Crystallization of Calcite Spherules around Designer Nuclei**

Jörg Küther, Ram Seshadri, and Wolfgang Tremel*

Dedicated to Professor Bernt Krebs
on the occasion of his 60th birthday

Living systems exercise considerable control over the crystallization of certain inorganic minerals.[1] This control extends to the nature and habit of the mineral polymorph and is usually guided towards a specific function. Sometimes this is achieved in seeming contradiction to thermodynamic expectation. An additional level of complexity is reached when living systems form composite structures that organize minerals in organic matrices.[2] The utility of organic–inorganic interfaces in mimicking these biomineralization processes have been exploited in the past. Langmuir monolayers,[3] protein-coated substrates,[4] polymer dispersions,[5] micellar media,[6] and self-assembled monolayers (SAMs)[7–9] have been used as templates or substrates for the crystallization of minerals such as calcium carbonate. We demonstrate here that standard SAM chemistry can be extended to produce controlled nanoscopic surfaces for the heterogeneous nucleation of inorganic minerals from aqueous solution. The seeds are about 5 nm large gold colloids coated with a *p*-sulfanylphenol SAM. An interesting aspect here is that while the nucleation is heterogeneous in the sense that it takes place at the liquid–solid interface, it commences from within a single homogeneous phase.

We have been interested in the crystallization of the carbonates of calcium and, to a lesser extent, strontium on self-assembled monolayers of long chain thiols, organized in two dimensions on gold-coated glass substrates.[8–11] Inspired in part by the kinds of processes taking place in living systems, we have examined how different substituents at the positions of the thiols can influence the nature and morphology of the calcium carbonate polymorph (calcite, aragonite, or vaterite) formed. In certain cases, we have also been able to establish a relationship between the specific 2D structure of the SAM and that of the growing crystal.[9] These studies complement existing work and have provided some insight into the templated crystallization of carbonate biominerals. Furthermore, they suggest mild routes to useful materials.

During the course of these studies, gold colloids attracted our attention. Their small size (in the range of 2–10 nm for the methods presented here) ensures that for a given quantity of gold a relatively large surface area is obtained. The self-assembly of thiols on gold colloids has in fact provided routes to preparing particles that are stabilized against aggregation and whose solubility in different solvents can be controlled through the size and functionality of the thiol molecules.[12, 13] Thiol-coated gold colloids can be purified by chromatography, evaporated, recondensed, precipitated, and redissolved; this is behavior that one usually associates with molecules.[12, 14, 15] Recently, we have been able to functionalize gold colloids with a Ru-containing polymerization catalyst to obtain a material that bridges homogeneous and heterogeneous catalytic behavior.[16] When coated with *p*-sulfanylphenol, the colloids are soluble in water at a pH value of about 12 or higher.[13] While solutions of these colloids are homogeneous in every sense, the colloids possess a surface capable of heterogeneous nucleation. These thiol-coated gold colloids can therefore be used to seed the crystallization of materials from saturated solutions. The different topologies of flat and spherical templates is to be noted. The use of gold colloids instead of flat gold surfaces should permit novel crystal or crystal-aggregate geometries to be obtained through templated crystallization.

Fritz et al.[17] have studied the formation of flat pearls on inorganic substrates inserted between the shell and mantle of the red abalone. They have determined that oriented calcite and template protein layers are initially formed. This is followed by the growth of stacks of aragonite along the pseudo-sixfold axis of the crystal. The proteins are generated within epithelial cells in the abalone mantle. Our approach is in contrast to this. We do not attempt to simulate natural pearls, but rather seek inspiration from the manner in which they are formed. The templating organic substance is the *p*-sulfanylphenol SAM. This is previously fixed to the substrate on which the crystallization is carried out rather than being in solution, which is the case in the formation of natural pearls.

