Highly organized assembly of barite crystals grown within thermally evaporated AOT thin films

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Control over the crystallography, morphology and hierarchical assembly of crystals are important goals in advanced materials engineering with important application potential. Most studies hitherto have concentrated on using different templates for the controlled nucleation and growth of ceramic crystals. In this paper, we demonstrate the crystallization of barium sulfate within thermally evaporated aerosol OT (AOT) thin films by a process of Ba^{2+} ion entrapment followed by SO_4^{2-} ion entrapment. This process leads to the formation of flat, barite crystals in highly organized assemblies. The process of crystal assembly was found to be dependent on the composition of the host matrix. Contact angle measurements of the barite–AOT films indicated that they were hydrophobic, thus pointing to the role of hydrophobic interaction between the AOT monolayer-covered barite crystals in the assembly process.

Introduction

Control over the crystallography and morphology of technologically important minerals is an important goal in the area of crystal engineering. Approaches leading to such crystallography/morphology control based on mimicking biological mineralization (biomineralization) procedures have gained in popularity. Development of protocols for the synthesis of advanced inorganic materials increasingly requires the ability to grow crystals of controllable structure, size, morphology and assembly of the crystals into predefined superstructures. In this context biominerals have served as an inspiration to crystal engineers. This is not surprising given the exquisite control that biological organisms exert over mineral nucleation and growth (both amorphous and crystalline) encompassing the abovementioned aspects.¹⁻⁴ It is now established that an important requirement for biomineralization is epitaxy between the crystal nucleating face and underlying bio-organic surface and consequently, biomimetic surfaces such as those presented by Langmuir monolayers,⁵⁻¹⁴ self-assembled monolayers (SAMs)^{15,16} and functionalized polymer surfaces^{17,18} have been studied in great detail. In addition to crystal growth at the air/water interface in the presence of Langmuir monolayers,⁵⁻¹⁴ nanocrystals of metals/metal sulfides¹⁹⁻²² as well as minerals/ oxides such as apatite²³ and mesostructured silica²⁴ have been synthesized by chemical treatment of metal ions within built-up Langmuir-Blodgett films. Attempts have also been made to control the morphology of crystals *via* addition of suitable crystallization inhibitors²⁵⁻²⁷ and carrying out crystal growth in constrained environments such as those afforded by microemulsions.^{28–30} The anionic surfactant sodium bis-2ethylhexyl-sulfosuccinate (aerosol OT, AOT) is a twin tailed surfactant and is most commonly used to make reverse micelles, because of its bulky hydrophobic group relative to its hydrophilic group. Such an anionic surfactant has been used in the synthesis of nanoparticles of barium chromate,³¹ barium sulfate,^{29,30} calcium sulfate,³² barium carbonate,³³ and silica.³⁴ The principal reason for using microemulsions is that particle sizes and corresponding size distributions can be readily controlled by reaction confinement.

In this laboratory, we have developed a process based on thermally evaporated ionizable lipid films for the electrostatic entrapment of inorganic ions,³⁵ surface-modified nano-particles,³⁶ proteins/enzymes³⁷ and DNA.³⁸ Electrostatically



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entrapped ions such as Cu2+ and Ni2+ within lipid matrices

such as stearic acid may be reduced in-situ to yield the corres-

ponding metal nanoparticles.³⁹ Interesting low-temperature

alloying of the Cu and Ni nanoparticles synthesized in such lipid bilayer stacks has been observed.³⁹ It is clear that metal

ions entrapped in such lipid bilayer stacks can be chemically

reacted to yield a variety of materials within the confines of

the bilayer stacks. One interesting possibility is the growth

of minerals within the bilayer stacks by suitable reaction of

entrapped metal cations. In this paper, we investigate the use

of such thermally evaporated lipid thin films as templates in the

growth of BaSO₄. We have chosen BaSO₄ as a model system

since a considerable body of information exists in the literature

on barite morphology control,^{11-14,25-30,40} possibly due to the

importance of this mineral in cosmetics, papermaking and off-

shore oil field applications. More specifically, we demonstrate

the crystallization of barium sulfate within thermally evapo-

rated AOT thin films by a process of sequential entrapment of

 Ba^{2+} and SO_4^{2-} ions. It is observed that the $BaSO_4$ crystals

grow with a flat morphology and exhibit interesting assembly

into quasi-linear superstructures. Control experiments on the

growth of BaSO₄ crystals in solution in the absence of AOT

thin films yielded well-separated, individual barite crystals. The assembly of the $BaSO_4$ crystals is believed to occur via

