

Self-organization of Inorganic Helical Crystals: Design of Structure, Chirality, and Function with an Exquisite Association of Molecular Recognition

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Helical morphologies emerged from inorganic crystals that were without molecular chirality through the assembly of tilted unit crystals under diffusion-controlled crystallization. The twisted twins of the achiral tilted units made up the backbone of inorganic helical crystals. The morphological chirality was precisely tuned with addition of chiral amino acids through stereochemical molecular recognition between the crystal faces and the chiral molecules. An exquisite using of polymer led to the formation of similar helical forms because the conjugation of the dual roles including habit modification and diffusion-controlled growth realized the growth condition of helical crystals. Moreover, ordered aggregate of organic dyes formed in the helical crystal at nanoscopic scale. Versatile design of helical inorganic materials is a significant step for the next stage of materials chemistry through self-organization.

Key words: helical morphology, crystal growth, chirality, polymer-mediated crystallization, biomimetic approach

1. INTRODUCTION

Designing crystals with a tailored morphology hold promise to be an essential technology toward the next stage in materials chemistry. Biomimetic crystallization by using polymer has attracted much interest because of their potential for morphological control [1]. The typical morphological variation is ascribed to habit modification with adsorption of polymeric additives on a specified crystal faces. Although the polymer-mediated crystallization has a great potential for morphological evolution, the recent morphological complexity is not always ascribed to the adsorption of polymer. A novel approach is required for real understanding and controlling crystal morphology through biomimetic approach.

Twisted and helical morphologies have one of the fascinating shapes in nature. Understanding helical architectures is of central importance to a broad range of scientific and technological investigations. The emergence of chirality is a hot topic, and the application of morphology as a functional material is an interesting challenge. Helical inorganic morphologies have reported in recent years; examples of such materials are carbonate [2], potassium dichromate [3], barium sulfate [4], silica-surfactant composite [5], manganese oxide [6], and zinc oxide [7]. However, the structure and the formation process were not clarified because the inorganic crystals were achiral.

Here we show recent approaches about versatile design of helical inorganic crystals. The backbone of inorganic helical crystals was the twisted twins consisting of the tilted units grown under diffusion-controlled condition. Molecular recognition that resulted from a specific interaction between the growing crystals and various organic molecules realized the design of chirality, structure, and function. The helical materials would be expected for their emergent optical, electric, and catalytic behavior toward the next stage of materials

chemistry. Moreover, the design strategies as described in this report are widely applicable for the other systems to prepare functional helical materials.

2. EXPERIMENTAL SECTION

Two triclinic crystals of potassium dichromate ($K_2Cr_2O_7$) and boric acid (H_3BO_3) and the one orthorhombic crystal of potassium sulfate (K_2SO_4) were grown in polymer matrices to achieve diffusion-controlled condition. Crystal growth proceeded in supersaturated solutions containing organic polymers, such as poly(acrylic acid) (PAA), poly(vinyl alcohol) (PVA), gelatin, agar, and pectin. Cubic crystals including barium nitrate ($Ba(NO_3)_2$) and ammonium chloride (NH_4Cl) were also demonstrated in the same condition to investigate the fundamental growth behavior of the crystals in the polymer medium. The detailed crystallization methods and the concentrations were given in our previous reports [8–11]. Crystal morphologies were observed by a optical microscopic (OM) and a field emission scanning electron microscope (FESEM).

3. RESULTS AND DISCUSSION

3.1. Morphological Evolution of Crystals Grown in Polymer Matrices.

The morphology of crystals grown in polymer matrix was remarkably changed from specific polyhedral habit into various dendritic forms as the gel density increased, regardless of the types of inorganic materials and organic polymers [8]. Figure 1 shows the images and their schematic representations of the morphological variation. The morphological evolution of crystals grown in gel medium was ascribed to diffusion-controlled growth, because the densified matrix decreased the apparent diffusion rate of the solutes and resulted in the diffusion-limited morphologies.

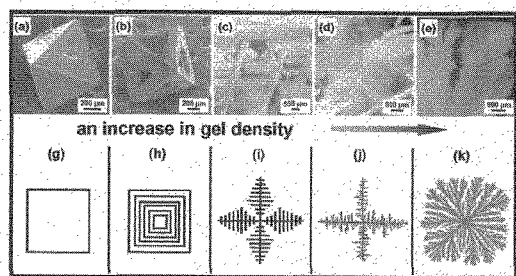


Figure 1. Morphological evolution of $\text{Ba}(\text{NO}_3)_2$ grown in agar matrix: (a) regular octahedron, (b) skeletal form, (c–e) various dendrites, (g–k) the schematic representations of morphological evolution

3.2. Emergence of Helical Morphology.

Helical morphology of inorganic crystals emerged from triclinic crystals under diffusion-controlled growth in various gel matrices [9]. It was reported in 1929 that several crystal systems, except for cubic systems, could induce twisted shapes. But the detailed structure and the formation process have been still unclear. We revealed that the backbone of the helix consisted of the twisted twinned assembly of the tilted unit crystals, as shown in Figure 2a,b. The tilted unit crystals resulting from triclinic system made up the backbone with a specified rotated connection both for $\text{K}_2\text{Cr}_2\text{O}_7$ and H_3BO_3 , even if the shape and the angle were different (Figure 2c–f).

