

Micro-nano zinc nitrate hexahydrate film fabricated by biomimetic mineralization

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In this work, $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ micro-nano rods are successfully fabricated by a biomimetic mineralization process. During synthetic process, the self-assembly monolayers with different terminal groups are used as templates to induce the nucleation and growth of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ crystals. The products obtained at different conditions are characterized by means of X-ray diffraction patterns, scanning electron microscopy. The results show that the orientation and morphology of the $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ crystals are controlled properly by tuning the terminal groups of the self-assembled monolayers.

Keywords: zinc nitrate hexahydrate, micro-nano structure, biocrystallization, self-assembly monolayers.

Изготовлены и исследованы микро-нано трубки $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ методом биомиметической минерализации. В процессе синтеза монослои с самосборкой с различными концевыми группами используются в качестве матриц для индукции нуклеации и роста кристаллов $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$. Образцы, полученные в различных условиях, исследованы рентгеновскими методами и сканирующей электронной микроскопии. Результаты показывают, что ориентация и морфология микро-нано трубок $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ должным образом контролируются путем настройки терминальной группы самосборных монослоев.

Мікро-нано гексагідрат нітрату цинку, отриманий біоміметичні мінералізацією.
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Виготовлені і досліджені мікро-нано трубки $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ методом біоміметичної мінералізації. У процесі синтезу моношарів з самозборкою з різними кінцевими групами використовуються в якості матриць для індукції нуклеації і росту кристалів $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$. Зразки, отримані у різних умовах, досліджено рентгенівськими методами і скануючою електронною мікроскопією. Результати показують, що орієнтація і морфологія мікро-нано трубок $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ належним чином контролюються шляхом надбудови термінальної групи самозбірних моношарів.

1. Introduction

The fabrication of functional nanomaterials via biomimetic mineralization is very meaningful due to their large variety of applications in biomedicine, catalysis, environment, and energy storage and conversion. For applications, it is needed to create inorganic crystal that are highly aligned and ordered, therefore, how to control the oriented growth of the crystals has recently

attracted much attention [1, 2]. As a typical example of induced nucleation, the biomimetalization are very actively studied currently because the materials made by the biomineralization have highly unified and orderly crystal morphology, size, and orientation [3, 4]. Inspired by this natural phenomenon, biomineralization method is widely used in the preparation of the special structures of the inorganic or organic/inorganic composite materials. The usually used

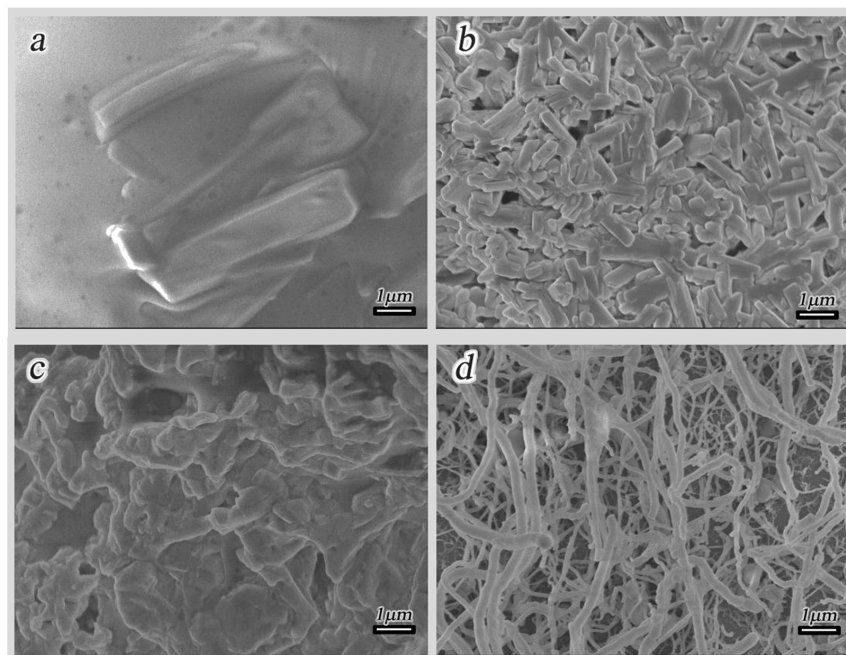


Fig. 1. SEM images of the $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ microcrystals nucleated on the SAMs template with the ending groups (a) hydroxyl-group; (b) amino group; (c) sulfonic group; (d) thiol group.

templates for biomineralization are bio or mimic bio films, such as polymer brushes, Langmuir films and self-assembly monolayers (SAMs) [5–7].

It is well known that the factors such as chemical binding, lattice matching and structural complementarity between crystals and organic ultra-thin film templates play great role in the biomineralization [8]. Our previous works have proved that the crystals with well-designed properties can be obtained under controlled conditions by changing the orientation and position of the LB template in solutions.