hydrophobic association of the crystallites that are covered by

a monolayer of AOT and is similar in principle to the assembly

observed in barium chromate crystals grown in AOT micro-

emulsions by Mann et al.³¹ Presented below are details of this

Aerosol OT, stearic acid, barium chloride and sodium sulfate

were obtained from Aldrich Chemicals and used without

300 Å thickness were thermally vacuum deposited in an

Edwards E306 vacuum coating unit operated at a pressure of 1×10^{-7} Torr onto gold-coated AT-cut quartz crystals

[for quartz crystal microgravimetry (QCM) studies] and onto

glass and Si (111) substrates for X-ray diffraction (XRD) and

scanning electron microscopy (SEM) measurements. The film thickness was monitored using a QCM fitted to the deposition

Thin films of aerosol OT ($C_{20}H_{37}NaO_7S$, MW = 444.56) of

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study.

purification.

Experimental details

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chamber and crosschecked by ellipsometry measurements. After deposition of the AOT films, the QCM crystal was immersed in 50 mL of 10^{-3} M aqueous BaCl₂ solution (pH 5.5) and the frequency change of the crystal was monitored ex-situ, as a function of time of immersion in the electrolyte solution, taking care to wash and dry the crystals thoroughly prior to frequency measurement. Frequency measurements were made on an Edwards FTM5 frequency counter (stability and resolution of 1 Hz). For the 6 MHz crystal used in this study, the mass resolution was 12.1 ng cm^{-2} and the frequency changes were converted to mass loading using the Sauerbrey equation.⁴¹ The optimum immersion time determined from the QCM kinetics measurements was used to load the AOT films on glass and Si (111) substrates with Ba²⁺ ions by similar immersion in 10^{-3} M BaCl₂ aqueous solution. After formation of Ba-AOT films, the films on glass were subjected to XRD analysis. Thereafter, the Ba-AOT film on the QCM crystal was immersed in 50 mL of 1.42×10^{-3} M Na₂SO₄ aqueous solution (pH 6) and the frequency change of the crystal was monitored as a function of time of immersion in the electrolyte solution. The growth of barium sulfate in AOT thin films for other studies was carried out using the optimum immersion times determined from the QCM kinetics measurements mentioned above. X-ray diffraction (XRD) measurements of the Ba-AOT and BaSO4-AOT films on glass were carried out in the transmission mode on a Philips PW 1830 instrument operating at a voltage of 40 kV and a current of 30 mA with Cu Kα radiation. Scanning electron microscopy (SEM) measurements and energy dispersive analysis of X-rays (EDAX) chemical studies of the BaSO₄-AOT films on Si (111) substrates were carried out on a Leica Stereoscan-440 instrument equipped with a Phoenix EDAX attachment. Prior to XRD and SEM studies, these films were subjected to mild ultrasonic agitation in water for ca. 3 min to dislodge any BaSO₄ crystals that had nucleated in the solution and had bound weakly to the AOT film surface. In order to determine whether the growth of these crystals was purely a surface process, contact angles were measured at various points on the films. Contact angle measurements were carried out by the sessile water drop method on a 1 µL water drop using a Rame-Hart 100 goniometer. Measurements were made on at least 10 different points on the film surface and these values were averaged before reporting.

In order to better understand better the role of the AOT thin film in determining the morphology and assembly of $BaSO_4$ crystals, kinetics of crystallization was monitored in the following manner. Thin films of AOT of 300 Å thickness were deposited on Si (111) substrates and immersed in aqueous $BaCl_2$ solution under the experimental conditions mentioned above using the optimum immersion time determined from the QCM measurements. After entrapment of Ba^{2+} ions, the barium sulfosuccinate film was immersed in Na_2SO_4 solution and the crystallization of $BaSO_4$ was monitored as a function of time of immersion by SEM.