The top right of Figure 1 shows schematically the thiol-coated particles used to nucleate the precipitation of calcium carbonate. At different seed concentrations (10–100 mg L^{-1}) and temperatures (4–45 °C) the only polymorph we observe is calcite; a sample X-ray diffraction pattern is displayed in Figure 1.[18] The effect of the colloid seeds on the crystallization is observed in the scanning electron micrographs. Figure 2a shows rhombohedral crystals of calcite formed when crystallization was carried out at 22 °C in the absence of the colloid seed. This is the expected morphology. The presence of the colloids (here 100 mg L^{-1}) initially gives the solution a deep pink color. By the end of the crystallization, the solution is colorless and the scanning electron micrographs of the grey-black precipitate display a completely different morphology (Figure 2b). At higher magnification (Figure 2c), a typical crystallite assembly shows the individual spherules of Figure 2b to comprise a complex assembly of the calcite rhombohedra. The direction radiating out from the center is the direction connecting opposite edges of the calcite rhombohedra, that is, the crystallographic [001] direction.

Crystallization experiments carried out under identical conditions on flat *p*-sulfanylphenol SAM/gold surfaces (as opposed to colloidal seeds) do not suggest any sort of epitaxy between substrate and crystal. The crystallization on the flat surfaces is inhibited and results in rather ill-defined morphologies, perhaps because the phenolic OH groups are ionized at the high pH used. This does not seem to affect the efficiency

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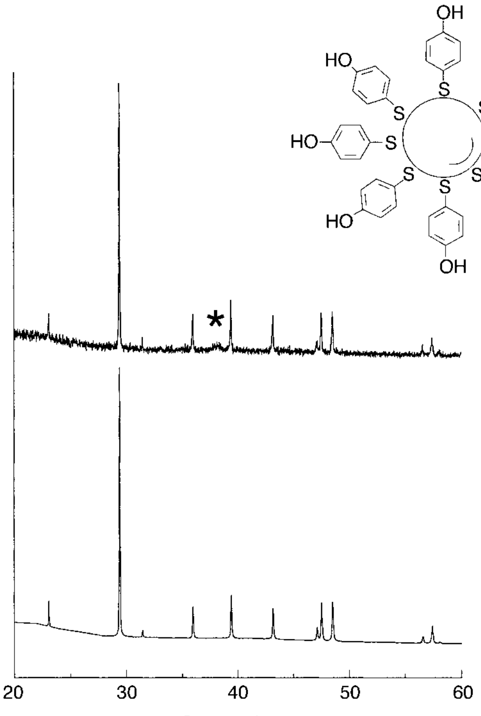

Figure 1. Measured and Rietveld-fitted X-ray diffraction profiles (transmission, $\theta-2\theta$) of $CaCO_3$ crystallized from solutions containing thiol-coated gold colloid seeds. The fit indicates pure calcite; the small hump marked by an asterisk is due to the (111) reflection of gold. The concentration of seeds used was 100 mg L^{-1} in solution, and the crystallization was carried out at 22 °C.

of the seeding, however. The organization of the calcite rhombohedra therefore arises from crystal–crystal interactions rather than crystal–substrate interactions, and from the fact that the crystals are obliged to pack around a sphere.[19] The manner in which the solution becomes clear after precipitation as well as the morphologies obtained in the presence of the colloid suggest that the colloids act as nuclei or seeds. We point out that the assemblies display a level of complexity that cannot be achieved with flat templates. The assemblies of the calcite rhombohedra are rather fragile. So far, attempts to fragment the spherules in order to better understand their structures have always resulted in the individual crystallites being damaged. It is possible that well-defined rhombohedra are found only near the outer surfaces of the spherules, and that within the spherules the morphology is quite different.

Figure 3a shows the precipitates obtained when the crystallization is carried out at about 4 °C instead of at 22 °C and fewer seed particles are used (30 mg L^{-1}). The morphology is still spheroidal, but at higher magnification (Figure 3b) it is seen to comprise spherulites rather than spherules, that is, needlelike crystals that radiate from a central point. Despite the changed morphology, X-ray diffraction experiments confirm that the samples are pure calcite.

