Journal of Crystal Growth I (IIII) III-III



Contents lists available at ScienceDirect

Journal of Crystal Growth

journal homepage: www.elsevier.com/locate/jcrysgro

Additive-induced morphological tuning of self-assembled silica-barium carbonate crystal aggregates

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ARTICLE INFO

Article history: Received 10 October 2008 Received in revised form 2 February 2009 Accepted 21 February 2009 Communicated by J. de Yoreo

PACS: 81.10.Dn 81.16.Dn

Keywords: A1. Biomimetic materials A2. Growth from solutions B1. Barium carbonate B1. Cetyltrimethylammonium bromide (CTAB) B1. Poly(diallyldimethylammonium chloride) (pDADMAC) B1. Silica biomorphs

ABSTRACT

Crystallisation of barium carbonate from alkaline silica solutions results in the formation of extraordinary micron-scale architectures exhibiting non-crystallographic curved shapes, such as helical filaments and worm-like braids. These so-called "silica biomorphs" consist of a textured assembly of uniform elongated witherite nanocrystallites, which is occasionally sheathed by a skin of amorphous silica. Although great efforts have been devoted to clarifying the physical origin of these fascinating materials, to date little is known about the processes underlying the observed self-organisation. Herein, we describe the effect of two selected additives, a cationic surfactant and a cationic polymer, on the morphology of the forming crystal aggregates, and relate changes to experiments conducted in the absence of additives. Minor amounts of both substances are shown to exert a significant influence on the growth process, leading to the formation of predominantly flower-like spherulitic aggregates. The observed effects are discussed in terms of feasible morphogenesis pathways. Based on the assumption of a template membrane steering biomorph formation, it is proposed that the two additives are capable of performing specific bridging functions promoting the aggregation of colloidal silica which constitutes the membrane. Morphological changes are tentatively ascribed to varying colloid coordination effecting distinct membrane curvatures.

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1. Introduction

The synthesis of "biomimetic" materials has aroused a great deal of interest throughout the last decade [1–6]. In most cases, the influence of organic additives or template structures on the crystallisation (or precipitation) of inorganic matter is exploited, modelled on the principles of nature, to build up microstructures of extraordinary and elaborate morphologies which potentially provoke superior macroscopic material properties [7,8]. The presence of suitable organic molecules or networks modifies the mineralization process leading to morphologies beyond crystallographic restraints. For instance, gelatin hydrogels and films have been employed as matrices for biologically inspired growth of calcium carbonate crystal assemblies [9,10]. Polymeric membranes were used to imprint desired morphologies on single $CaCO_3$ crystals [11]. Moreover, specifically designed doublehydrophilic block copolymers have proven to be versatile additives for directing non-classical structure formation of various inorganic materials [12–14].

The self-assembly of alkaline-earth metal carbonates in the presence of silicate is an outstanding example in this context, as *purely inorganic* precursors cooperate in this case to constitute hierarchical structures and shapes strongly reminiscent of biological forms [15–19]. Precipitation of barium carbonate (witherite) from alkaline silica solutions or gels results in a variety of complex curved, non-crystallographic ultrastructures, including helicoidal filaments and sinuous sheets. Indeed, some of the observed aggregates closely mimic the morphology of certain putative microfossils [20–22]. These so-called "silica biomorphs" consist of a crystalline phase of quite monodisperse, defect-free aragonite-type carbonate nanorods in a compact array exhibiting

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^{0022-0248/\$ -} see front matter \circledcirc 2009 Elsevier B.V. All rights reserved. doi:10.1016/j.jcrysgro.2009.02.044

liquid crystal-like long-range orientational ordering with a constant mutual twist between neighbouring rods [19]. The whole assembly of crystallites is often surrounded by an outer amorphous silica skin which is composed of densely aggregated siliceous nanospheres [23,24]. Similar composite architectures have also been observed for strontium carbonate [25]. Recently, the structural concept of biomorphs has been successfully transferred onto calcium carbonate (aragonite phase) at elevated temperature, yielding coral- and floral dumbbell-like morphologies [26].

Despite numerous studies, the physicochemical processes underlying the formation of biomorphs are still not fully understood. One feasible "top-down" mechanism acts on the assumption of a silica membrane which templates subsequent carbonate precipitation and deposits finally on the crystalline ensemble. The putative template membrane is supposed to originate from negatively charged colloidal silica spheres which form upon addition of alkaline-earth metal cations to silica sols at high pH, and aggregate to sheets due to charge screening by the cations. In an alternative, "bottom-up" scenario, the emergence of these complex morphologies from rather simple inorganic precursors is ascribed to interactions between initially formed carbonate nanocrystallites and soluble silicate species, with local constraints between crystallites being responsible for the observed selfassembly [23]. Similar mesoscale self-ordering processes have been claimed for organic-coated nanocrystals exhibiting high shape anisotropy [27]. Interestingly, helical arrangements consisting of BaCO₃ nanocrystals, though on a smaller global scale than in the case of witherite biomorphs, were synthesized using a racemic block copolymer as additive [28]. Selective adsorption of the additive onto specific faces of the primary building blocks and subsequent interparticle attachment in a preferentially staggered arrangement leads to helix formation in this case. Helical CaCO₃ aggregates (vaterite phase) grown in the presence of charged polyelectrolytes were reported by Gower et al. [29].