In control experiments, the crystallization of BaSO₄ was accomplished directly in solution by reaction of aqueous solutions of BaCl₂ (50 mL of 10^{-3} M) and Na₂SO₄ (50 mL of 1.42×10^{-3} M). The crystals were formed predominantly in the bulk of the solution and slowly settled down at the bottom of the container. The crystals were separated by filtration, washed with water and drop-coated on Si (111) substrates for further analysis. In another important control experiment, BaSO₄ crystals were grown in 300 Å thick stearic acid films under conditions identical to those used for AOT thin films.

Results and discussion

The kinetics of incorporation of Ba²⁺ ions in a 300 Å thick AOT film was followed by QCM and the data recorded as a function of time of immersion in the BaCl₂ solution and thereafter in the Na₂SO₄ solution is shown in Fig. 1A. During immersion in the BaCl₂ solution, a fairly large mass increase is seen and is attributed to electrostatically controlled diffusion (and entrapment) of the Ba²⁺ ions in the AOT matrix. At pH 5.5, the sulfosuccinate ions of the AOT matrix are expected to be fully negatively charged leading to maximum attractive electrostatic interaction with the Ba^{2+} cations. It is observed that equilibration of the Ba^{2+} ion density in the film occurs within 6300 s of immersion of the AOT film in the BaCl₂ solution. From the equilibrium mass uptake of Ba^{2+} ions (ca. 7000 ng cm⁻²) and the mass of the AOT film, a Ba^{2+} : AOT molar ratio of 7 : 1 was calculated. This result indicates considerable over compensation of the negative charge in the anionic matrix by the Ba²⁺ ions. Such charge over-compensation is known to occur in layer-by-layer electrostatically assembled systems.^{42,43} However, we would like to caution here that there is a number of factors that could contribute to an error in estimation of the Ba^{2+} : AOT molar ratio. One source of error could be a change in the acoustic properties of the AOT film after complexation with Ba²⁺ ions. We believe binding of the Ba²⁺ ions to the AOT molecules would lead to it becoming acoustically 'stiffer' and could account for (to a large extent) the seemingly unreasonable charge overcompensation



Fig. 1 (A) QCM mass uptake recorded *ex-situ* during immersion of a 300 Å thick AOT film sequentially in Ba^{2+} and SO_4^{2-} ion solutions. The inset shows a cartoon of the lamellar structure of the thermally evaporated AOT film after entrapment of Ba^{2+} counterions. (B) EDAX spectra recorded from an as-deposited 300 Å thick AOT film on a Si (111) substrate (curve 1), the AOT film after incorporation of Ba^{2+} ions (curve 2) and the Ba-AOT film after reaction with SO_4^{2-} ions (curve 3).

observed. To our knowledge, such effects have not been addressed in the literature and we are performing measurements to make a start in understanding this interesting discrepancy. In thermally evaporated films, it is likely that there are a number of defect structures such as pores in the film, which would result in creation of water channels for transport of ions into the lipid. The lamellar structure of the lipid matrix and the swelling observed on immersion in water³⁵ would also lead to aqueous pathways for the transport of Ba²⁺ ions into the film. Thus, the hydrocarbon layers need not necessarily be viewed as barriers to ion transport since lateral diffusion *via* hydrophilic water channels perpendicular to the lamellae is highly possible.

After Ba²⁺ ion entrapment, the Ba²⁺–AOT covered QCM crystal was immersed in Na₂SO₄ solution (pH 6) and the frequency change of the crystal was monitored as a function of time of immersion in the electrolyte solution. A large mass increase is observed during this cycle of immersion as well and is due to electrostatically controlled diffusion (and entrapment) of the SO₄²⁻ ions in the Ba–AOT film. As in the case of Ba²⁺ : SO₄²⁻ molar ratio. The QCM measurements were thus merely used as an indicator of the optimum time of immersion in the BaCl₂ (6300 s) and Na₂SO₄ solutions (4360 s).