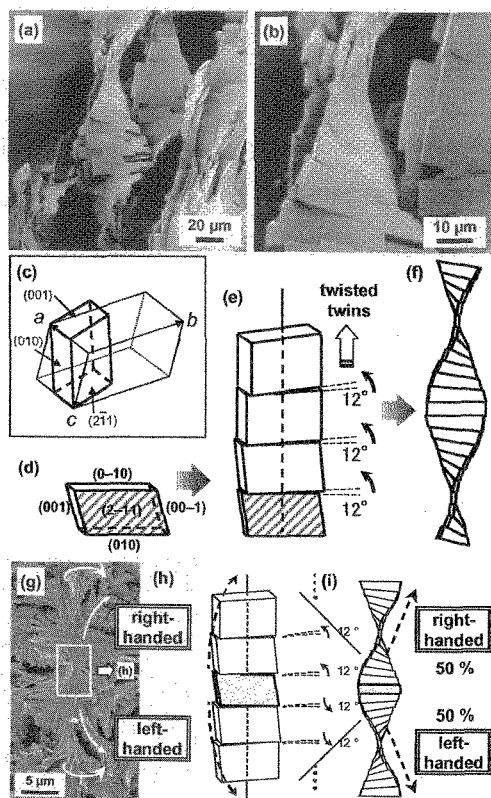


Figure 2. The structure of $\text{K}_2\text{Cr}_2\text{O}_7$ helical crystal. (a–b) FESEM images of helical crystal consisting of the twisted twins of the tilted units, (c) Schematic illustration of the tilted unit, (d–f) formation of the backbone with twisted twinned crystals, (g–i) the growth behavior of right- and left-handed helices from the starting point.

The emergence of helical morphology was deduced to be a diffusion-limited growth of the tilted units through the formation of twisted twins. If the tilted units were placed in a diffusion-controlled condition, the concentration gradient around the growing crystals strongly influenced on the morphology. The contour lines around the tilted units would be nonsymmetric, as illustrated in Figure 3. Although the original growth direction is direction Z_1 , the higher driving force for crystal growth is changed to direction Z_2 because of the nonsymmetric diffusion field around the tilted unit (Figure 3a). Therefore, the reversed twin is introduced and then is repeated for the further growth (Figure 3b).

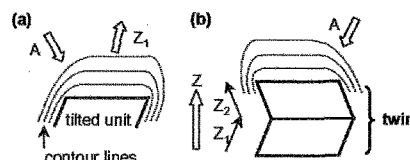


Figure 3. Schematic illustration of the concentration gradients around the tilted unit.

In a three-dimensional system, the growth behavior with formation of twins is the same as that of two-dimensional model. The nucleation probability of the completely reversed twins, as shown in Figure 3b, would be relatively small. The formation of slightly rotated twins is more favorable in a three-dimensional diffusion field. The angle of rotation is determined by lattice matching on the twin plane. Consequently, the slightly rotated twins induce the formation of helical crystals (Figure 2d–f).

The right- and left-handed twists were produced on the opposite sides of the starting point (Figure 2g). The tilted units are aligned along the $[010]$ and $[0\bar{1}0]$ directions with a counterclockwise rotation of ca. 12° (Figure 2h,i). This model indicates that the right- and left-handed helices are equally produced with regard to the opposite directions from the primary unit (Figure 2i).

3.3. Chirality in Helical Morphology and Its Precise Tuning through Stereochemical Molecular Recognition.

An equal amount of right- and left-handed helical morphologies were obtained in gel medium consisting of synthetic polymers such as PVA and PAA. Interestingly, the gel matrices originating from natural polymer including gelatin, agar, and pectin induced the right-handed dominancy. We investigate the fundamental effects of chiral additives on the macroscopic helical shapes and its potential for chiral tuning behavior [10]. The $\text{K}_2\text{Cr}_2\text{O}_7$ helices were grown in PAA matrices containing various achiral and chiral additives because the right- and left-handed structures were equally obtained in PAA matrix.