Here we describe the influence of two selected additives on the morphology of silica-barium carbonate biomorphs. The performed experiments have been designed to explore mechanistic principles underlying the multiple-scale structuring of biomorphs. For this purpose, a common cationic surfactant, cetyltrimethylammonium bromide (CTAB), and a cationic polymer consisting of monomers with a guaternary ammonium functionality, poly(diallyldimethylammonium chloride) (pDADMAC, see Fig. 1) were chosen as additives in a typical biomorph synthesis. Both substances are known to maintain strong interactions with silicate species in solution. For example, CTAB 'templates' the well-known mesoporous silica materials [30,31]. During the formation process, anionic silicate species adhere to the cationic head of the surfactant and subsequently mineralize the structure of supramolecular surfactant assemblies in solution. The polymeric additive pDADMAC has also been successfully employed to create mesopores in siliceous material [32], pointing to significant interactions with silica in this case also. In the present work, CTAB and

Fig. 1. Molecular structure of the repetitive unit of poly(diallyldimethylammonium chloride) (pDADMAC).

pDADMAC were used as "secondary" additives to influence *in situ* the "primary" additive, silica. The observed morphological changes in the silica–carbonate materials are discussed in view of feasible morphogenesis pathways. Cooperative effects of two distinct additives on the crystallisation of inorganic matter have been reported previously. For instance, CTAB was added to solutions of certain block copolymers and of certain dendrimers used for the mineralization of calcium carbonate, resulting in uniform pine-cone shaped calcite crystals and in calcite rhombohedra covered with disc-shaped vaterite crystals, respectively [33,34].

2. Experimental section

2.1. Materials

Silica-witherite biomorphs were obtained by precipitating barium carbonate from alkaline silica sols at ambient temperature and pressure. Barium chloride dihydrate (Sigma-Aldrich, \geq 99%) was used as soluble barium salt, commercial water glass (Sigma-Aldrich, reagent grade, 27% as SiO₂) as silica source. Cetyltrimethylammonium bromide was purchased from Fluka ($\geq 99\%$) and used without further purification. Poly(diallyldimethylammonium chloride) was received as a powder ("Magnafloc 368") from Ciba Specialty Chemicals (Lampertheim, Germany), with a purity specification of 90-100% due to varying water content. The product was dried in a vacuum oven at 60 °C for at least 48 h prior to use. The average molecular weight of the polymer was \sim 750 kDa, corresponding to about 4640 monomer units per polymer chain. The main field of application of "Magnafloc 368" is its use as primary coagulant inducing flocculation of colloidal suspensions of negatively charged particles. All solutions and dilutions were freshly prepared using exclusively Millipore water.

2.2. Crystallisation experiments

Biomorph synthesis is carried out by mixing equal volumes of aqueous barium chloride and sodium silicate solution to give typical final concentrations of 5 and 8.9 mM (as SiO₂), respectively. For this purpose, the water glass stock is diluted 1:350 (v/v), followed by addition of small aliquots of 0.1 M sodium hydroxide (Merck) to adjust the pH to about 11.3. After mixing 1:1 (v/v) with 10 mM BaCl₂ solution, the pH was determined to 11.0 ± 0.1 pH measurements were done using a Schott laboratory pH-meter (model CG-843) equipped with a Metrohm combined glass electrode (model 6.0238.000). All manipulations and experiments were performed at 20°C. Additives were dissolved in the BaCl₂ solution by vigorous stirring overnight before mixing with the silicate solution, with final concentrations ranging from 0.1 to 10 mM (referred to total monomer concentrations in case of the polymer). All solutions were filtered before use. Both additives did not affect noticeably the pH of the mixture. Reaction mixtures are subsequently transferred into plastic cylindrical wells (Linbro Tissue Culture, ICN Biomedicals Inc.) of 1.7 cm in depth and 1.6 cm in diameter, and left with loose covers to avoid contamination but to allow diffusion of atmospheric carbon dioxide into the system. Continuous dissolution of CO₂ and formation of carbonate species in the alkaline mixture leads to BaCO₃ precipitation and biomorph formation. Growth is terminated after 8-10h in additive-free experiments. In the presence of the studied additives, growth time was reduced to roughly 6 h. Finally, mother solutions are removed, and the formed precipitates are washed several times with water, eventually with ethanol (Baker, p.a.), followed by drying in air.

Selective dissolution of the silica skin and the carbonate core of the as-prepared biomorphs were achieved by immersion of the

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Fig. 2. SEM images of (A) dendritically branched and spherulitic BaCO3 (witherite) microcrystals grown in the absence both of silica and organic additives under gas diffusion-controlled conditions ([BaCl₂]=5 mM, pH=11), and (B) a twisted-ribbon silica-witherite "biomorph" grown from solutions free of organic additives ([BaCl₂]=5 mM, [SiO₂]=8.9 mM, pH=11, Growth time: 9 h). Scale bar in (A): 10 μm.

aggregates in 0.1 M NaOH and 0.01 M acetic acid (Merck), respectively.

2.3. Analytical methods

Biomorph specimens were routinely examined by optical microscopy using a Wild microscope (Model M420). Selected aggregates were mounted on carbon adhesive tabs and gold- or carbon-coated for electron microscopy (Polaron E5200 SEM autocoating sputter unit and Balzers MED 010 sputter coater, respectively). Scanning electron microscopy (SEM) was performed using a Jeol JSM-840 microscope operated at 5 kV. Field-emission scanning electron microscopy (FESEM) studies were done using either a LEO 1530 or a Hitachi S4500 microscope, both working at 0.1-30 kV. Cryogenic transmission electron microscopy (cryo-TEM) was carried out using a Zeiss EM922 EF microscope working at an acceleration voltage of 200 kV. Samples were prepared by placing a small drop of solution on a plain carbon grid, removing subsequently excess liquid with a filter paper and finally plunging the grid into liquid ethane. TEM studies were performed at temperatures around 90 K. Images were recorded with a CCD camera (Gatan Ultrascan 1000) and processed using the Digital Micrograph 3.10 software package. The elementary composition of as-synthesized biomorphs was determined by means of energydispersive X-ray (EDX) analysis. Therefore, a number of specimens was collected and subsequently crushed and pressed to give a flat layer of material for proper analysis. EDX measurements were performed at a working voltage of 15 kV using an EDAX microanalyser installed on a FEI Quanta 400T scanning electron microscope. For X-ray diffraction (XRD) studies, selected crystal aggregates were mounted individually on cryo-loops (Hampton Research). Measurements were done at beamline XRD1 of the synchrotron radiation facility ELETTRA in Trieste, Italy. Data were collected under rotation at a fixed wavelength of 0.1 nm, using a two-dimensional CCD detector from Mar Research having 2048×2048 pixels with a pixel size of 78.1 μ m. The size of the incident beam was about $300 \times 400 \,\mu\text{m}^2$. Diffraction was thus taken from single aggregates in this work.