To determine whether the sodium ions in aerosol OT are completely replaced by Ba2+ ions during immersion in BaCl2 solution, a chemical analysis of the as-deposited 300 Å thick AOT film on a Si (111) substrate before and after immersion in $BaCl_2$ solution and after reaction with SO_4^{2-} ions was done using EDAX (Fig. 1B, curves 1, 2 and 3, respectively). It is seen that the as-deposited AOT thin film shows the presence of Na, S, C and O signals (curve 1). A quantitative analysis of the Na and S components yielded a 1: 1.22 atomic ratio for Na: S in agreement with the expected stoichiometry. After immersion of the AOT film in BaCl₂ solution, the Na signal is reduced significantly (curve 2) and a strong Ba signal appears and indicates replacement of the Na⁺ ions by Ba²⁺ ions in the AOT thin film. A quantitative analysis of the Ba and S components yielded a 1:1.69 atomic ratio for Ba: S. This is in reasonable agreement with the expected Ba : S ratio of 1 : 2 based on charge neutrality considerations. Thereafter, immersion of Ba²⁺-AOT film in Na₂SO₄ solution resulted in an increase in the S and O signals (curve 3) indicating the formation of BaSO₄ crystals.

As briefly mentioned in the introduction, it has been shown in this laboratory that thermally evaporated fatty acid films when immersed in electrolyte solutions such as PbCl₂ and CdCl₂ resulted in the electrostatic entrapment of the metal cations and the spontaneous ordering of the lipid films into a lamellar *c*-axis oriented structure.³⁵ We have used this approach to form barium sulfosuccinate films by immersion of 300 Å thick AOT films in BaCl₂ solution. The formation of lamellar barium sulfosuccinate was ascertained by the presence of characteristic odd–even intensity oscillations in the (0 0 1) Bragg reflections in the XRD pattern of the film³⁵ (curve 2, inset of Fig. 2). These Bragg reflections are not observed in the as-deposited AOT films (curve 1, inset of Fig. 2). The *c*-axis oriented lamellar structure of a barium sulfosuccinate bilayer is illustrated in the schematic in the inset of Fig. 1A.

SEM pictures recorded from a 300 Å thick AOT film on a Si (111) substrate after formation of $BaSO_4$ are shown in Fig. 3A, B and C at different levels of magnification. The SEM image (Fig. 3A and B) shows a well-formed assembly of barite crystals organized into quasi-linear super-structures. EDAX analysis of the $BaSO_4$ crystals yielded a Ba : S : O atomic ratio of 1 : 1.56 : 12 (curve 3 in Fig. 1B). While the Ba : S ratio is in fair agreement with the expected stoichiometry, excess oxygen is due to sampling from the silica substrate. The XRD pattern recorded from the $BaSO_4$ crystals shown in Fig. 3 is displayed in curve 2, Fig. 2. A number of Bragg reflections are identified



Fig. 2 XRD patterns recorded from $BaSO_4$ crystals grown in solution (curve 1) and within a 300 Å thick thermally evaporated AOT film (curve 2). The inset shows the XRD patterns recorded from a 300 Å thick as-deposited AOT film (curve 1) and this film after entrapment of Ba^{2+} ions (curve 2). The (0 0 1) Bragg reflections are identified in this figure.



Fig. 3 A, B & C are representative SEM images at different magnifications of $BaSO_4$ crystals formed in a 300 Å thick thermally evaporated aerosol OT film.

and have been indexed with reference to the unit cell of the barite structure (a = 8.87 Å, b = 5.45 Å, c = 7.15 Å; space group *Pnma*).⁴⁴ For comparison, the XRD pattern recorded from barite crystals grown in solution in one of the control experiments is shown in Fig. 2 (curve 1). It is observed that the intensity ratios of the different Bragg reflections in the barite crystals grown in the AOT film is quite different from those obtained in the control experiment. The crystals grown in the thermally evaporated AOT thin film have pronounced orientational order, the predominant nucleating planes being (2 0 0), (1 1 2) and (2 2 1). The presence of intense (2 0 0) and (2 2 1) reflections in the XRD pattern suggests oriented growth of the barite crystals along these crystallographic planes and that the nature of growth in this constrained environments may play a role in face-specific nucleation of the barite crystals. The role of epitaxy in directing face-specific nucleation of calcite crystals grown within thermally evaporated stearic acid films has recently been demonstrated by some of us.⁴⁵ In analogy with this report, we believe that favorable epitaxy between the AOT molecules and the Ba²⁺ ions is responsible for the highly preferred oriented growth of barite crystals within the lipid bilayer stacks.

