Crystallization of SrCO$_3$ within thermally evaporated fatty acid films: unusual morphology of crystal aggregates

Murali Sastry,[*a] **Ashavani Kumar,**[a] **Chinmay Damle,**[a] **S. R. Sainkar,**[a] **Mahesh Bhagwat**[b] **and Veda Ramaswamy**[b]

[a] *Materials Chemistry Division, National Chemical Laboratory, Pune-411 008, India. E-mail: sastry@ems.ncl.res.in*
[b] *Catalysis Division, National Chemical Laboratory, Pune-411 008, India*

Paper

Reaction of CO$_2$ with electrostatically entrapped Sr^{2+} ions within thermally evaporated stearic acid films leads to the *in-situ* growth of SrCO$_3$ crystals in highly organized assemblies, the organization possibly occurring due to hydrophobic association of the crystallites covered by a monolayer of stearic acid.

There is currently considerable interest in the use of biomimetic templates for the crystallization of inorganic materials.[1] Many different templates have been used, some examples of which are surfaces modified with proteins,[2] Langmuir monolayers,[3] polymer surfaces,[4] self-assembled monolayers with differing terminal functionality,[5] monolayer films of gold nanoparticles[6] as well as free nanoparticles in solution.[7] In 1995, some of us demonstrated the spontaneous organization of thermally evaporated fatty acid films during immersion in suitable electrolytes.[8] It was observed that cations such as Cd^{2+} and Pb^{2+} from solution were electrostatically complexed with carboxylate ions of the fatty acid molecules and that this process led to the organization of the lipid film into a *c*-axis oriented structure, similar to that obtained by the conventional Langmuir–Blodgett deposition procedure.[8] Here, we develop on this theme and demonstrate for the first time the crystallization of biominerals such as strontium carbonate within thermally evaporated fatty acid films. SrCO$_3$ was chosen in this study since it almost always crystallizes in the strontianite form and thus is a simpler prototypical system than the more thoroughly studied CaCO$_3$, which is known to crystallize in three different crystallographic forms.[5a,7] Reaction of CO$_2$ with Sr^{2+} ions entrapped within stearic acid films leads to the growth of beautiful, flower-like structures of close-packed strontianite needles, such an aggregated morphology not normally observed using other surfaces as templates.[5a,7] Possible reasons for the unusual aggregated structures composed of strontianite crystals are briefly discussed.

Stearic acid (Aldrich, used as-received) films of 500 Å thickness were deposited by vacuum evaporation on to a 6 MHz gold-coated quartz crystal [for quartz crystal microgravimetry (QCM) studies] and on to Si(111) substrates [for Fourier transform infrared (FTIR), X-ray diffraction and scanning electron microscopy (SEM) studies]. As a control, a 500 Å thick octadecylamine (ODA; Aldrich, used-as received) film was also vacuum evaporated on to the QCM crystal as well as on to Si(111) substrates. The film thickness was monitored using a QCM fitted to the deposition chamber and cross-checked by ellipsometry measurements. After deposition of the stearic acid film, the QCM crystal was immersed in 10^{-4} M SrCl$_2$ solution (pH 6) and the frequency change of the crystal was monitored as a function of time of immersion in the electrolyte solution *ex-situ*, taking care to wash and dry the crystal thoroughly prior to frequency measurement. Fig. 1A shows the QCM mass uptake recorded from the stearic acid film as a function of time of immersion in the electrolyte

solution (red squares).[9] It is seen that there is a fairly large mass increase and this is attributed to electrostatically controlled diffusion (and entrapment) of the Sr^{2+} ions into the fatty acid film. At pH 6, the carboxylate ions of the fatty acid matrix are expected to be fully charged leading to maximum electrostatic interaction with the metal cations. From the equilibrium mass uptake of Sr^{2+} ions (*ca.* 23 000 ng cm^{-2}) and the mass of the stearic acid film, a Sr^{2+} : stearic acid molar ratio of 14 : 1 was easily calculated. This result indicates considerable over-compensation of the negative charge in the acid matrix by the Sr^{2+} ions. Such charge overcompensation is known to occur in layer-by-layer electrostatically assembled systems.[10] Fig. 1A also shows the mass uptake recorded from a 500 Å thick ODA film during immersion in SrCl$_2$ solution (blue circles). At pH 6, the amine groups of the ODA matrix are fully protonated and therefore entrapment of Sr^{2+} ions in this lipid film is electrostatically unfavorable. Indeed, energy dispersive X-ray analysis (EDAX)[11] of this film indicates that the mass uptake is almost entirely due to entrapment of chloride anions in the positively charged ODA matrix. From the QCM measurements shown in Fig. 1A an optimum time of immersion of the stearic acid film within the SrCl$_2$ solution was determined to be 60 min.