3. Results

3.1. Control experiments

Barium carbonate was precipitated from dilute aqueous solutions at high pH using atmospheric carbon dioxide as the

carbonate source. In the absence of both silicate species and organic additives, characteristic microcrystalline BaCO₃ dendrites and spherulitic bundles of needles are found in the growth cells after several hours in contact with the atmosphere (see Fig. 2), as reported previously for barium carbonate grown by gas diffusion reactions [12]. The presence of sufficiently high amounts of silicate during precipitation changes the situation dramatically. Micron-scale curved morphologies with non-crystallographic symmetries are observed at silica and barium concentrations ranging between about 7-15 mM (as SiO₂) and 5-500 mM, respectively, at starting pH values of about 9.5-12. We focus here on mixtures containing 8.9 mM silica and 5 mM BaCl₂ with a starting pH of 11. In the absence of any further additive, silica-barium carbonate self-assembly results in this case typically in racemates of regularly wound helical filaments (Fig. 2), curvilinear sheets as well as thicker croissant-like braids ("worms"), as documented in detail in earlier work [18,23,24].

In this work, the influence of a cationic surfactant (CTAB) and a cationic polymer (pDADMAC) on the morphology of barium carbonate biomorphs was studied. In a series of control experiments, BaCO₃ was precipitated in the presence of varying amounts of both substances at pH 11, with no added silica. Within the investigated additive concentration range (0.1–5 mM for CTAB, 0.1–10 mM as monomer for pDADMAC), there was little pronounced effect on the morphology of the crystals discernible in both cases, with classical faceted forms found in all batches. We note that the presence of the surfactant resulted in a larger number of smaller crystals, most of them being single pseudohexagonal witherite needles. The latter finding might be due to noticeable adsorption of CTAB on the surface of the crystals, as reported earlier for calcium carbonate [35].

3.2. Effect of the cationic surfactant CTAB

By contrast, adding CTAB to alkaline mixtures of barium chloride and silicate provokes significant morphological changes in the forming crystal aggregates at sufficiently high additive concentrations. First, when increasing the CTAB concentration from 0.1 to about 0.4 mM, typical biomorph forms such as spirals and worms are replaced by an increasing fraction of less regular clusters, mainly aggregates of globules with scrolled braid-like excrescences in most cases. Helical filaments were rarely observed in all additive-containing experiments. Indeed, uniformly twisted aggregates were never observed in growth media containing more 0.5 mM surfactant. Instead, increasing areas of rather flat, sheetlike regions appeared in the precipitates, with (hemi)spherical

overall aggregate shape becoming more and more predominant. At 1 mM CTAB, floral spherulites reminiscent of cloves are found in the growth cells after about 6 h. A second major fraction of particles formed under these conditions were spherulitic aggregates composed of straight filaments emanating radially from a common core, resembling to some degree certain sea anemones. Aggregate diameters vary roughly between 50 and 150 μ m in both cases. Fig. 3 shows typical biomorphic forms grown in the presence of CTAB.

The aggregate seen in Fig. 3D, obtained at 0.5 mM CTAB, is representative for the morphological transition observed when adding the surfactant: globular domains, typical for rather low CTAB fractions, co-exist with branched petalloid sheet-like regions. The latter form predominates at higher CTAB concentrations, giving floral spherulites. It is also worth noting that virtually all spherulites grown at 1 mM CTAB have flat bases exhibiting a central origin that is presumably the initial nucleation point, from which aggregate segments appear to radiate outwards (see Fig. 3E). These flat faces are likely to be cast from the walls of the plastic growth wells or the solution interface, since the aggregates frequently adhere to the walls or the surface of the solution. Similar observations were reported earlier for coralline calcium carbonate biomorphs [26].

3.3. Effect of the cationic polymer pDADMAC

Introducing the cationic polymer pDADMAC during the synthesis of silica-witherite biomorphs also induces significant changes in the morphology of the final crystal aggregates. Fig. 4 shows typical forms found after 6 h when adding 1 mM pDADMAC (monomer concentration) to the mother solution.

As in the case of added CTAB, a gradual morphological transition from regularly wound helices and worms (no added polymer) to flower-like shapes (1 mM referred to monomer) can

clearly be discerned. Overall, biomorphs realised on addition of the polymer are somewhat less regular than those grown in the presence of the surfactant, resembling (slightly withered) petalloid flowers. In turn, aggregates obtained in the presence of pDADMAC are slightly bigger than their CTAB analogues, with diameters typically between about 100 and 200 μ m. The bases of these flower-like architectures are likewise flat, as observed for the CTAB-induced spherulites, which is again probably due to the affinity of the crystal assemblies with the walls of the plastic wells. In other words, nucleation appears to be favoured at (or near) the walls, and growth then proceeds by continuous transport of reagents (or crystallites) from the solution to the initial nucleation site.

With both organic additives, another type of morphology is frequently found throughout most batches, which we refer to as "cauliflower-like" aggregates. Fig. 5 shows "cauliflowers" grown in the presence of 1 mM CTAB and pDADMAC, respectively. These ultrastructures are almost exclusively encountered at the surface of the reaction mixture after several hours of growth, in contrast to the flower-like morphologies that predominantly nucleate and grow on the walls.

The distinct morphological discrepancy between the aggregates formed on the cell walls and those grown at the surface can at this point be tentatively ascribed to different reaction kinetics prevailing deep in the solution and at its surface. Diffusion of atmospheric CO_2 into the reaction mixture and the resulting local concentration and pH variations are likely to be the governing parameters in this context. In the following discussion, we will focus on the flower-like morphologies shown in Figs. 3 and 4.