The helical morphologies were generated on the branches of a spherulitic morphology (Figure 4a,b). Addition of chiral molecules significantly influenced the chirality of macroscopic helical morphologies. About 70% of right- and left-handed helices were obtained with the addition of D- and L-additives, respectively. In contrast to chiral glutamic and aspartic acids, the macroscopic chirality was not influenced by the achiral additives; examples of the achiral additives are imidodiacetic acid, citric acid, and malonic acid.

As crystal growth proceeded, the chiral symmetry breaking was more extreme in the area farthest from the starting point at the center. The right-handed helical forms, which account for 70% in region A in the presence of D-additives, increased with growth into region B and then completely occupied in region C (Figure 4a). On the other hand, the left-handed types disappeared by the dominant growth of right-handed helices with frequent branching (Figure 4b). The addition of L-additives, in contrast, led to the left-handed dominance with the disappearance of right-handed structures.

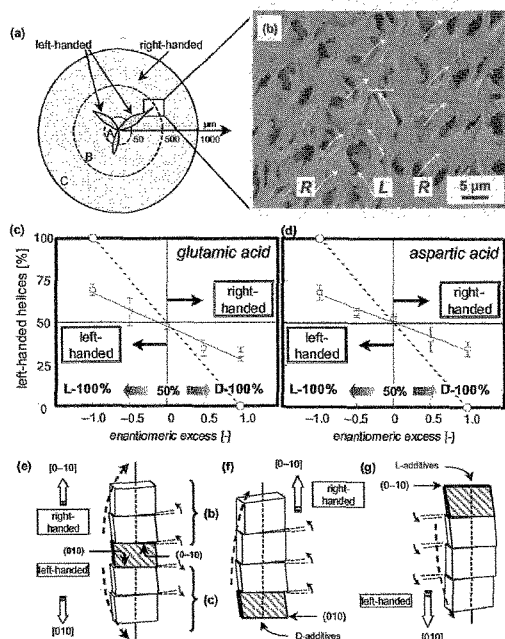


Figure 4. Macroscopic chiral symmetry breaking with addition of chiral molecules. (a) schematic illustration for distribution of the right- and left-handed helical forms, (b) A typical FESEM image for the disappearance of left-handed helices, (c and d) macroscopic chiral tuning with a variation of enantiomeric excess of Glu and Asp, respectively, (e-g) Schematic representations of stereochemical recognition leading to chiral symmetry breaking.

Moreover, we successfully tuned the proportion of right- and left-handed helices by a change of enantiomeric excess (ee) of glutamic acid (Glu) and aspartic acid (Asp) (Figure 4c,d). The initial proportion of the left-handed structures about 70% at $ee = -1.0$ decreased to approximately 55% at $ee = -0.5$, and then changed into racemic (50%) at $ee = 0$. Finally, the dominance was changed into 70% of the right-handed structures at $ee = 1.0$. The precise tuning of macroscopic chirality was realized using ee value.

Stereochemical molecular recognition played an important role for the chiral tuning. Recently, it has been accepted that crystal surface in lower symmetry of crystal systems is chiral, even if the bulk structure is not chiral. Crystal faces that are represented same Mirror index such as $\{010\}$ have positive (010) face and negative (0-10) face. Thus, the chiral molecule recognizes the chiral crystal surface such as (010) and (0-10) faces and then changes the growth behavior of

helical crystal in a specified direction (Figure 4e-g). As depicted in Figure 4e, the right- and the left-handed twisted assembly were grown from (0-10) and (010) faces with the formation of counterclockwise rotation, respectively. If D-additives stereochemically interacts the (010) face, the growth in [010] direction leading to the left-handed growth would be inhibited. As a consequence, the right-handed structures were dominantly obtained with addition of D-additives (Figure 4b). In a similar manner, the selective adsorption of L-additives inhibited the right-handed growth in the [0-10] direction and then resulted in the left-handed dominance (Figure 4c). Therefore, the microscopic chirality at a molecular level was precisely transferred into the macroscopic level through stereochemical molecular recognition. The molecular recognition mediating chirality is significant for understanding biological systems and designing a novel type of materials.

3.4. Morphological Evolution into Zigzag and Helical Morphologies with an Exquisite Association of Polymer.

The triclinic crystals are not always required for the formation of the tilted units. We successfully led to the tilted units from orthorhombic K_2SO_4 crystal through habit modification of PAA and then resulted in formation of zigzag and twisted assembly under diffusion-controlled condition [11].

Figure 5 shows typical FESEM images for morphological evolution of K_2SO_4 crystals grown in PAA matrix. Thin platy morphology was observed in relatively low PAA concentration. As PAA concentration increased, tilted columnar assembly (Figure 5a) was changed into zigzag (Figure 5b) and twisted morphologies (Figure 5c,d). The controlled assembly of the tilted platy units, as shown in Figure 6b, made up these unique morphologies.

