A Selective Crystal Growth under a Monolayer

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The crystallization are selective when the monolayer of 9-(hexadecyl)imino-4,5-diazafluorene was spread on the surface of the mixed supersaturated solution of $CuSO_4 \cdot 5H_2O$ and Na_2SO_4. In the experiment, $CuSO_4 \cdot 5H_2O$ and its (010) face are chosen to form under the monolayer; but the crystallization of Na_2SO_4 still occurs at the bottom of the solution.

A new field that usually called biomineralization (the crystallization of inorganic solids in biological system) has been developing rapidly recently.[1] In the past time, Mann, Addai, and Fendler *et al.* have reported the nucleation of some minerals under the monolayer.[2,5-9]

In this paper, we report the selective nucleation between two crystals(chalcanthite and sodium sulfate) and their faces under the monolayer of 9-(hexadecyl)imino-4,5-diazafluorene (**L**). 20g Na_2SO_4 and 38g $CuSO_4$ were put into 100g water at 40°C. After the solutes were dissolved, it was filted carefully at 30°C and the filtrate was the mixed saturated solution of both $Na_2SO_4 \cdot 7H_2O$ and $CuSO_4 \cdot 5H_2O$. On the surface of the filtrate, the monolayer of **L** was carefully and slowly spread from a 1×10^{-3} mol·dm^{-3} solution of **L** in chloroform. The volume of spreading solution was estimated from the cross section of the crystallization vessel and limiting area per molecule, 35Å^2, obtained from surface pressure-area isotherm of **L** amphiphile on the subphase containing copper ions.[10] After the chloroform was volatilized, the stable monolayer of **L** was formed (limiting area is 35Å^2, surface pressure is 35 mN·M^{-1}) on the water/air interface. Then the temperature of the solution was slowly dropped and the crystals of both $Na_2SO_4 \cdot 7H_2O$ and $CuSO_4 \cdot 5H_2O$ would separate out from the mixed supersaturated (supercooled) solution.

In general, if there are two solutes in a solution and these solutes are supersaturated, they will separated out of the solution and the crystals coexisted at the bottom of the container. However, in our experiment, when the monolayer was spread on the mixed solution of chalcanthite and sodium sulfate, the results were different. The crystals of $Na_2SO_4 \cdot 7H_2O$ were gathered at the bottom, but $CuSO_4 \cdot 5H_2O$ were separated from the $Na_2SO_4 \cdot 7H_2O$, and they were preferablely formed at the monolayer/water interface (Figure 1). It is noted that the millimeter-dimension crystals of $CuSO_4 \cdot 5H_2O$ removed form the monolayer were ladder-shaped. This morphology is different from the plated crystals obtained from the normal solution. Compared with the plated ones, a new crystal face was found on the surface of the ladder-shaped crystals, which was adhered to the monolayer during the nucleation and growth(Figure 2). The crystal faces were examined by a D/Max-γA Rotating Anod X-Ray Diffractometer (Rigaku, Japan). The results show that the three main crystal faces of the plated-shaped crystal are (110), (1$\bar{1}$0), (001) and the special face of the ladder-shaped crystal that remove from the monolayer is (010), which does not exist on the surface of the normal crystals.

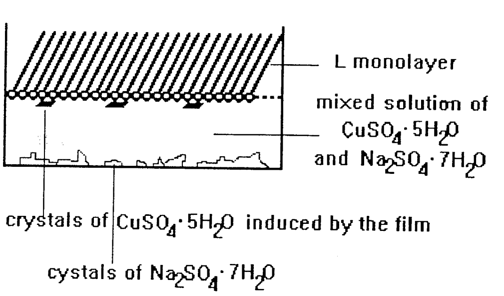

Figure 1. When the L monolayer formed on the surface, the crystallization of the two solutes $Na_2SO_4 \cdot 7H_2O$ and $CuSO_4 \cdot 5H_2O$ were separated, the former was occurred at bottom of the container and the latter was happened on the surface.

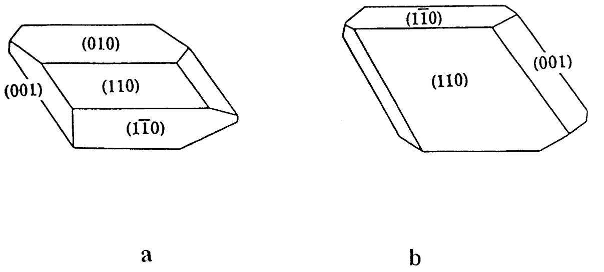

Figure 2. The morphologies of the $CuSO_4 \cdot 5H_2O$ crystals removed from the monolayer(a) is distinction from the normal ones which grown without L monolayer(b). It is clear that a new crystal face (010) appears on the surface of former and this special face is attached to the monolayer plane during the growth.