The higher magnification SEM image (Fig. 3C) recorded from the barite–AOT film clearly shows the presence of highly organized assemblies of mature barite crystals. The barite crystals are flat and needle-like in shape. This image also indicates two levels of hierarchy in the assembly of barite crystals. At the first level, the flat barite crystals are assembled into flower-like patterns (Fig. 3A, B and C). These flower-like assemblies are in turn assembled into quasi-linear superstructures of length often in excess of 20 μ m. It is pertinent to mention here that we had observed such assembly of strontianite needles grown in thermally evaporated stearic acid films into flower-like structures.⁴⁶ However, no further assembly of the flower-like structures was seen.⁴⁶

It is possible that the growth of the barite crystals occurs in solution by a process of leaching out of Ba^{2+} ions from the barium sulfosuccinate film followed by reaction with sulfate ions and attachment of the crystals thus formed to the surface of the AOT film. This possibility is to be discounted before in-situ growth of the barite crystals within the AOT matrix can be accepted as the true mechanism. One possible method to ascertain the mechanism is to monitor the growth of the barite crystals as a function of time of immersion in the Na₂SO₄ solution. SEM pictures recorded from a 300 Å thick barium sulfosuccinate film on a Si (111) wafer after immersion in Na₂SO₄ solution for 30, 45, 60 and 80 min are shown in Fig. 4A-D, respectively. After 30 min of reaction, the SEM image (Fig. 4A) shows the growth of very small barite crystallites on the substrate surface. After a further 15 min of reaction, the growth of flat disk/needle like plates of BaSO₄ assembled in flower-like pattern is observed (Fig. 4B). Reaction of the barium sulfosuccinate film for 60 min leads to selfassembly of the flower-like aggregates into higher order superstructure (Fig. 4C). Immersion of the barium sulfosuccinate film for 80 min in the Na₂SO₄ solution clearly shows assembly of the barite crystals into quasi-linear superstructures. The size of the barite crystals in Fig. 4C and D is not very different indicating that the crystal growth is complete within 60 min of reaction and that further immersion in the electrolyte solution facilitates assembly of the barite crystals. Thus, the SEM images recorded from the barium sulfosuccinate film during growth of the barite crystals suggest that the growth process occurs within the AOT matrix and not externally by a leaching process.

A simple calculation may be performed to show that formation of barite crystals by reaction of barium ions leached out from the AOT film and sulfate ions in solution is not a physically meaningful alternative. The barium sulfosuccinate films used in this study were typically of $1 \text{ cm} \times 1 \text{ cm}$ dimensions. Assuming that the QCM mass loading in these



Fig. 4 A, B, C and D are representative SEM images of $BaSO_4$ crystals grown in a 300 Å thick thermally evaporated aerosol OT film as a function of time of reaction of the barium sulfosuccinate film with SO_4^{2-} ions.

films is reasonable at *ca.* 7000 ng cm⁻² (Fig. 1A) and if all the barium ions in this film are leached out into the 50 mL 1.42×10^{-3} M Na₂SO₄ solution, it can easily be shown that the concentration of the barium ions in this solution would be nearly 1.02×10^{-6} M. Clearly, this would lead to a supersaturation ratio far too small to yield nucleation and growth of BaSO₄ crystals in solution. Together with the SEM studies on the kinetics of growth presented earlier, these calculations show that growth of the crystals occurs within the AOT thin films.