3.4. Variation of species concentrations

For both additives investigated, the optimal (monomer) concentration regarding a structuring effect was found to be



Fig. 3. FESEM images of witherite crystal aggregates grown in the presence of both silica and the cationic surfactant CTAB ([BaCl₂]=5 mM, [SiO₂]=8.9 mM, [CTAB]=1 mM (except for D), pH=11, Growth time: 6 h). (A) and (C) "Floral spherulites". (B) "Anemone-like" spherulite. (D) "Transitory" morphology obtained at 0.5 mM CTAB. (E) Bottom view of a floral spherulite. (F) and (G) Higher magnifications taken from sections of a floral spherulite. Scale bars: (A) 10 µm, (B) 10 µm, (C) 25 µm, (D) 25 µm, (E) 10 µm, (F) 1 µm, and (G) 5 µm.

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Fig. 4. FESEM images of BaCO₃ aggregates formed under the influence of both silica and the cationic polymer pDADMAC ([BaCl₂]=5 mM, [SiO₂]=8.9 mM, [pDADMAC]=1 mM (monomer concentration), pH=11, Growth time: 6 h). (A–C) "Flower-like" spherulites. (D) Bottom view of an aggregate. (E–G) Zoom sequence into a typical flower-like spherulite. Scale bars: (A) 10 µm, (B) 20 µm, (C) 20 µm, (D) 10 µm, (E) 20 µm, (F) 4 µm, and (G) 2 µm.



Fig. 5. FESEM images of "cauliflower-like" barium carbonate architectures grown in the presence of 8.9 mM silica and 1 mM of (A) the cationic surfactant CTAB, and (B) the cationic polymer pDADMAC. [BaCl₂]=5 mM, pH=11, Growth time: 6 h. In both cases, "cauliflowers" are found exclusively at the surface of the reaction mixture.

around 1 mM. Lesser amounts of additive also affected the final aggregate morphology, however their primary effect was simply to contort the regular helical or worm-like silica biomorphs. These "intermediate" morphologies can still be classified as noncrystallographic witherite biomorphs, not least due to their internal microstructure (see below). Increasing the additive concentration above 1 mM does initially not change the final product of the crystallisation reaction. However, above a certain threshold, biomorphic forms are no longer evident in the growth cells; rather, "classical" witherite microcrystals are obtained, as grown in the absence of both silica and organic additive (cf. Fig. 1A). Obviously, high fractions of surfactant and polymer effectively prevent the silica from interacting with barium and/or barium carbonate species, thus resulting in "regular" crystallisation. This finding can be attributed to the strong interactions between silica and both additives in alkaline solutions, as mentioned above. Recall that free (excess) additive likewise has little effect on conventional witherite crystallisation.

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Varying the silica concentration, while maintaining the content of organic additive, also changes the situation under certain conditions. Increasing significantly the amount of silica present during the syntheses suppresses of the influence of the additives. For example, regular silica biomorphs with familiar morphologies including spirals, sheets and worms form at 15 mM SiO₂ and 1 mM additive (cf. Fig. 1B). Presumably, the excess silica effectively locks up the organic additive in this case, leaving

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Fig. 6. Left: EDX spectrum of flower-like spherulites grown in the presence of pDADMAC (cf. Fig. 4). Right: X-ray diffraction data acquired from single floral spherulites, confirming the witherite crystal lattice. The shown diffractograms were calculated by averaging over all angles in the original diffraction image (see inset).

additional silica exempt from the influence of the additive to exert its specific effect on witherite crystallisation, resulting in usual silica biomorphs. When decreasing the effective silica concentration, at first no noticeable change can be observed, until finally biomorph formation succumbs, giving way to conventional BaCO₃ crystallisation. The lower silica limit necessary for the formation of biomorphic aggregates in the presence of CTAB and pDADMAC is found to be somewhat higher than in additive-free experiments (about 4 mM SiO₂, cf. Ref. [23]). Consequently, it can be concluded that both additives compete with barium (carbonate) species for interaction "sites" at the silica in solution.

3.5. Effect of the nature of the added cationic surfactant

In a further suite of experiments, the nature of the added cationic surfactant was varied both in terms of chain length and headgroup type. It was found that morphologies as shown in Fig. 3 form when the number of carbon atoms in the hydrophobic chain is equal to or higher than 13. Below this threshold, no noticeable effect of the additives on the morphology and structure of silica biomorphs could be discerned at comparable concentrations (i.e. helices and worms are formed). Significantly higher additive concentrations (50 mM or more) in turn affect aggregate morphology in a similar manner as simple salts such as sodium chloride, resulting in raspberry-like shapes [36]. All investigated surfactants with chains longer than C_{13} (up to C_{20}) appeared to exert virtually the same influence during biomorph growth, with flower-like shapes being predominant in all cases. A number of experiments were also done with distinct surfactant headgroups. The methyl moieties in CTAB were replaced by ethyl groups, and imidazolium was substituted for the quaternary ammonium. In addition, the bromide counter-ion of CTAB was exchanged by chloride and tetrafluoroborate. None of these changes imparted significant influence on the resulting morphologies.

3.6. Chemical analysis

The composition of the as-prepared flower-like biomorphs was verified by means of both X-ray diffraction and energy-dispersive X-ray analysis. For the former technique, single aggregates were selected, mounted on a cryo-loop and diffraction images were collected using synchrotron radiation while rotating the sample. Thus, diffraction data were collected from individual aggregates in this work. For EDX studies, a collection of biomorphs were subsequently ground and pressed to give a flat layer on a SEM stub. This sample preparation procedure was applied to ensure accurate quantitative EDX analysis, avoiding erroneous effects caused by locally varying sample height. Fig. 6 shows a typical EDX spectrum of a pDADMAC-induced flower-like aggregate, together with XRD data for both sample types.