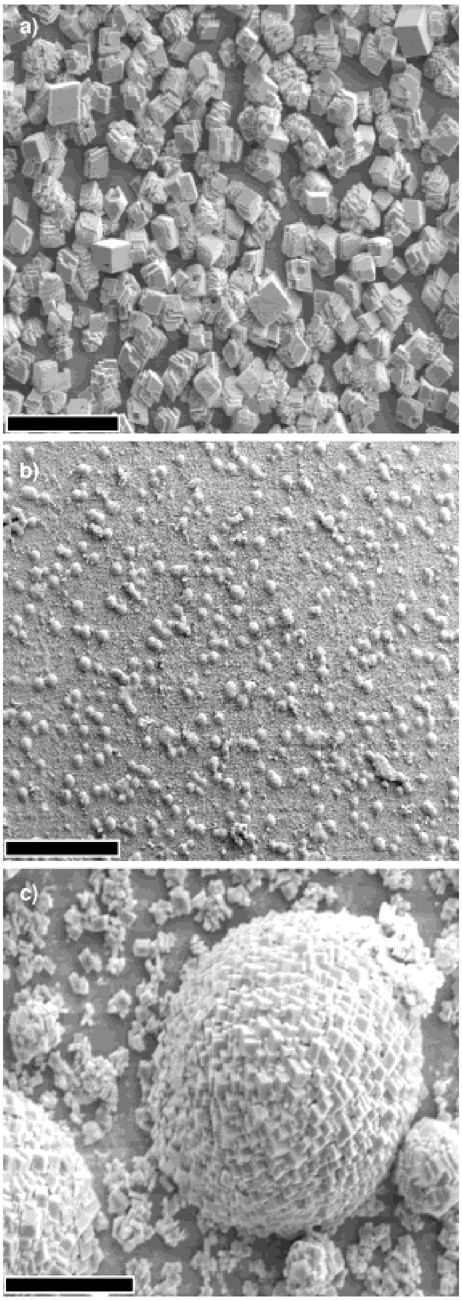

Figure 2. a) Scanning electron micrograph of the crystals formed by precipitation of $CaCO_3$ from solution at 22 °C. The rhombohedra are crystals of calcite displaying {104} faces. b) Scanning electron micrograph of the crystals formed on crystallization in the presence of the seeds (100 mg L^{-1} at 22 °C). A typical crystallite assembly seen at higher magnification is shown in c); the rhombohedra arrange spherically around some central point. The scale bars correspond to 50, 500, and 20 μm, respectively.

The precipitates formed at 22 °C, unlike those formed at about 4 °C, comprise crystals with well-defined morphologies. Correspondingly, the X-ray diffraction profiles possess narrower linewidths. This is expected from considerations of the supersaturation ratios at the two temperatures. However, the dependence of the size of the precipitates on the amount of seed colloids used does not follow expectation. This could be because the distribution of sizes is not monomodal, as suggested from a closer analysis of the micrographs. Additionally, the number of seeds used are far in excess of the spherules that are formed. It is possible that some the seeds are incorporated into the spherules during the later stages of the crystallization. The spherelike nature of a large proportion

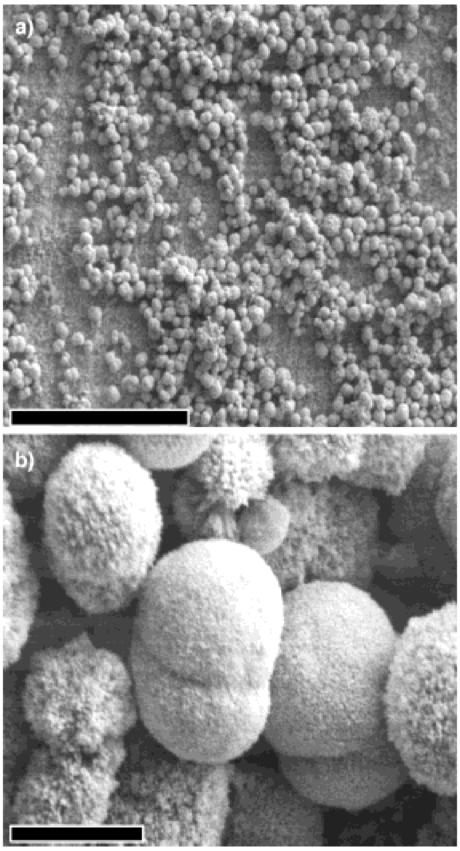

Figure 3. Scanning electron micrographs of precipitates obtained from crystallizations (30 mgL^{-1}) at about 4°C. The spherelike morphology is retained (a), while at higher magnifications (b) differences become visible. The individual crystallites making up the assemblies are no longer rhombohedral, but fluffy and branched. Some bilobed structures are also observed. The scale bars correspond to 200 and 10 μm, respectively.

of the products also indicates that the spherules fall out of solution onto the witness glass slides only after nearly all the calcium in solution is depleted, as there is little or no growth of the assemblies after they settle.

