DALTON

Selective crystallization between $CuSO_4 \cdot 5H_2O$ and $Na_2SO_4 \cdot 7H_2O$ under a monolayer

Ruikang Tang,[a] Zihou Tai *[,a] and Yiqun Chao[b]

[a] *State Key Laboratory of Coordination Chemistry, Institute of Coordination Chemistry, Nanjing University, Nanjing 210093, China*
[b] *Institute of Solid State Physics, Department of Physics, Nanjing University, Nanjing 210093, China*

Two selections have been found to occur in the crystal growth induced by a monolayer of 9-(hexadecylimino)-4,5-diazafluorene. Between $CuSO_4 \cdot 5H_2O$ and $Na_2SO_4 \cdot 7H_2O$, although both were supersaturated, only the former was chosen to nucleate under the monolayer and the latter formed at the bottom of the container. Furthermore, among all of the crystal faces of $CuSO_4 \cdot 5H_2O$, the (010) face was selected by the monolayer and the crystallization was oriented. In these processes, the monolayer plays a very important role and acts as a template which can recognize a certain crystal and a certain crystal face. This is due to specific molecular interactions between ions and the hydrophilic head groups of the monolayer, and the influence of some factors including ion binding, lattice matching and structural complementarity. Using the principles of hard–soft acid–base theory, coordination theory and by computer simulation, it was found that the dimensions of the (010) face of $CuSO_4 \cdot 5H_2O$ match those of the monolayer very well.

Recently, a new field of inorganic chemistry, usually called biomineralization, has been developing rapidly as the crystallization of inorganic solids in biological systems proceeds in an oriented fashion.[1–4] In these systems the substrates are often various organic frameworks. Unlike inorganic surfaces, the chemical, steric and structural properties of these organic substrates will be critical factors in the control and organization of bioinorganic solid formation. A central tenet of biomineralization is that the nucleation, growth morphology and aggregation of the inorganic crystals are regulated by organized assemblies of organic matrices.[4]

A different approach is the use of simplified organized surfaces, which are compressed monolayer surfactant films formed at air–water interfaces, as substrates for inorganic crystallization from supersaturated subphases. Addadi and co-workers[5,6] have used compressed amino acid monolayers as templates for the nucleation of inorganic and chiral organic crystals. Mann, Fendler and Addadi and co-workers[5,7–13] have studied the nucleation of some inorganic minerals such as $CaCO_3$ and PbS using compressed monolayers formed at the air–water interface as the organic matrix. Their results show how organized organic surfaces control the nucleation of inorganic materials by geometric, electrostatic and stereochemical complementarity between incipient nuclei and functionalized substrates.

In this paper we report the selective crystal growth between two soluble inorganic compounds under a monolayer. In general, crystals are formed as a new phase (solid state) arising from a less stable phase (supersaturated solution). During this process, an important function is the supersaturation ratio S defined as c/c_0, where c is the concentration of ions in the solution and c_0 the ionic concentration at equilibrium. Nucleation will occur and progress if the value of S is higher than 1 since the supersaturated solution is unstable. Assuming that there are two kinds of solutes in a mixed solution and these solutes are supersaturated, as a general rule of thumb, both solutes will separate out of the solution and coexist as crystals at the bottom of the container. However, in the present work, when a monolayer film of 9-(hexadecylimino)-4,5-diazafluorene (L) was spread on a solution containing $Na_2SO_4 \cdot 7H_2O$ and $CuSO_4 \cdot 5H_2O$ the results were different. Upon crystallization from the supersaturated solution, $Na_2SO_4 \cdot 7H_2O$ was always deposited at the bottom; but $CuSO_4 \cdot 5H_2O$ appeared at the monolayer–water interface and the millimeter-sized crystals had a special face (010) on their surface. This indicates that selective crystallization occurred under the L monolayer, and is closely related to the inorganic–organic interface, and the influence of some factors such as ion binding, lattice matching and structural complementarity between the crystals and the monolayer.[7–12]