The XRD data clearly prove the presence of crystalline aragonite-type barium carbonate (witherite structure) inside the samples. Furthermore, the diffraction images display complete rings, rather than discrete reflections or arcs (see inset in Fig. 6). This indicates that the aggregates consist of multiple crystallites whose orientation must be isotropic in average throughout the assembly. This finding differs from previous data on sheet-like silica-witherite biomorphs, which revealed to some degree preferred orientation of the crystallites within whole aggregates [20]. These differences can be ascribed to the different biomorph fractions sampled by the beam during XRD measurements. In particular, the floral structures consist of several (intergrown) sheets with distinct orientations within the aggregate, which leads to multiple overlapping patterns caused by individual sheets, giving rise to powder-like diffraction images. Indeed, we confirm below that local orientational ordering of the crystallites is also observed in biomorphs grown in the presence of additives, though the length scale of that ordering is rather small.

The EDX data confirm the presence of barium carbonate, and further identify certain amounts of silica. Quantitative elemental analysis averaged over several independent positions in the samples yielded the aggregate compositions shown in Table 1.

The Si content of the aggregates was thus found to be 11.79% and 7.08% relative to the Ba atomic count for CTAB- and pDADMAC-induced floral spherulites, respectively. Previous studies on the Si/Ba ratio in silica biomorphs led to a diverse range of values, depending on the type of morphology as well as on the respective position within an aggregate. For instance, Si/Ba percentages of 15–29% were reported for biomorph helices, while 6–35% was found for worms [18,37]. Coralline CaCO₃ biomorphs were claimed to contain 35–40% Si relative to Ca²⁶. However, as all

these analyses were performed on intact biomorphic architectures rather than ground and pressed powders, it is hardly possible to directly compare the present values to those previously reported. Further, the composite nature of biomorphs with their frequently occurring outer silica skin (see below) calls EDX studies on intact architectures into question, considering the limited penetration depth of the method. Light microscopy and FESEM images suggest that the silica content of the aggregates synthesized in this work is somewhat lower than that of silica biomorphs grown in the absence of additives.

Table 1

Elemental compositions and the silicon-barium atomic ratio of floral aggregates grown in the presence of CTAB and pDADMAC, respectively.

Additive	At% C (K)	At% O (K)	At% Si (K)	At% Ba (L)	% Si/Ba
CTAB	34.73	45.16	2.37	17.73	11.79
pDADMAC	37.64	45.13	1.22	16.02	7.08

Carbon, oxygen and silicon contents were calculated based on the K edge, while the L edge was used for barium. Values for the C and O content are less reliable due to background contributions.

3.7. Microstructure of flower-like spherulites

The microstructure of the flower-like morphologies produced with the aid of CTAB and pDADMAC is generally the same as that of classical silica biomorphs [18,23,24]. The interior of the aggregates is composed of an array of single elongated witherite nanorods, with a preferred orientation of the rods over the image area. The whole crystallite assembly is in turn occasionally sheathed by an outer amorphous silica skin, which consists of densely agglomerated siliceous nanospheres, as evidenced by the high-magnification FESEM images shown in Fig. 7.

The nanorods constituting the carbonate core were found to be about 300–400 nm in length and 50–100 nm in width, in good agreement with earlier work [17]. The diameter of the silica spheres establishing the outer skin is around 100 nm. The witherite nanorods are roughly aligned along the growth direction of the aggregates, i.e. radially outwards from the central origin, and appear to share a similar, but still slightly varying vector regarding their long axis. However, the long-range orientation field, characteristic of silica biomorphs, appears to be less regular here than reported elsewhere [23]. More detailed FESEM analysis and selected-area X-ray diffraction might clarify this question.



Fig. 7. The microstructure of flower-like morphologies produced by introducing CTAB (A) and pDADMAC (B) into the synthesis of silica biomorphs. Aggregates consist of an inner carbonate core which is constituted by single elongated BaCO₃ crystallites (right), and an outer amorphous silica skin composed of aggregated colloidal spheres (left). In order to reveal the inner core (rightward images), samples were leached in 0.1 M NaOH prior to FESEM studies.

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Nevertheless, given the nanometric microstructure as well the observed complex curved ultrastructures, crystal aggregates grown here in the presence of modest amounts of organic additives can unambiguously be classified as "silica–carbonate biomorphs" due to their composite microstructures, with intimate intergrowths of nanocrystalline witherite and (amorphous) silica.

3.8. Leaching experiments

The composite nature of such biomorphs can further be clearly visualized by selective dissolution of single components. On the one hand, immersion in dilute base removes the outer silica sheath, leaving an intact silica-free carbonate core (see Fig. 7). On the other, leaching with dilute acid has shown to be effective to dissolve any carbonate material, resulting in a hollow silica "ghost" whose ultrastructure thereby remains unchanged [20,23,24,26]. A typical time-lapse sequence of optical micrographs showing the dissolution of the carbonate core from flower-like aggregates grown in the presence of pDADMAC is given in Fig. 8.

We note, however, that many aggregates in a single batch do not exhibit distinct silica skins; the fraction of sheathed aggregates varies from batch to batch. Comparative carbonate dissolution studies with additive-induced morphologies and additive-free silica biomorph forms (helices and worms) give the impression that silica skins are less frequently found on the former than on the latter, as already suggested above. Irrespective of this, there were no differences in sheathed fractions across distinct morphologies induced by the same additive (e.g., between floral and anemone-like spherulites in the case of CTAB). Finally, it became obvious over the course of these studies that on average a lower fraction of particles possess an outer silica skin when using pDADMAC as additive than with CTAB. This finding is also reflected in the EDX data (cf. Table 1).

4. Discussion

The self-assembly of alkaline-earth metal carbonates in the presence of silica is a fascinating process from both crystallographic and colloidal perspectives, with significant implications for the increasingly important field of biomimetic materials. Although growing attention has been paid to these materials over recent years, resulting in manifold complex architectures, still little is known about their physical origin [15–26]. This is not least due to the many parameters governing the precipitation process, all cooperating and changing simultaneously on different time and length scales during the growth process. In the present study, selected additives were employed in order to firstly investigate their influence on the morphology (and structure) of "classical" barium carbonate biomorphs. In particular, additives were chosen that are capable of strongly interacting with the primary additive silica, namely the cationic surfactant CTAB and the cationic polymer pDADMAC. Since these substances are likely to affect the silica speciation in solution, changes in final aggregate morphology can provide indirect hints on the interplay between barium (or barium carbonate) and silica species resulting in silica biomorphs.