The high initial pH value at which the crystallizations are carried out seems to favor the formation of calcite at the expense of aragonite. To simulate the formation of aragonite spherules, we crystallized $SrCO_3$, whose stable modification strontianite has the same structure. The different crystal structure (orthorhombic *Pmcn* for strontianite/aragonite, rhombohedral $R\bar{3}c$ for calcite) usually results in the phases precipitating from solution with completely different morphologies.[9] An attempt to make strontianite spherules is shown in Figure 4. The usual strontianite (or aragonite) morphology is needlelike. The use of the colloid seeds seems to induce the needles to cluster around a central point. This additionally demonstrates the utility of our designer nuclei.

Self-assembled monolayers of thiols on gold (or other) substrates can induce the controlled crystallization of inorganic materials, whereas gold colloids provide a novel way of looking at gold surfaces. The marriage of these concepts yields a method for controlled heterogeneous nucleation with the result that the crystallite assemblies so formed are very different from what one obtains (and what one can possibly obtain) with flat templates. The seeds are in solution and, hence, perfectly wetted. Classical theory predicts that they should act very much like homogeneous nuclei.[20] This is not observed in the micrographs. The examples outlined here testify to the ease with which nanoscopic seeds can be designed and used for controlled crystallizations.

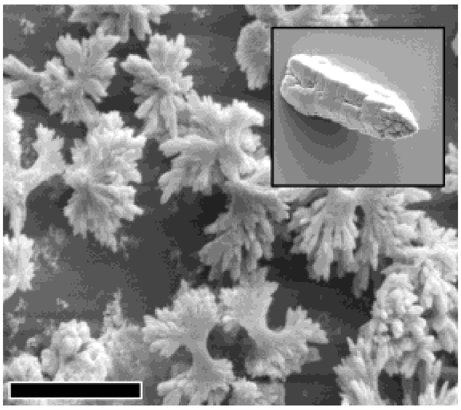

Figure 4. Scanning electron micrograph of $SrCO_3$ crystals precipitated from solutions containing the colloid seeds (30 mgL^{-1} at 4°C). The scale bar corresponds to 10 μm. The inset shows a needle (ca. 15 μm long) of $SrCO_3$ in the strontianite modification obtained from precipitation in the absence of colloids. The needle grows along a pseudohexagonal [001] trilling axis.

Experimental Section

The gold colloids (diameters near 5 nm) were prepared in two-phase toluene–water systems by reported procedures.[11, 12] The organic phase was isolated and then mixed with a solution of *p*-sulfanylphenol in toluene, causing the colloids to precipitate. Surface plasmon spectroscopic measurements confirm that *p*-sulfanylphenol forms densely packed monolayers on gold surfaces. Attempts to obtain the 2D structure of the *p*-sulfanylphenol SAMs (on gold/mica) through atomic force microscopy failed due to the high acidity of phenolic OH group. Also the small size of the *p*-sulfanylphenol molecule might prevent its forming crystalline monolayers. The precipitate was washed and dried before being dissolved in 10 mM solutions of calcium or strontium chloride, whose initial pH value was raised to 12–13 with aqueous NaOH. The rather alkaline pH are necessary in order to take the colloids into homogeneous solution.[13] Precipitation of the carbonate was induced in closed desiccators through the slow diffusion of CO_2 from solid $(NH_4)_2CO_3$ placed within the desiccator. After 48 h the precipitates, which were collected on glass slides, were removed and fixed to aluminum stubs using conducting carbon glue. Before transferring to the microscope, gold was sputtered on to the glass slides.

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[18] When the crystallizations are performed on *p*-sulfanylphenol SAMs on gold/glass substrates rather than on colloids, no modification other than calcite is observed. However, when the pH value is lowered to about 10.5, the aragonite:calcite ratio of crystals deposited on *p*-sulfanylphenol SAMs on gold/glass is about 40:60 at 22 °C and 85:15 at 45 °C, as determined from the Rietveld refinement of powder X-ray profiles. These are the highest aragonite weight fractions that we have been able to obtain at 22 °C on SAMs of simple thiols. We are now attempting to prepare colloids coated with thiols that permit dissolution of the colloids in water at neutral pH values in the hope of inducing aragonite.