The results indicate that the **L** monolayer has the ability to change some factors of the crystal growth from the mixed solution and there are two selections in this experiment. Firstly, the **L** monolayer choose $CuSO_4 \cdot 5H_2O$, 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 is oriented.

As we know, the **L** is a special amphiphilic ligand,[10] which has a rigid diazafluorenone Schiff base segment containing two nitrogen atoms with lone pair electrons as hydrophilic head group. So **L** is a preferable ligand for some soft acids such as copper ion. In this experiment, Na^+ ions coexisted in the solution but they belong to hard acids. The **L** monolayer prefers to accumulate copper ions, so the surface concentration of copper ions and the supersaturation ratio S of $CuSO_4 \cdot 5H_2O$ is increased. As the result, the nucleation of $CuSO_4 \cdot 5H_2O$ can be easily occurred under the monolayer. That's why

$CuSO_4 \cdot 5H_2O$ crystal is selected by the **L** monolayer.

But what about the special crystal face (010) of $CuSO_4 \cdot 5H_2O$? This is correspondent to the interaction between the crystal face and monolayer. The key to the specificity in nucleation is the presence of some forms of molecular complementarity between function head groups of **L** and copper ions[1,3,5], which determines the specificity in nucleation and orientation of the crystals. As a matter of fact, the monolayer is an organized organic aggregation and has a definite lattice structure, with the parameters *a, b and* θ, like a crystal face. To some extent, the monolayer play as a template, only the crystal face which matches with it well can be selected by the **L** monolayer. In quest of this problem, we studied the lattice structure of **L** monolayer on subphase of copper ions by computer simulation techniques.[11-13] The calculation shows the structure of the monolayer is: $a = 6.20$ Å, $b = 6.00$ Å, $\theta = 73.0°$ (Figure 3). The corresponding lattice parameters of (010) crystal face of $CuSO_4 \cdot 5H_2O$ are: *6.12* Å, *5.96* Å and 72.8°. It is clearly that the crystal face of (010) matches with the **L** monolayer perfectly. It also means that the (010) face of $CuSO_4 \cdot 5H_2O$ was firstly formed as the Cu^{2+}-**L** structure: the **L** is the template for copper ions, and the copper ions play as the template for (010) crystal face on which the further growth of the crystal is based.

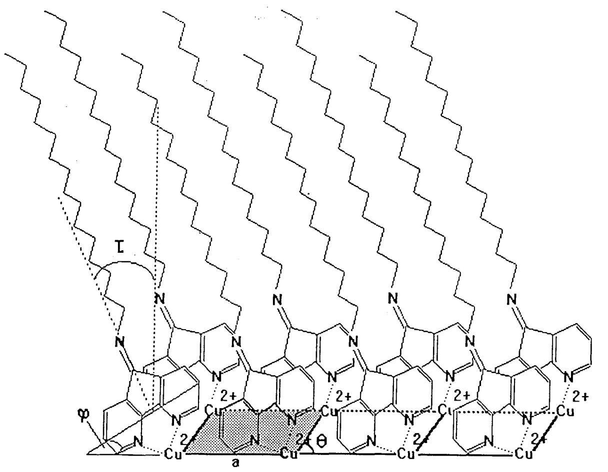

Figure 3. The structure of L monolayer on the subphase containing copper ions, it is simulated by computer techniques: a=6.20 Å, b=6.00 Å, θ=73.0°, φ=20 °, and τ=53°. The shadow part illustrates that the arrangement of the copper ions under the L monolayer is close agreement with that on (010) face of $CuSO_4 \cdot 5H_2O$.

In conclusion, since the **L** monolayer has an organized structure like a crystal face and the hydrophilic head group has the selectivity of ions, it can play as a template in the crystal growth. It can not only choose the crystal (ion), but also can choose the crystal face(arrangement of the ions). Obviously, in these processes, the structure and properties of inorganic/ organic interface are very important in the regulation of the selective inorganic crystal growth and in the specificity to crystal morphology and particle aggregation, and some factors including lattice geometry, spatial charge distribution, molecular interactions between inorganic crystals and organic film framework play a very important role.

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