The effect of the additives can be summarised as follows. Relatively small amounts of both substances clearly shift the morphology of the forming aggregates, from helices and worms in the absence of additives to predominantly flower-like spherulites at 1 mM. In the case of the surfactant, moreover "anemone-like" spherulites were frequently isolated throughout the syntheses. Despite this change in aggregate ultrastructure on the multi-µm scale, the typical nanometric-scale microstructure of silica biomorphs apparently remained unaltered, with single elongated witherite nanocrystallites found throughout the assemblies. Aggregates grown in the presence of additives were occasionally sheathed by an amorphous silica skin, though to a somewhat lesser extent than in the absence of additives. Possible ramifications for



Fig. 8. Time-lapse sequence of carbonate dissolution from pDADMAC-induced flower-like aggregates by leaching in 0.01 M acetic acid (from top left to bottom right), leaving a structurally intact silica "ghost". Time interval between frames: 220 s. Scale bar: 100 µm.

the theory of biomorph growth mechanism(s) are worth canvassing in the light of these observations.

Recent ideas on the formation mechanism of silica biomorphs fall into two classes [23]. The first model posits a "bottom-up" mechanism, where the primary building blocks of the final aggregates, i.e. the carbonate nanocrystallites, form first and subsequently self-assemble, mediated by silica, to yield the characteristic curvilinear morphologies of biomorphs. In this context, it is probable that carbonate nuclei and/or nanoscale particles readily interact with silicate species, the latter potentially stabilising such particles and promoting their aggregation, perhaps also inducing curved forms through successive branching of silica-coated crystallites [25]. Differential adsorption of silica on crystallographically distinct faces of the carbonate nanocrystals may steer the crystallite self-assembly, as described recently for the system BaCO₃—double-hydrophilic block copolymer [28]. The model then implies that the local orientational order observed in biomorphs is induced by particular interactions between individual nanorods, possibly caused by locally varying surface charge due to their shape anisotropy.

The second model supposes a "top-down" mechanism, whereby a membrane of silica colloids, extant in the alkaline mixtures of silica and divalent cations prior to commencement of carbonate precipitation, templates the large-scale biomorph structure [23]. From this perspective, addition to the silica sols of alkaline-earth cations triggers condensation of silica, resulting in mesoscale spherical colloids whose naked surface charge is negative at the elevated pH. The cations provoke further aggregation of the silica, by screening the electrostatic repulsion in-between colloids. The latter possibility was already postulated by Iler in the 1950s [38]. A pre-requisite for this explanation for biomorph growth via cation-induced aggregation of silica colloids is the formation of a membrane which directs structured carbonate crystallisation. A possible candidate for that membrane is the silica skin observed on many of the aggregates, composed of a quasi-monolayer of densely packed siliceous nanospheres (cf. Fig. 7). Geometrical considerations lead to the possibility of the membrane shape being induced by the preferred coordination of the silica spheres making up the membrane; a roughly constant coordination number of (equal) spheres is expected to lead to a template membrane whose Gaussian curvature is also close to constant. Indeed, some biomorph shapes resemble certain standard surfaces of differential geometry with constant Gaussian curvature. On that basis, different biomorph morphologies, i.e. membrane curvatures, can be explained by locally differing charge and pH balances [23]. However, this membrane-templating model offers no insights into the origin of orientational order between the crystallites.

In view of this "top–down" model for biomorph formation, the effect of the studied additives on the final morphology must be discussed primarily in terms of their possible roles during silica colloid aggregation. It is well-known that both CTAB and pDADMAC tend to flocculate silica sols, though usually at significantly higher silica concentrations than in the present experiments. Indeed, ller reported the formation of more or less flat layers of agglomerated silica spheres when adding CTAB to alkaline silica sols [38]. It was claimed that charge screening and simultaneous bridging of the colloids by cationic micelles leads to pronounced aggregation and layer formation. Similar bridging effects were expected for cationic polymers. This concept is schematically reproduced in Fig. 9.

A possible check on the validity of a membrane-templating model arises from a comparison of biomorphs grown in the presence of additives with additive-free silica-witherite biomorphs. In the latter case, a membrane can form by aggregation of silica colloids due to naked Ba²⁺ ions, whereas those grown in the presence of additives are formed by additive-bridged colloid sphere association. Clearly, the coordination number of the spherical colloids within the membrane – and consequently also the curvature of the template membrane - depend on colloidal interactions at work in the solution, themselves dependent on local concentrations and pH. It is reasonable to expect that added cationic surfactant or polymer would "support" the inorganic cations in arranging the colloids, as depicted in Fig. 9. Additives are therefore likely to affect the final morphology, assuming that the shape of a feasible template membrane is imprinted on the later crystal assembly. The observed flower-like morphologies, found in the presence of additives, are rich in rather flat, sheet-like domains. Bridging conformations as seen in Fig. 9 can allow growth of extended layers via accretion at the sheet edges, if the additives preferentially attach at these edges (due, for example, to higher local negative charge at the edges compared to the sheet faces). The detailed origin of two-dimensional forms, strikingly present in biomorph architectures also in the absence of additives, remains a mystery at this point.

Interestingly, floral spherulites have been observed previously in additive-free biomorphs when the Ba^{2+} concentration is high, typically around 0.5 M [23]. That earlier observation is consistent



Fig. 9. Bridging and consequential aggregation of negatively charged siliceous colloidal spheres induced by the presence of (A) a cationic surfactant and (B) a cationic polymer.

