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Research Article

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Oriented growth of KCl crystals induced by the self-assembled monolayers

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ABSTRACT

In the present work, KCl crystals with single crystal face were induced by using the method of bio-mimetic mineralization and self-assembled monolayers of (3-Mercaptopropyl) trimethoxysilane(MPTS) as the template. The crystals were characterized by optical microscope and X-Ray Diffraction (XRD). The crystals were observed in regular shape with uniform size and they were found by XRD to grow along the (110) plane. From these experiments, we can conclude that the good selection of the（110）crystal face of KCl is due to the match between this crystal face and definite lattice structure of the SAMs film.

Keywords: KCl, Biomineralization, SAMs , Oriention growth

INTRODUCTION

In recent years, with the understanding of biological system, lots of biomineralization materials are found in the nature[1].Because of the special participation and control life processes, biomineralization materials play great role whether in the several meters mammals or in one micron blue – green algae. Compared to the synthetic materials, biomineralization materials have significant structure and assembly method [2]. Therefore, biomineralization materials unique properties, such as high strength, fracture toughness, optical, electric, magnetic, heat, sound, catalytic activity[3]. Among materials preparation method, becaused of the crystallization process by the regulation of organic matrix and other life activities, materials made by the biomineralization have highly unified and orderly crystal morphology, size, and orientation [4].Inspired by this natural phenomenon, biomimetic mineralization method is widely used in the preparation of the special structure of the inorganic or organic/ inorganic composite materials. Application of these methods, people have fabricated $CaCO_3$, Cu_2S, CdS, CdSe, et al [5-6]. The usual template is biofilm，such as polymer template, Langmuir film, Self-assembled Monolayers (SAms)[7]. Potassium chloride crystal belongs to the cubic system, and its solubility increases with temperature in a solution, which is suitable for cooling crystallization. Therefore, KCl has been selected as a suitable material in this study.

In this study, self-assembled monolayers of (3-Mercaptopropyl) trimethoxysilane (MPTS) was used as template to induce the nucleation and growth of KCl crystals. The preparation and characterization of the KCl crystals were investigated. Optical Microscopy was applied to examine the morphological quality of the crystal. X-ray diffraction (XRD) was used to characterize the structure of obtained structure. There are comparatively obvious morphological and XRD differences between the spontaneous solution-formed crystal and crystal induced by the SAMs films. In addition, the reason that aroused above - mentioned phenomena was also discussed.

EXPERIMENTAL SECTION

Pretreating of substrates Glass plates were used as substrates. They were immersed for 30 min in Piranha solution (H_2SO_4:H_2O_2=7:3 (V/V)) at 90 °C to make hydroxy radicals on the surfaces. Then the substrates were carefully rinsed with deionised water, and dried later on. Preparation of MPTS Monolayers. The pretreated substrates were immersed in dehydrated benzene solution containing 0.5 mmol/L of MPTS for 40 min. In order to remove other physisorbed ions or molecules, the substrates were cleaned in turn ultrasonically with chloroform, acetone and deionised water, and then dried for 60 min at 120 °C, and cooled in a desiccator.The concentration of a KCl-saturated solution is 35.54 g KCl/100g water at 25 ℃.

Preparation of KCl crystal. The KCl solution (419.4 g KCl/kg water) was poured into a 60 ml beaker and warmed by a water bath to 50 ℃, where KCl was completely dissolved in water. For the induced crystallite, an Sams film was dipped into the KCl solution at 50 ℃. The position and orientation of the LB films in the solutions are illustrated in Fig. 1.When the solution was slowly cooled down to 25 ℃ at a rate of approximately 16℃/h, the crystals were formed on the SAMs films. For comparison, a blank glass was also placed on the bottom of the container. After that, the substrates were drawn from the solution and dried for the test.

RESULTS AND DISCUSSION

The concentration of a KCl-saturated solution is 355.4 g KCl/kg water at 25℃. Therefore, spontaneous crystallization will take place if a KCl solution with the concentration of 41.94 g KCl/100g water is cooled down from 50 to 25 ℃ at a rate of 4℃/h. As a result of sedimentation, the crystals are located at the bottom of the beaker . These spontaneous solution-formed crystals display parasite morphology as shown in Fig. 1a.

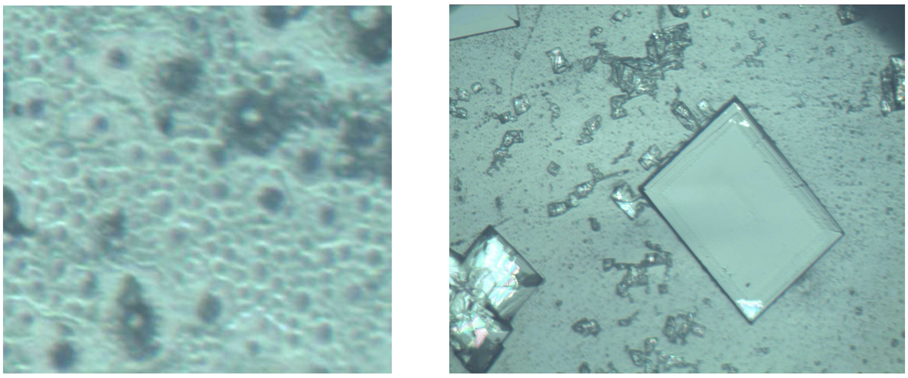

Fig.1 Optical microscopy images of prepared crystals (a) solution-formed, (b) induced by SAMs film of MPTS