In the present study, we have provided a simple biomimetic mineralization for the fabrication of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ micro-nano structures. First, different group-terminated self-assembly monolayers are employed to control the deposition and crystallization of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ on their surfaces. Various crystal habit of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ microcrystals have been synthesized on the surface of different group-terminated SAMs.

2. Experimental

(3-Mercaptopropyl) trimethoxysilane (MPTS), (3-aminopropyl)trimethoxysilane (APTMS), and 4-Mpy were purchased from Sigma Aldrich. $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, benzene, chloroform, acetone, concentrated sulfuric acid, hydrogen peroxide, acetic acid were

obtained from Shanghai Chemical Reagents Co. All of chemical were of A.R. grade and used without further purification.

Pretreatment of ITO and quartz wafer substrates. The ITO conductive glass and quartz wafer were immersed in Piranha solution ($\text{H}_2\text{SO}_4:\text{H}_2\text{O}_2 = 7:3$, V/V) at 90°C for 30 min to make hydroxy radicals on their surfaces. Then the substrates were carefully rinsed with deionized water and dried in the air condition.

Preparation of thiol group-terminated SAMs on the substrate. The as-pretreated substrates were immersed in dehydrated cyclohexane solution containing 0.5 mmol/L of MPTS for 6 h. In order to remove other physically adsorbed ions or molecules, the substrates were cleaned in turn ultrasonically with chloroform, acetone, and ultrapure water.

Preparation of sulfonic group-terminated SAMs. MPTS SAMs on the substrate was put in a solution of 30 % $\text{H}_2\text{O}_2/\text{HOAc}$ (1:5 v/v) and maintained at 45°C for the oxidation of thiol group to generate sulfonic group-terminated SAMs. The substrate was withdrawn after 60 min and cleaned with chloroform, acetone, and ultrapure water.

Preparation of amino group-terminated SAMs. The pretreated substrates were immersed in dehydrated methyl alcohol solution containing 0.3 mmol/L of APTMS for 6 h. In order to remove other physically ad-

sorbed ions or molecules, the substrates were cleaned with methyl alcohol.

Preparation of $Zn(NO_3)_2 \cdot 6H_2O$ crystals. The solubility of $Zn(NO_3)_2$ is 211 g at 40°C, while at 30°C, the solubility is 138 g. The $Zn(NO_3)_2$ undersaturated solutions were prepared by dissolving 140 g of $Zn(NO_3)_2$ into 100 mL of deionized water at 40°C in the water bath. The solutions were precisely dissolved for 1 h and then the solutions cooled to 30°C. Thus supersaturated solutions were obtained.

The SAMs modified substrates and hydroxyl substrate were vertically inserted into the above solution at 30°C. After a soaking time of 8 h, the substrates were drawn from the solution and dried for the test.

The morphologies of the products were characterized by a field-emission scanning electron microscope (JEOL JSM-6700F). The X-ray diffraction (XRD) measurement was recorded with a D/Max-RA X-ray diffractometer using $Cu K\alpha$ ($k = 1.5406$) radiation.

3. Results and discussion

When different groups-terminated SAMs modified substrates and hydroxyl substrates are vertically soaked in the $Zn(NO_3)_2$ solution, the induced nucleation and growth of crystals occur on the surface of substrates. Morphologies of as-synthesized products are firstly characterized by SEM images. As shown in Fig. 1, $Zn(NO_3)_2 \cdot 6H_2O$ crystals composed of cuboids are observed on the surface of hydroxyl substrate and amino group-terminated SAMs modified substrate. The size of $Zn(NO_3)_2 \cdot 6H_2O$ crystals on hydroxyl substrate is larger than those deposited on amino group-terminated SAMs modified substrate. Massive aggregate $Zn(NO_3)_2 \cdot 6H_2O$ crystals built up on sulfonic surfaces, fibrous $Zn(NO_3)_2 \cdot 6H_2O$ crystals nucleated on the mercapto surfaces. The highest density of the $Zn(NO_3)_2 \cdot 6H_2O$ crystals is on sulfonic substrate, then on mercapto surfaces, on amino surface, on hydroxyl substrate in sequence.

The corresponding XRD analysis on the surface of hydroxyl substrate and amino group-terminated SAMs modified substrate show characteristic peaks at 17.8°, which are assigned to the diffraction of the (111) plane of the orthorhombic $Zn(NO_3)_2 \cdot 6H_2O$ crystals (Fig. 2). The result indicates that the {111} faces of the orthorhombic $Zn(NO_3)_2 \cdot 6H_2O$ crystals are arranged paral-