Please cite this article as: M. Kellermeier, et al., J. Crystal Growth (2009), doi:10.1016/j.jcrysgro.2009.02.044

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with our hypothetical scenario, since it is reasonable to assume that high cation density in solution allows increased cation screening at the growing edges, promoting colloidal accretion there. However, the cations are obviously significantly less effective in this context than the two additives, as 1 mM of the latter induce comparable changes to an additional 495 mM of the former. This finding is expected in the case of biomorphs grown with CTAB, since the cations promote colloidal accretion via electrostatic screening, whereas the surfactant additives assist accretion via hydrophobic interactions, which promote aggregation of bare additive chains protruding from the additivedecorated silica colloids. Note also that the surfactant additive chain length must be sufficiently long (at least tetradecyl, see above) to establish conformations as depicted in Fig. 9, presumably due to insufficient hydrophobic driving force for shorter-chain analogues. In this latter case, surfactant molecules contribute to silica charge screening and agglomeration in a similar manner as simple monovalent salts below the cmc. Above the cmc, surfactant micelles are expected to interact with the silica colloids like multivalent cations.

It is also worth noting that the "anemone-like" spherulites found as second main morphology in the case of CTAB appear to be ancestors of the floral structures. No such precursor morphologies could in turn be discerned for pDADMAC-induced flowerlike forms. Evidently, the growth mechanism in the presence of pDADMAC differs at least to some degree from that of CTAB. The frequent incidence of these spherulites in our experiments indicates that growth is not terminated at individual aggregates after 6 h, meaning that the formation process is either slower in these cases, or that nucleation occurs continuously over a certain timeframe. Whereas the anemones have a short growing front exposed to the solution at their tips, the floral structures have a much longer boundary, corresponding to the sheet edges. Sheetlike domains form by lateral growth of single members, ending in fusion, induced by a slow turnover from high line energy to low line tension of the growing tips in solution. This transition is likely due to changes in chemical affinity of the growing edge for the mother solution.

The detailed nature of the interstitial material that effects condensation of colloidal silica in the case of CTAB remains uncertain. It may be coupled with the formation of CTAB aggregates on the silica surfaces, though the cmc for CTAB on silica is unknown. In any case, there were no structural changes detectable in this study whose onset correlated with a critical concentration, although the cmc of CTAB in aqueous solution (0.9–1.3 mM [39]) lies just in the concentration region of optimum structuring influence. Morphological transitions were found to occur smoothly as a function of additive concentration, rather than abruptly, perhaps reflecting a distribution of chemical species on growing edges within a batch, depending on local physicochemical conditions. It is therefore possible that silica condensation is caused by supramolecular assemblies of CTAB, such as micelles, or analogous pDADMAC aggregates, given sufficient concentration, allowing the growing edges to be coated with hydrophilic material (as in micellar surfaces). Lower concentrations could result in a "pseudo-hydrophobic phase" between the colloids as shown in Fig. 9.

A potentially fatal flaw in this model is the lack of a visible membrane on some of the aggregates. Indeed, the temporal sequence of membrane appearance (and possibly, disappearance) relative to carbonate growth is difficult to ascertain unequivocally. We find a certain portion of silica ghosts remain intact on acid leaching of the biomorphs in all batches, suggesting the presence of a silica skin of some type in biomorphs. Unfortunately, at this stage, it remains difficult to definitively accept or reject a membrane-templating model. For example, the possibility that silica membranes are secondary precipitates, condensed on extant biomorphs, cannot be excluded. Further, when assuming a top-down scenario, one may suspect that template membranes should also form in solutions containing only barium ions and silica, in the absence of any carbonate. Indeed, we observe that silica agglomeration occurs in a similar manner in carbonate-free mixtures as well (dynamic light scattering (DLS) data, not shown). However, silica membranes with characteristic shapes could not be imaged in these solutions to date. In summary then, a top-down model explaining the observed biomimetic morphologies in terms of membrane templating is not inconsistent with the experimental data, but compelling objections remain.

Discussion of the effect of the two additives on the basis of an alternative "bottom-up" model proves to be by far more speculative, since little information regarding specific adsorption of silica and organic additives on witherite faces at the atomic scale is available to date. Nevertheless, it is reasonable to infer from the model that silica species influence primary carbonate building blocks by short-range interactions. Regardless of whether there are selective adsorption effects, the speciation of the silica in solution, especially its degree of oligomerisation, must be an important parameter throughout any such interactions. This parameter is in turn expected to be sensitive to the presence of additives like CTAB and pDADMAC, since the latter will induce increased oligomerisation of the silica. In other words, the character of the "primary" additive silica in the reaction solution is affected by the introduction of "secondary" additives. The adsorption of silicate species onto carbonate crystallites under these conditions will follow different laws and kinetics. If the selfassembly of carbonate nanorods in the realm of a "bottom-up" model is governed by the action of silica species, then the additives are expected to interfere with the growth process, probably changing interaction energies and conformations between the crystallites (possibly by altering their surface charge distribution). This would readily lead to large-scale morphological differences compared with the additive-free preparations, as observed. In this scenario, the silica skin occasionally sheathing crystal assemblies must be a secondary effect, presumably resulting from the continuous pH lowering during growth.

We emphasise that both additives are not incorporated into the forming aggregates. This is verified by the EDX measurements (see Fig. 6), that reveal an absence of nitrogen peaks (although particular efforts were made to look for them during the analyses). IR spectra further support this finding, as all detected bands can be assigned to either silica or carbonate and no organic vibrations could be traced (data not shown). This is an interesting result, since one may expect the additives to be trapped within occluded silica between witherite crystallites in the bottom–up scenario, or within the template membrane responsible for biomorph formation in the top–down model. Washing processes may lead to effective removal of the organics.

However, cryo-TEM micrographs of particles taken from solutions at different growth times suggest an alternative "sink" for both additives in the course of the experiments. It was found that nanoscale mesoporous silica particles form during (or parallel to) growth, as shown in Fig. 10.