When an MPTS SAMs film is vertically kept in the KCl solution, and temperature decreases from 50 to 25 ℃,

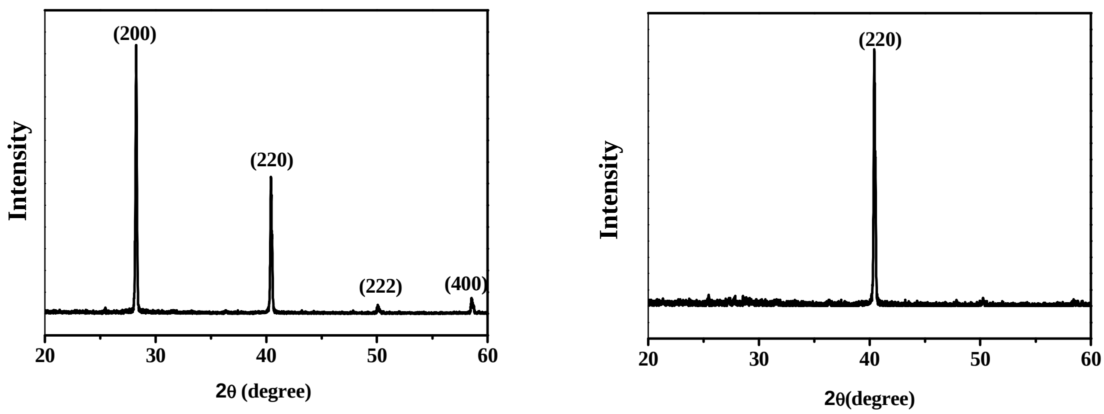

Fig.2 X-ray diffraction patterns of crystals: (a) solution-formed, (b) induced by SAMs film of MPTS

induced nucleation and growth of crystals occur. The morphologies of the induced crystals on the SAMs films are quite different from those of the solution-formed crystals. As shown in Fig. 1b, the induced crystals show a rectangle structure.

The XRD patterns of the KCl crystals formed under different experimental conditions are shown in Fig. 2. The XRD analysis of solution-formed crystals shows (200), (220), and (222) peaks at 28.3°, 40.5°, and 50.2° corresponding to the (100), (110), and (111) faces of KCl crystals (Fig. 2a), respectively. These results agree with the previous reports[8-10]; for example, the appearance of the (111) face in the KCl microcrystals. When an MPTS SAMs film is vertically dipped into the solution, the XRD pattern of induced crystals shows just the (220) reflection at 40.5°, indicating that the crystallite is (110)-oriented (Fig. 2b).

The lattice matching, the degree of supersaturation and electrostatic interactions are important factors responsible for the induced crystallization of inorganic materials on organic templates[11-13].As for KCl crystals on SAMs films of MPTS, only (110) oriented crystals are induced and formed when a template is vertically placed into the solution. This behavior can be explained as follows: MTPS SAMs film is a highly ordered molecular film, the structure has detail studied. According to I. Piwon´ski et al., [14] MTPS SAMs films have rectangle close-packed structure with a=1.2nm, b=0.6nm. KCl is known to crystallize in a cubic crystalline lattice with a lattice constant of a=0.63nm. In comparison, the superimposition of a rectangular lattice of the SAMs template on the (110) face of the cubic KCl crystal provides a good lattice matching. Thus, when the SAMs template is dipped into the solution, (110)-oriented KCl is obtained. The K-K distance in the <110> direction of (110) face is 1.5 times than b of SAMs film. Meanwhile, the K-K distance in the <110> direction of (110) face is half of b of SAMs film. The misfits along a and b directions in the SAMs film templates are 1%. (110)-oriented KCl is obtained owing to the matching regulation between KCl (110) face and MTPS SAMs films.

CONCLUSION

By dipping vertically an SA LB film into a KCl solution, (110) oriented cubic KCl with a uniform size has been prepared. Based on the structure of the MTPS SAMs film and (110) face of KCl crystal, it can conclude that lattice matching is key factors responsible for the induced crystallization of inorganic materials on SAMs templates.

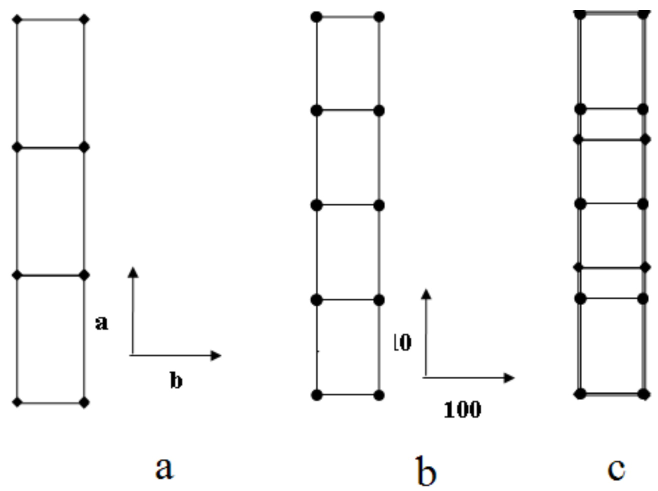

Fig 3. proposed matching between the (110) planes of KCl and the headgroups of MPTS SAMs film

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