[19] On the other hand, the use of (flat) SAM/gold templates with a well-defined hexagonal 2D crystal structure, such as SAMs of hexadecanethiol, result in calcite crystallizing with the [001] direction nearly always perpendicular to the substrate, suggesting the role of epitaxy.[9]

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Enantioselective Allylic Substitution of Cyclic Substrates by Catalysis with Palladium Complexes of P,N-Chelate Ligands with a Cymantrene Unit**

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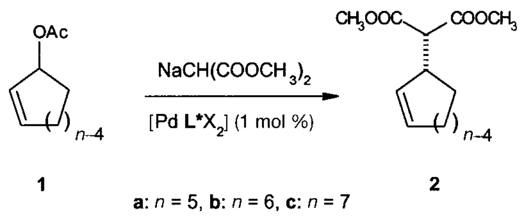
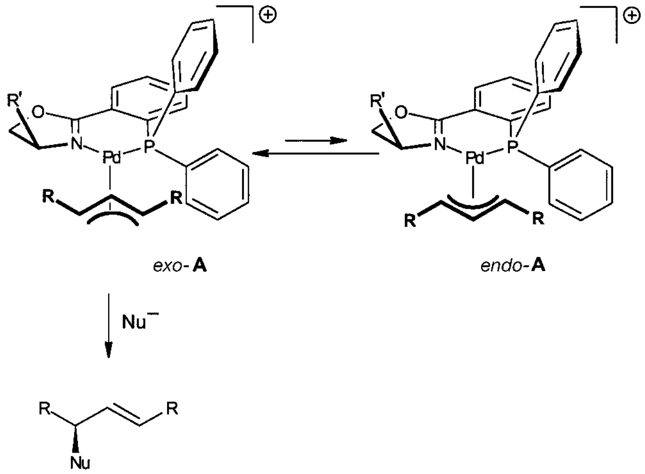
Palladium complex catalyzed asymmetric C–C bond forming reactions with allylic compounds are being investigated with great intensity.[1] As ligands, modular C_2 diphosphanes[2] and phosphanylcarboxylic acids[3] gave good results, particularly with small cyclic substrates. For acyclic substrates, chiral phosphanyldihydrooxazoles were successfully used as ligands,[4] and enantioselectivities of up to more than 99:1 were achieved. However, cyclic substrates **1** (Scheme 1) furnished low enantioselectivities with these ligands. Because of the favorable properties of phosphanyldihydrooxazoles, such as ease of synthesis and high turnover numbers in catalysis, it was of interest to develop ligands of this type that are suitable for cyclic substrates. We found such compounds on the basis of mechanistic considerations.



Scheme 1. Palladium complex catalyzed allylic substitution of cyclic allyl acetates.

Key concepts of the reactions with dihydrooxazoles and other P,N ligands[5] are a) the assumption of preferred attack of the nucleophile at the carbon atom of the allyl group in the position *trans* to the phosphorus atom and b) the postulate that of the diastereomeric *exo*- and *endo*-π-allyl complexes **A** (Scheme 2), the *exo* isomer reacts faster. As the relative reactivities of these diastereomers are nearly equal, the ratio of their concentrations mainly determines the enantioselectivity of the substitution. The reason for the low selectivity with cyclic substrates is insufficient differentiation, that is, equal populations of *exo* and *endo* isomers.



Scheme 2. The *exo*–*endo* isomerism of π-allylpalladium complexes with phosphanyldihydrooxazole ligands (R' = *i*Pr, *t*Bu).

With second-generation ligands, the enantioselectivity for cyclic substrates was increased significantly by substituting the pseudoaxial phenyl group by a 2-biphenylyl group;[6] *ee* values of 50–80% were obtained. The higher enantioselectivity had been anticipated, since the crystal structure of complex **B** with R = *i*Pr and $n = 6$ displayed only the conformer in which the terminal phenyl group is directly above the allyl system. This conformer is the most favorable for achieving high selectivity. According to ^{1}H NMR NOE measurements,[7] conformer **B** is in equilibrium with conformer **C**, in which the 2-biphenylyl group is rotated away from the palladium center and does not interact with the allyl group. To restrict rotational freedom of

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