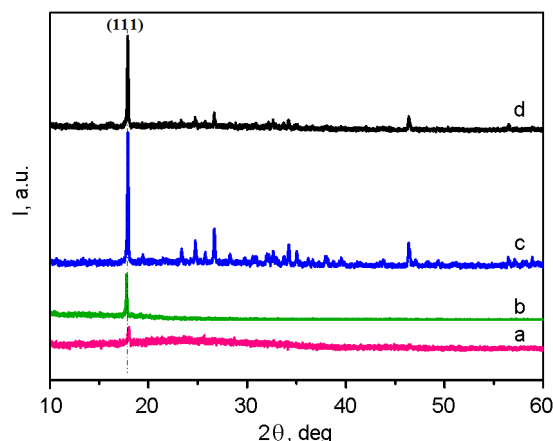


Fig. 2. X-ray diffraction patterns of the $Zn(NO_3)_2 \cdot 6H_2O$ microcrystals nucleated on the SAMs template with the ending groups (a) hydroxyl-group; (b) amino group; (c) sulfonic group; (d) thiol group.

lel to the surfaces of the substrate, and their growth direction was [111].

It is known that several factors including the lattice matching, the degree of supersaturation, and electrostatic interactions hydrogen bonding influence the induced crystallization of inorganic materials on organic ultrathin films templates [9, 10]. XRD results further demonstrates that $Zn(NO_3)_2 \cdot 6H_2O$ cuboids have {111} planes parallel to hydroxyl substrate and amino group-terminated SAMs modified substrate. The ITO glass is amorphous phase, and ATMPS possesses orthorhombic structure [11]. Therefore, it can conclude that the lattice matching is not the factor for the orientation growth of crystals [12]. Fig. 3a and 3b shows the schematic models of the unit cell of orthorhombic $Zn(NO_3)_2 \cdot 6H_2O$ and its (111) plane, respectively. As indicated in physical principle of the orthorhombic structured $Zn(NO_3)_2 \cdot 6H_2O$ crystals, the set of (111) planes is the closest packed plane. Therefore, the {111} planes correspond to the lowest free energy surfaces [13]. The {111} plane should be first to emerge in solution, however if no additives, the crystal facets of $Zn(NO_3)_2 \cdot 6H_2O$ crystals are not just the {111} plane due to the crystal kinetic process. In case of the presence of APTMS SAMs, the NH_2 groups of ATMPS are almost dissociated in neutral solution. Therefore, the electrostatic interactions exist between APTMS SAMs and $Zn(NO_3)_2 \cdot 6H_2O$ crystals. The (111) orientation may be due to the adsorption of {111} plane in a preferred orientation with re-

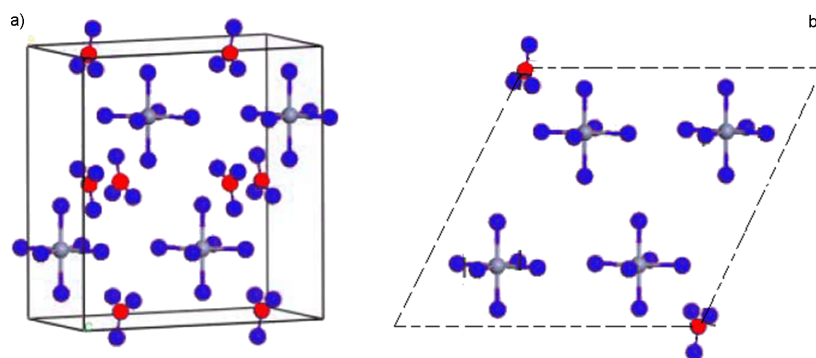


Fig. 3. (a) Unit cell of orthorhombic $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$. For clarity, H atoms of the water molecules are not shown. (b) (111) plane of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$. (Zn in green, O in blue, N in green).

spect to the substrate. Moreover, in the crystals, the Zn^{2+} is in the form of $\text{Zn}(\text{H}_2\text{O})_6^{2+}$ cations[15], H-bonding interactions between the $\text{Zn}(\text{H}_2\text{O})_6^{2+}$, nitrate and the surface amino groups of ATPMS SAMs will be another contributes to the adsorption of {111} plane to the substrate. The hydroxyl ITO glass is a negative template, the electrostatic interactions will drive the {111} plane to the ITO glass. At the same time, H-bonding seems to be an important factor for the orientation growth of crystals.

While on the surface of thiol and sulfonic groups-terminated SAMs modified substrates, there are additional typical peaks appearing in the curves besides the maximum intensity at 17.8° . The thiol and sulfonic groups in the solutions are both dissociated so that they can absorb the $\text{Zn}(\text{H}_2\text{O})_6^{2+}$ cations in the {111} plane of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ crystals which caused that (111) direction is mainly crystal growth direction. However there are no H-bonding between the template and $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ crystals so that thiol and sulfonic groups-terminated SAMs modified substrates not completely promoted (111) growth and inhibited the other crystal orientation growth.

4. Conclusions

We have demonstrated the successful fabrication of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ micro-nanostructures via biomimetic mineralization technique and annealing treatment. SAM templates are used to induce the nucleation and growth of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ crystals. The

crystal orientation and morphology are controlled by tuning the terminal group of the SAM templates in the solutions.

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