The inset of Fig. 1A shows the FTIR spectra[12] recorded from the as-deposited 500 Å thick stearic acid film on a Si(111) substrate (curve 1), the stearic acid film after immersion in SrCl$_2$ solution for 60 min (curve 2) and the strontium stearate film after reaction with CO$_2$ for 72 h (curve 3). In all of the films used in this study, growth of SrCO$_3$ crystals was carried out by immersing the films in a vertical position in the SrCl$_2$ solution and passing CO$_2$ gas [produced by decomposition of (NH$_4$)$_2$CO$_3$] through the solution for the correct time period.[5a,7] Prior to measurement of the FTIR spectra (as well as before the XRD and SEM studies), the films were subjected to mild ultrasonic agitation for 3 min to dislodge any weakly surface-bound SrCO$_3$ crystals that had nucleated in solution. A prominent absorption is seen at 1700 cm^{-1} in the case of the as-deposited stearic acid film (curve 1) as well as with the fatty acid film after immersion in SrCl$_2$ solution (curve 2). This band is due to excitation of carbonyl stretch vibrations in the carboxylic acid groups of the fatty lipid film.[13] In addition to this band, the strontium stearate film shows an additional absorption at *ca.* 1515 cm^{-1} (curve 2). This band is assigned to the carbonyl stretch of the carboxylate groups of the salt of stearic acid.[13] The presence of the 1700 cm^{-1} band in the strontium stearate film indicates that complete salt formation
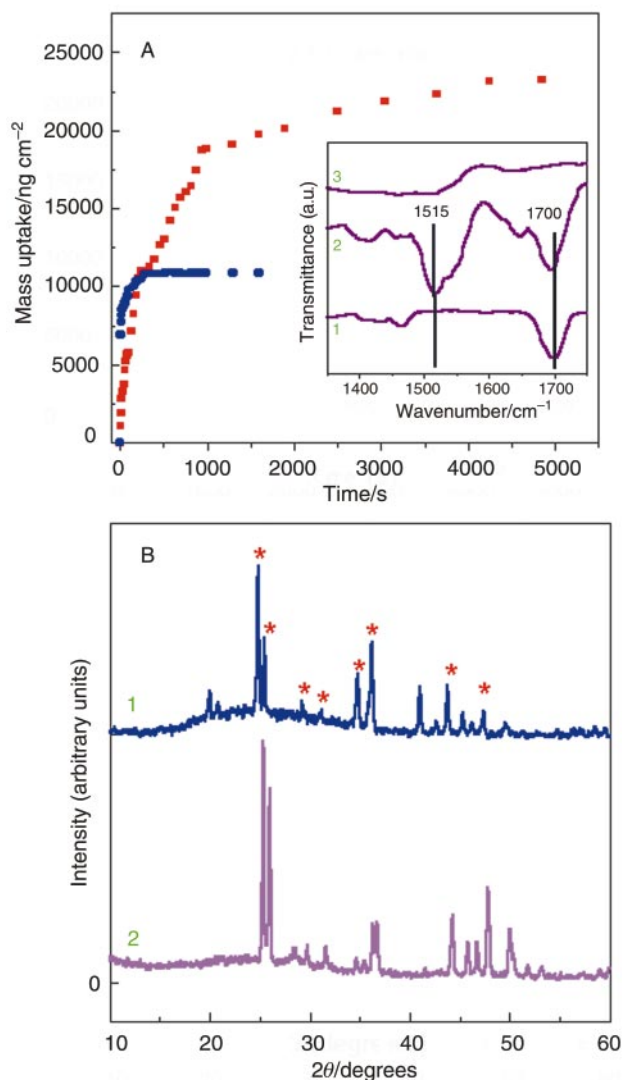
Fig. 1 (A) QCM mass uptake data recorded as a function of time of immersion of a 500 Å thick stearic acid film (squares) and a 500 Å thick ODA film (circles) in 10^{-4} M $SrCl_2$ solution. The inset shows the FTIR spectra recorded from a 500 Å thick stearic acid film on a Si(111) substrate (curve 1), the stearic acid film after immersion in 10^{-4} M $SrCl_2$ solution for 60 min (curve 2), and the strontium stearate film after reaction with CO_2 for 72 h (curve 3; see text for details). (B) XRD patterns obtained from $SrCO_3$ crystals grown on glass (curve 1) and within a 500 Å thick stearic acid film as described in the text (curve 2). The Bragg reflections arising from the strontianite phase are indicated by asterisks.

had not occurred. The FTIR spectrum recorded from the strontium stearate film after reaction with CO_2 (curve 3) is essentially featureless.

Fig. 1B shows the XRD spectra recorded from a glass substrate immersed in $SrCl_2$ solution and reacted with CO_2 for 72 h (curve 1) and within a 500 Å thick stearic acid film after growth of $SrCO_3$ crystals as mentioned earlier (curve 2). The XRD pattern recorded from the ODA film after formation of $SrCO_3$ was identical to that recorded from the glass substrate and, for brevity, has not been shown. A number of Bragg reflections are observed and those corresponding to the strontianite phase have been identified and labeled by asterisks within the figure. The major Bragg reflections agree very well with those reported by Künther *et al.* for strontianite crystals grown on self-assembled monolayers.[5a] We would like to add here that $SrCO_3$ crystals were grown in the strontium stearate film on the QCM crystal and that the additional mass uptake due to strontianite formation was measured. It was observed that almost all the Sr^{2+} ions were converted to $SrCO_3$.