Experimental

The synthesis and aggregation behaviour of L has been reported previously.[14] In the experiment, $Na_2SO_4 \cdot 7H_2O$ (20 g) and $CuSO_4 \cdot 5H_2O$ (38 g) were added to water (100 g) at 40 °C; the water used was doubly distilled and purified by ion exchange. When the solutes had dissolved the temperature was reduced to 30 °C. Then, the solution was filtered carefully and the filtrate comprised a saturated solution of both $Na_2SO_4 \cdot 7H_2O$ and $CuSO_4 \cdot 5H_2O$ at 30 °C, to be used later. On the surface of the filtrate, a monolayer of L was carefully and slowly spread from a 1×10^{-3} mol dm^{-3} solution in chloroform. The volume of the spreading solution was estimated from the cross-section of the crystallization vessel and limiting area per molecule, 35 Å^2, obtained from the surface pressure *vs.* area isotherm of L on a subphase containing copper ions.[14] After the chloroform had been volatilized, a stable monolayer of L was formed (limiting area 35 Å^2, surface pressure about 35 mN m^{-1}). Then the temperature was slowly decreased and crystals of both $Na_2SO_4 \cdot 7H_2O$ and $CuSO_4 \cdot 5H_2O$ separated from the mixed supersaturated (supercooled) solution.

The experiment was recorded photographically. The $CuSO_4 \cdot 5H_2O$ crystals formed at interfaces or in solution were studied by optical microscopy and the crystal faces of the samples examined by a rotating-anode X-ray diffractometer (D/Max-RA, Rigaku, Japan).

Results and Discussion

In the absence of the monolayer, the crystallization of $Na_2SO_4 \cdot 7H_2O$ and $CuSO_4 \cdot 5H_2O$ was uncontrolled. Both kinds

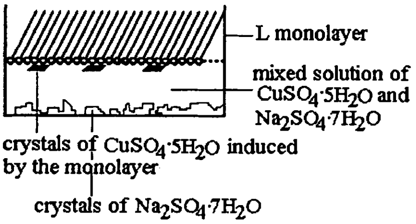

Fig. 1 Crystallization of solutes $Na_2SO_4 \cdot 7H_2O$ and $CuSO_4 \cdot 5H_2O$ in the presence of a monolayer of compound

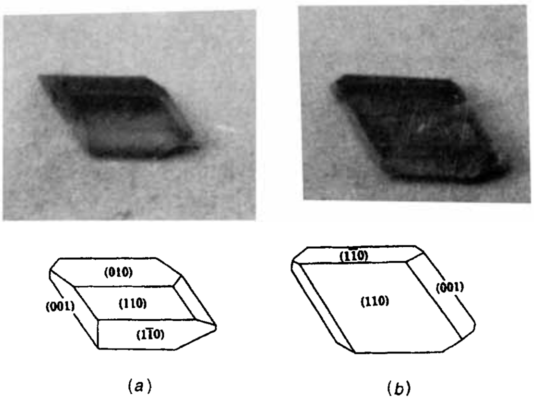

Fig. 2 Topographies of the $CuSO_4 \cdot 5H_2O$ crystals. The morphology of the $CuSO_4 \cdot 5H_2O$ crystals removed from the monolayer(*a*) is distinct from those grown without the monolayer(*b*). A new crystal face (010) appears on the surface of the former and this special face is attached to the monolayer plane during crystal growth