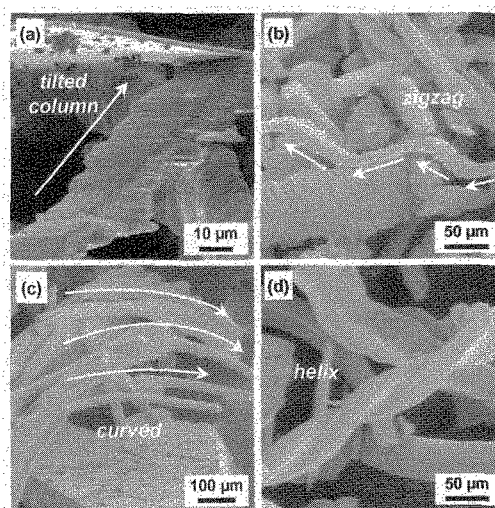


Figure 5. Morphological evolution of K_2SO_4 crystals grown in PAA matrix. (a) tilted columnar assembly, (b) zigzag morphology, (c) and (d) curved and helical forms, respectively.

The habit modification and the diffusion-controlled growth were exquisitely conjugated in the mineralization process. Adsorption of PAA on the (010) face

fundamentally changes the basic form into platy shapes (Figure 6a). The further selective adsorption results in the formation of tilted platy units (Figure 6b). In this way, the tilted platy unit was fundamentally formed with addition of PAA. As PAA concentration increases, an excess amount of PAA provides a steep concentration gradient around the platy units and promotes further morphological evolution through diffusion-limited growth. The diffusion-controlled assembly of tilted units made up various unique architectures through formation of the twinned connection, as previously reported. The columnar assembly of the tilted units was produced in relatively low PAA concentration because the concentration gradient was not so steep (Figures 5a and 6c). An increase in PAA concentration led to the formation of branched and the zigzag morphology consisting of the completely reversed twins (Figures 5b and 6e). Finally, the curved and helical shapes were generated with the formation of slightly rotated twins in relatively high PAA concentration (Figures 5c,d and 6e,f).

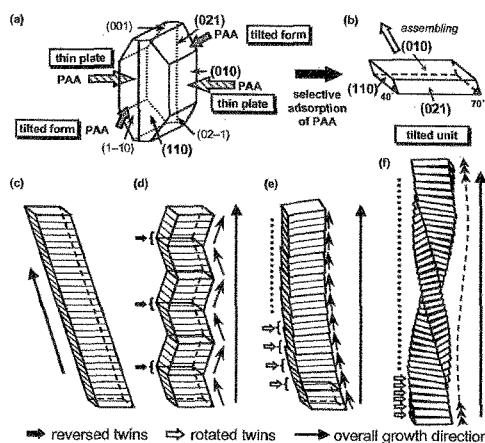


Figure 6. Schematic illustrations of the morphological variation into helical morphology. (a) basic form of the K_2SO_4 unit crystal, (b) tilted platy unit, (c–f) the diffusion-controlled assembly with twinned connections leading to various unique morphologies.

The dual roles of PAA including the habit modification and the diffusion-controlled assembly realized the emergence of helical morphology from the symmetric crystal. TG-DTA analysis indicates that the PAA molecules were incorporated in the composite by the two different styles. This is the first time that polymeric additives remarkably fulfill two significant roles in crystallization at the same time. The approach can be widely applicable for other systems.

3.5. Dye Inclusion in Helical Architectures.

We introduced various organic dye molecules in the K_2SO_4 /PAA composite. The strong photoluminescence (PL) from the incorporated rhodamine B (RB) molecules was observed with an ultraviolet-light excitation (Figure 7a). According to previous reports [12], the RB molecules organized J-aggregate in the K_2SO_4 composite (Figure 7b). Several organic dye molecules were also included in the K_2SO_4 /PAA composite. The detailed incorporation style and the designing emergent properties are now under investigation.

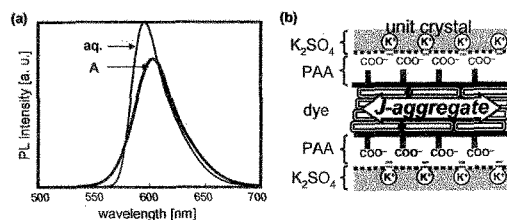


Figure 7. Dye inclusion in the helical morphology of K_2SO_4 and PAA. (a) PL spectra of K_2SO_4 /PAA/RB composite (excitation at 420 nm), (b) schematic model of incorporation style of dye molecules.

4. CONCLUSIONS

We showed design strategies of helical inorganic crystals toward a novel type of functional materials. The structure and the formation process were clarified. The chirality, the structure, and the function can be designed by manipulation of organic molecules for crystal growth. Our approaches are significant for the next stage of materials chemistry.

5. ACKNOWLEDGEMENT

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