The XRD results discussed above do not indicate any dramatic differences in the crystallography of the $SrCO_3$ crystals formed either on the glass/ODA film surface or within the strontium stearate film. This is not surprising given that the thermally evaporated fatty acid film is known to be highly disordered insofar as the organization of the carboxylic acid groups in the film is concerned.[8] Consequently, the presence of a highly ordered organic template that may direct the crystallization of $SrCO_3$ in a specific manner does not exist in the present study. However, interesting differences were observed in the SEM pictures of the crystallite morphology. Fig. 2 shows the SEM pictures obtained from strontianite crystals grown on a glass substrate (A) (please note that a similar ultrasonic treatment was given to this film prior to SEM measurement), on a 500 Å thick ODA film (B) and within a 500 Å thick strontium stearate film (C).

While well separated, individual strontianite needles are observed to form on glass (A) and at the surface of the ODA film (B), the morphology of the strontianite needles is more interesting in the case of the strontium stearate film (C). The strontianite crystals clearly aggregate into dense, flower-like structures, and these structures were observed to cover the whole film surface with very high surface coverage. To the best of our knowledge, such close-packed aggregates of strontianite needles have not been observed in other biomimetic approaches
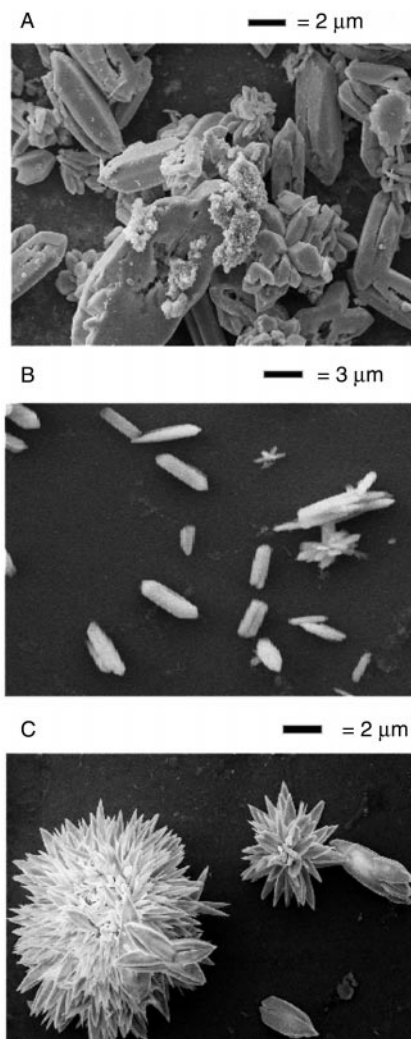

Fig. 2 (A) SEM picture of $SrCO_3$ crystals grown on a glass substrate showing well separated stontianite needles. (B) SEM picture of $SrCO_3$ crystals, grown on a 500 Å thick ODA film, showing individual strontianite needles. (C) SEM picture of $SrCO_3$ crystals, grown in a 500 Å thick strontium stearate film, showing the aggregation of strontianite needles into flower-like superstructures.

to the growth of SrCO₃ crystals. In order to determine whether the growth of these crystals was purely a surface process (as would be the case for the glass surface and the ODA film), we measured the contact angle[14] at various points on the film surface and found that the surface was fairly hydrophobic (mean contact angle of 84°). This is to be contrasted with a contact angle of 48° obtained for films of strontianite crystals grown in solution and picked up on to a Si(111) wafer. This interesting result clearly shows that the strontianite aggregates of Fig. 2C are covered with a monolayer of stearic acid which renders them hydrophobic. The likely mechanism is therefore nucleation and growth of the strontianite crystals within the hydrophilic regions of the bilayers in the strontium stearate film accompanied by expansion of the lipid matrix (and consequent surface coating) to accommodate the large crystals. The hydrophobic nature of the crystallites indicates also a possible reason for formation of the superstructures of strontianite needles. Since the growth of the crystals occurs in an aqueous environment, hydrophobic forces between the lipid monolayer-covered strontianite crystals (at least in the very early stages of crystal growth) could lead to aggregation of the crystals as observed. It is clear that such hydrophobic interactions cannot occur in the case of SrCO₃ crystals grown on, for example, self-assembled monolayer surfaces.[5a] Another factor that cannot be discounted is the kinetics of crystallization which, in the case of growth within the fatty acid matrix, are expected to be much slower than for homogeneous nucleation in solution. Indeed, Künther *et al.* have observed that carrying out the growth of SrCO₃ crystals at reduced temperatures on self-assembled monolayer surfaces did result in some aggregation of the strontianite crystals.[5a] However, the extent of aggregation was considerably less than that observed in this study. It is possible that both hydrophobic and kinetic effects contribute to the interesting strontianite superstructures observed in the case of strontium stearate films. This result is expected to be of importance in understanding the hierarchical assembly of crystallites in biominerals.

Acknowledgements

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9 The QCM resonance frequency was measured using an Edwards FTM5 frequency counter (resolution = 1 Hz) and converted to mass loading using the expression $\Delta m = 12.1 \Delta f$ (ng cm⁻²).

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