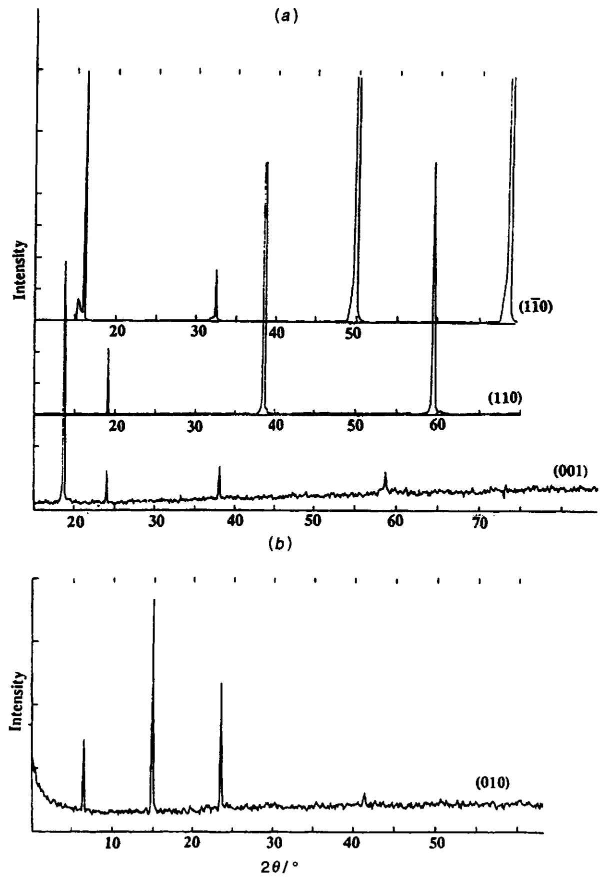

Fig. 3 X-Ray diffraction patterns of (*a*) the surface of a plated $CuSO_4 \cdot 5H_2O$ crystal grown in the absence of the monolayer, revealing (110), (1$\bar{1}$0), (001) crystal faces, and (*b*) of a crystal removed from the monolayer and having the special (010) face

of crystals coexisted at the bottom of the container and were randomly aggregated. However, when the L monolayer was present on the surface the crystal growth was induced by the organized film. The crystals of $Na_2SO_4 \cdot 7H_2O$ still appeared at the bottom, but $CuSO_4 \cdot 5H_2O$ was separated from the $Na_2SO_4 \cdot 7H_2O$, and preferably formed at the monolayer–water interface (Fig. 1) The millimetre-sized crystals of $CuSO_4 \cdot 5H_2O$ removed from the monolayer are ladder-shaped (Fig. 2). This morphology is different from that of the crystals grown from solution in the absence of the monolayer, which are plated with three main faces (110), (1$\bar{1}$0) and (001) (Fig. 2). X-Ray diffraction patterns revealed that the special crystal face found on the laddered crystal surface was (010) (Fig. 3). These studies also showed that this is not the initial face of $CuSO_4 \cdot 5H_2O$ growing from solution but it is formed under the monolayer.

The above results indicate that the L monolayer has the ability to change some factors of the crystal growth from the mixed solution and that two selections are made. First, the L monolayer chooses $CuSO_4 \cdot 5H_2O$, but not $Na_2SO_4 \cdot 7H_2O$, to nucleate under it. Secondly, among all the crystal faces of $CuSO_4 \cdot 5H_2O$, the (010) face was selected by the L monolayer and the crystallization was oriented. Obviously, the structure and properties of the inorganic–organic interface[4,7,9–12] are very important in the selective inorganic crystal growth and in the specificity of the crystal morphology and particle aggregation.

How does the L monolayer choose $CuSO_4 \cdot 5H_2O$? As we know, L is a special amphiphilic molecule composed of two structural elements:[14] a rigid diazafluorene Schiff-base segment containing two nitrogen atoms with lone-pair electrons as the hydrophilic head group, and an alkyl chain containing sixteen carbon atoms as the hydrophobic part. According to the principles of co-ordination and the hard–soft acid–base theory, L is a preferable ligand for some soft acids such as copper ion. In this experiment, Na^+ ions coexist in the mixed solution but they are associated with hard acids. Therefore, the L monolayer preferentially accumulates copper ions and their local concentration under the monolayer is much higher than that in solution. Owing to ion exclusion, the concentration of Na^+ decreases. So the value of *S* of the $CuSO_4 \cdot 5H_2O$ is increased and that of $Na_2SO_4 \cdot 7H_2O$ is decreased in proximity to the monolayer. As a result[15] the nucleation of $CuSO_4 \cdot 5H_2O$ can easily occur under the monolayer.

What about the special crystal face (010) of $CuSO_4 \cdot 5H_2O$? This is related to the interaction between the crystal and monolayer. The key to the specificity in nucleation in this case is the presence of some form of molecular complementarity between the head groups of L and copper ions.[4,7,9] The monolayer is an organized organic aggregation and has a definite lattice structure, with the parameters *a*, *b* and θ, like a crystal face. When it is formed on the surface of the solution, the local environment under it also becomes organized, undergoing changes in physical functions such as the electric field, energy and mass transmission, *etc.*, and some other chemical functions which are related to the crystallization. To some extent the monolayer acts as a template; only the crystal face which matches well with it is selected. In our experiment this means that the (010) face of $CuSO_4 \cdot 5H_2O$ fits the monolayer and its local environment. To elucidate this we studied the lattice structure of an L monolayer on a subphase of copper ions by computer-simulation techniques.[16–18] The parameters of the monolayer obtained were $a = 6.20$, $b = 6.00$ Å and $\theta = 73.0°$. The area per molecule is 35.57 Å^2, in close agreement with the experimental result, 35 Å^2. This shows that L can interact with Cu^{2+} giving a 1 : 1 complex Cu^{2+}–L. The corresponding lattice parameters of the (010) crystal face of $CuSO_4 \cdot 5H_2O$ are 6.12, 5.96 and 72.8°, and the area per Cu^{2+} ion on the (010) face is 34.76 Å^2. Clearly the (010) crystal face matches the L monolayer perfectly. On the other hand, this means that the (010) face is formed first as the Cu^{2+}–L structure: this L is the template for copper ions, and the copper ions also act as the template for the (010) crystal face on which further growth is based.