The size distribution of these particles is overall quite narrow, with diameters ranging approximately from 100–200 and 30–50 nm for CTAB and pDADMAC, respectively. The mesoporosity of the particles is in both cases clearly seen in the micrographs. Pore sizes were determined roughly from fast Fourier transforms (FFT) of the images (cf. inset in Fig. 10A). In the case of the surfactant, regular pores arranged mostly in a hexagonal or lamellar lattice could be discerned, with pore dimensions around 4.5 nm, which is in good agreement with previously described materials of the M41S family [31]. The pores found in the



Fig. 10. Cryo-TEM micrographs of isolated particles of mesoporous silica found in mother solutions of silica biomorphs growing in the presence of (A) the cationic surfactant CTAB, and (B) the cationic polymer pDADMAC. Samples were taken after 80 min of growth. Particles grown in the presence of CTAB exhibit domains of mesopores in regular arrays, as seen from Fourier transforms of the images (inset in (A), taken from the area marked in white, reveals regular hexagonal arrangement of pores).

nanoparticles formed in the presence of the polymer are not staggered in a regular manner, but seem to be interconnected, establishing a sponge-like structure throughout the particles with pore diameters of around 2.5 nm. Particles of similar morphology, size and internal structure were found in aqueous dispersions of certain lipid mesophases [40]. Recent studies on porous silica materials based on pDADMAC as structuring agent (Beta-H zeolite) reported both hierarchical mesopores of 5–20 nm in diameter and ordered micropores in the range of 0.8 nm in the samples [32].

Reasons for the apparent discrepancies as well as structural details concerning both pore systems will not be discussed further here. Nonetheless, it is worth noting that in the present systems isolated nanoparticles of mesoporous silica are found, whereas most other syntheses of such materials yield at least micron-scale, or larger, bulk phases. Furthermore, these particles have proven to be stable in our reaction mixtures for a minimum of 6 h, remaining suspended in solution instead of aggregating or even flocculating, and thereby giving a slightly turbid, bluish appearance to the mixtures. Moreover, it appears that mesoporous particles form continuously over a certain frame of time. Particles of sizes and shapes similar to those shown in Fig. 10A have been described in previous work on CTAB-induced mesoporous silica [41–43]. Both the dilution of the reaction mixtures and their pH have proven to be crucial parameters for particle size distributions in mesoporous silica materials (rather than the presence of alkaline-earth cations, as one might suppose).

There is a remarkable congruency in size of the mesostructured particles shown in Fig. 10 and those establishing the silica sheath of biomorphs. However, despite explicit efforts, no noticeable difference between the silica particles composing the skin in the absence and in the presence of the additives could be detected (though in particular the CTAB-induced particles are clearly featured by angled edges rather than being round). The observed size consistency may simply arise due to the tendency of silica to form colloids of such dimensions under the governing physicochemical conditions in solution, regardless of the presence of additives. We currently suspect that the formation of these rather monodisperse mesoporous particles is a process occurring parallel to the steps decisive for biomorph growth. In a set of control experiments, silica and additives were mixed in the absence of barium and carbonate species under otherwise identical conditions. It was found that particles as shown in Fig. 10 form nonetheless, with virtually identical size, structure and number (as evidenced by cryo-TEM and DLS data, not shown). Also, the kinetics of particle formation seems to remain unchanged when removing barium and carbonate ions from the mixture. These findings suggest that the formation of mesoporous particles indeed is a process uncoupled from biomorph growth.

On balance then, a top-down model affords a more ready explanation of the complex suite of observations described here. Current work is exploring the influence of other species capable of influencing in a similar manner the membrane geometry, such as added multivalent cations [36]. Our dichotomy of growth models may however, prove overly simple. Taking into account the present results and the (at least local) orientational order between the crystallites, a mechanism invoking both the action of a template and the self-organisation of carbonate nanorods may eventually afford a more thorough account.

We note that there is a previous study on the influence of additive species on the morphology of silica biomorphs [44]. Therein, the effect of added amino acids on the formation of biomorphs in silica gels was explored at different pH. In the light of our study, the results reported for the amino acids with positively charged side chains, i.e. Arg, Lys and His, are particularly interesting, as these too have ammonium functionalities. In the earlier work, a transition from filamentous braids to disc-like morphologies was found to occur at the highest pH investigated (pH 10). Changes were interpreted roughly in terms of selective adsorption onto either carbonate or silica species. The reported morphologies too are featured by regions of low degree of curvature and longer edge lengths. Although no detailed structural analysis is given in that work, the additives may well influence the biomorph growth process in a similar fashion to that proposed here, assuming that the amino acids can also perform certain bridging functions, analogous to our additives.

5. Conclusion

In the present study, the influence of two selected additives on the formation process and in particular the final morphology of "silica biomorphs" was investigated. For this purpose, a cationic surfactant (CTAB) and a cationic polymer (pDADMAC) were chosen, as both substances are known to maintain pronounced interactions with silicate species. It was found that flower-like spherulitic architectures primarily form at relatively low additive concentrations. These aggregates were characterized in terms of morphology, composition and structure. Based on the observed changes, conclusions could be drawn regarding possible morphogenesis pathways of silica biomorphs in general. It is proposed that both additives may enhance the formation of a silica membrane through aggregation of colloidal siliceous spheres, which later templates structured carbonate crystallisation. The shift in morphology resulting when adding surfactant or polymer was in this context ascribed to changes in the solvophobicity of the membrane growing front and hence also in membrane curvature, caused by specific bridging of the colloids by the additives. Taking into account the present results and previously reported studies, a mechanism comprising both the action of a template membrane and the self-assembly of primary building blocks seems most likely to be responsible for the formation of silica biomorphs at the moment.

Acknowledgements

The authors thank Alberto Cassetta and Luisa Barba from the ELETTRA Synchrotron Light Source (Trieste, Italy) for their helpful support during beamtime at XRD1. Emilio Melero García and Duane Choquesillo Lazarte (Laboratorio de Estudios Cristalográficos, IACT, Granada, Spain) are kindly acknowledged for valuable discussions and their help with the XRD measurements. We are further grateful to Björn Bartel (University of Regensburg) for carrying out the EDX measurements. Matthias Kellermeier appreciates the granting of a scholarship by the Fonds der Chemischen Industrie. Markus Drechsler and Benjamin Gossler acknowledge financial support by the Deutsche Forschungsgemeinschaft (SFB 481). Stephen Hyde is grateful to the Australian Research Council for the award of a Federation Fellowship.

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