While it is clear that crystal growth occurs within the film, reasons leading to assembly of the barite crystals into linear superstructures need to be established. Control experiments were performed wherein barite crystals were grown both in solution and in thermally evaporated stearic acid films under similar conditions used for the AOT studies. Stearic acid films also spontaneously assemble into lamellar structures upon electrostatic binding with Ba²⁺ ions and may thus be used to grow barite crystals on reaction with SO_4^{2-} ions.⁴⁷ Fig. 5A shows the morphology of BaSO4 crystals grown within stearic acid bilayers, wherein a number of very small crystallites of disk/needle shape can be seen. Clearly, there is no evidence of flower patterns in the crystal assembly or linear superstructures as seen in the AOT films. The barite crystals grown in solution are shown in Fig. 5B and here too, the barite crystals are flat with no signs of assembly. The overall crystal morphology of barite formed within thermally evaporated AOT bilayers is very different from that of barite grown within thermally evaporated fatty acid films (Fig. 5A)⁴⁷ as well as in solution using AOT microemulsions.^{29,30} While the exact mechanism leading to the morphology variation in the barite crystals within the AOT bilayers is not fully understood and may be a consequence of inhibition of growth along certain crystallographic directions by the anionic molecules in the bilayer, another factor that could contribute is the kinetics of crystal growth and the built-in anisotropy of the bilayer geometry. Yet another factor could be the difference in periodicity of the carboxylate ions in stearic acid and the sulfate groups in AOT which would clearly affect face-specific nucleation of the mineral in both cases. It is possible that the bulky nature of the AOT headgroup forces it to pack in a rectangular pattern whereas stearic acid with smaller carboxylic acid headgroups would pack hexagonally in the respective thermally evaporated films. The issue of crystal morphology variation in different templating matrices requires more study and will be dealt with in future reports.

The interesting hierarchical assembly of barite crystals could be hydrophobic interactions between individual crystallites covered by a monolayer of aerosol OT. During the initial stages of growth of the crystals, the AOT bilayers would distort to accommodate the large structures and eventually rupture to form a monolayer around the crystals. In order to determine whether the growth of these crystals was purely a surface process, we measured the contact angle at various points on the film surface and found that the surface was quite hydrophobic (mean contact angle of 95°). This is to be contrasted with a contact angle of 65° measured for films of barite crystals grown



Fig. 5 (A) SEM image of $BaSO_4$ crystals formed in a thermally evaporated stearic acid thin film. (B) SEM image of $BaSO_4$ crystals grown in solution by reaction of aqueous solutions of $BaCl_2$ and Na_2SO_4 .

in solution and picked up on to a Si (111) wafer coated with a 300 Å thick AOT film. We would like to emphasize here that the contact angle measurements were carried out by the sessile water drop method. This interesting result clearly shows that the barite aggregates of Fig. 3 are covered with a monolayer of AOT which renders them hydrophobic. The likely mechanism is therefore nucleation and growth of the barite crystals within the hydrophilic regions of the bilayers in the barium sulfosuccinate film accompanied by expansion of the lipid matrix (and consequent surface coating) to accommodate the large crystals. The hydrophobic nature of the crystallites points to a possible reason for formation of barite superstructures. Since the growth of the crystals occurs in an aqueous environment, hydrophobic forces between the AOT monolayercovered barite crystals (at least in the very early stages of crystal growth) could lead to aggregation of the crystals into flower-like structures as observed. This sequence of events is borne out by the SEM results presented earlier that clearly identified a nucleation and growth stage followed by assembly of the crystals (Fig. 4). As mentioned earlier, a similar mechanism has been implicated in the assembly of prismatic barium chromate crystals into linear superstructures grown in AOT microemulsions.¹¹ The fact that AOT molecules in a highly condensed solid thin film state result in similar hydrophobic association-driven assembly indicates considerable swelling of the barite-AOT films during immersion in water. The further assembly of the barite flowers into quasilinear structures may be rationalized in terms of interleaving of the petals of neighbouring flowers, this process also presumably driven by hydrophobic interactions between AOT molecules bound to the individual barite crystals. That such an assembly process does not occur for films grown in stearic acid films clearly underlines the special role of the AOT molecules in the assembly. The hierarchical assembly of barite crystals in the AOT matrix is a salient feature of the work.

Conclusions

The crystallization of barium sulfate within thermally evaporated AOT films by a process of Ba^{2+} ion entrapment and thereafter, reaction with SO_4^{2-} ions has been demonstrated. Under conditions where there is good registry between the Ba^{2+} ions and the underlying AOT template, oriented growth of predominantly barite crystals is observed. The barite crystals show two levels of hierarchical assembly. The first level consists of the formation of barite flower-like structures that assemble into quasi-linear structures at the second level. This process of barite crystal association is believed to occur *via* hydrophobic interactions between AOT monolayer-covered barite crystals. The ability to assemble barite crystals into superstructures on a solid support suggests possible extension to more intricate superstructures by suitable patterning/templating of the substrate surface.

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