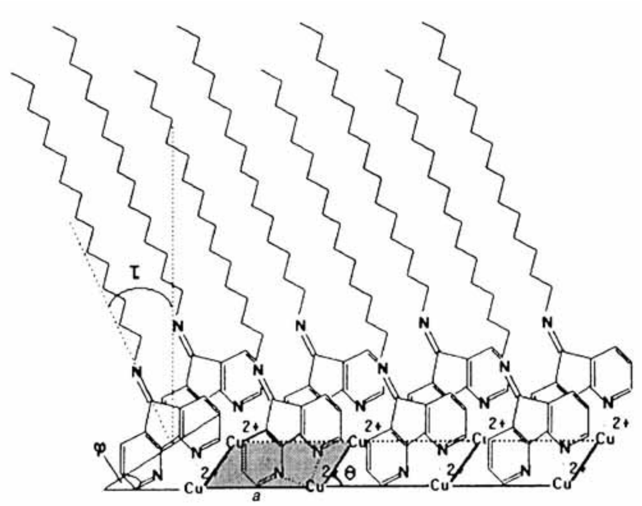

Fig. 4 Structure of the L monolayer on the subphase containing copper ions as simulated by computer techniques. The calculations were performed in two steps: first the conformation of L was determined by Alligner's MM2&P1 program; secondly the monolayer energy was minimized using Backinghame-Jean's atom–atom potential formula. The simulation result is: a = 6.20, b = 6.00 Å, θ = 73.0, φ = 20 and τ = 53°. The shaded part illustrates that the arrangement of the copper ions under the L monolayer is in close agreement with that on the (010) face of $CuSO_4 \cdot 5H_2O$

It is also well known that the shape of a crystal and the crystal faces appearing on a crystal surface depend on the different rates of growth of each face. A faster one is covered by a slower one and the latter is regarded as the initial face on the surface of the crystal. Since the rate of growth of each face is constant, single crystals grown from solution always have a certain shape and initial faces. In the crystallization of $CuSO_4 \cdot 5H_2O$ from solution, the rate of growth of the (010) face is fast and it cannot be found on surface of a plated single crystal. Under the L monolayer, the (010) face cannot grow in the direction of the monolayer. As a consequence, it can exist and be stable under the monolayer. However, the monolayer cannot bear a tremendous weight, so as further growth occurs the crystal will separate from the monolayer and drop down to the bottom of the container. Without the monolayer, the (010) face grows freely and rapidly and the crystal shape changes from ladder to plate, as those obtained in the absence of the monolayer. It is clear that the control of the monolayer is limited at the inorganic–organic surface, for the monolayer itself has a two-dimensional nature at the surface.

Conclusion

We have shown that, as the monolayer has an organized structure like a crystal face and the head group has selectivity for ions, it can show selectivity in crystal growth. The monolayer can not only choose the crystal (ion), but also the crystal face (arrangement of the ions). This selectivity is due to electrostatic, structural matching and molecular complementarity between the crystal and the organic surface. Some factors including lattice geometry, spatial charge distribution, molecular interactions between inorganic crystals and organic film framework play a very important role in the control of crystallization.

The lack of control over local ordering and the inability to direct crystal growth in three dimensions may cause some limitations. However, the selectivity for crystal and oriented crystal growth of this method shows that the integration of supermolecular self-assembly, organized molecular film and inorganic material chemistry provides the opportunity to develop rational synthetic routes to select a certain crystal from a mixture and a product having uniform crystal shape-tailored morphologies and crystallographic orientation. The molecular recognition between the monolayer and the crystals represents an important milestone in the realization of crystal engineering.

Acknowledgements

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