Electronic Supplementary Information

Morphology and orientation control of guanine crystals: A biogenic architecture and its structure mimetics

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Contents

Experimental Methods

Surface skin of a fish: A banded blue-sprat (*Spratelloides gracilis*) was purchased from a shop of fishery products in Japan. The surface skin exhibiting the silver luster was peeled and then washed with purified water. The specimens were dried at room temperature.

Recrystallization of guanine, hypoxanthine, and uric acid dihydrate: Guanine (Kanto-Acros, 99 %), hypoxanthine (Wako, 97.0 %), and uric acid anhydrous (Wako, 98.0 %) were used for the recrystallization experiments without further purification. The precursor solutions containing 0.1 wt. % of these organic molecules were prepared with 28 wt. % of aqueous ammonia solution. The following additive organic molecules were dissolved in the precursor solutions: PAA (Aldrich, Mw=2×10^3, 90×10^3, and 25×10^4), PEI (Kanto-Acros, Mw=60×10^3, 50 wt. % of aqueous solution), PAH (Aldrich, Mw=70×10^3), PVA (Junsei, Mw=22×10^3), PVP (Wako, Mw=35×10^3 (K25) and 360×10^3 (K90)), PSS (Aldrich, Mw=70×10^3), Asp (Tokyo Kasei), and Glu (Junsei, 99 %). The molar ratio of these additive organic molecules to guanine was adjusted to 1, 0.5, 0.33, 0.2, 0.1, and 0.02. As for the polymers, the concentration was calculated on the basis of the concentration of the functional groups. After these materials completely dissolved, 3 cm^3 of the precursor solution was poured into the polystyrene vessels (35 mm in width, 65 mm in length, and 10 mm in height) with a glass substrate lined at the bottom of the vessels. When the modified substrates were used to study the influence of the substrates, the volume of the precursor solution was set to 1 cm^3 in the polystyrene vessel. The recrystallization experiments were performed with evaporation of water from the precursor solutions in a fume hood at room temperature.

Preparation of substrates: A glass substrate was cleaned before the use. For the preparation of the hydrophilic surface, the cleaned glass substrate was immersed in the mixed solution of water (100 cm^3) and ethanol (110 cm^3) containing 2.5 g of potassium hydroxide (KOH). The substrates immersed in the solution was treated in an ultrasonic bath for 5 min and then

immersed in purified water for 3 min. The cycle was repeated twice. For the surface modification by amino groups, the cleaned glass substrate was immersed in the toluene solution of 1 wt.-% 3-aminopropyltriethoxysilane (Tokyo Kasei) for 72 h at room temperature under stirring. Then, the modified substrate was washed with toluene and dried at room temperature in air. The hydrophobic surface was prepared by the immersion of a glass substrate in the toluene solution of 1 wt.-% dodecyltrichlorosilane at room temperature ˚C for 24 h under stirring. After that, the modified substrate was washed with toluene and dried at room temperature in air. Chitosan was coated by spin-coating of the acetic acid solution. The methods were referred to the previous reports. About 1 wt. % of chitosan powder (Wako) was dissolved in 1 wt. % of acetic acid aqueous solution. The chitosan solution was coated on a glass substrate with a spinning rate of 4000 rpm for 60 sec. Then, the substrate was annealed at 105 ˚C for 1 h.

Characterization: The morphologies were observed by optical microscopes (Keyence, VHX-1000 and Olympus, BX-51) and field-emission scanning electron microscopes (Hitachi, S-4700 and FEI, Sirion). The crystallographic orientation was analyzed by XRD (Rigaku, MiniFlex II).

Size of biogenic guanine crystals compared with the other fishes

Table 1 Size of guanine crystals in the surface skin of fishes

Species	Length [μm]	Width [μm]	Thickness [nm]	Color
Banded blue-sprat[a]	50	6.0	120	silver
Pilchard[b]	25	5.0	100	silver
Carp (Japanese Koi)[c]	15	6.0	20	yellow
Neon tetra[d]	10	3.0	60	blue

[a] *Spratelloides gracilis*, [b] *Clupea sprattus*,[19c] [c] *Cyprinus capio*,[19h] [d] *Paracheirodon innesi*.[19i]

Table 1 shows that a banded blue-sprat has the platy guanine crystals with the larger size compared with the other fishes. However, the structure-property relationship is not focused in the present work.

Influence of additive organic molecules on the size of the recrystallized guanine

Table S2. Size of the recrystallized guanine plates on a glass substrate in the presence of additive organic molecules.

Additive molecules	Length [μm]	Width [μm]	Thickness [nm]
None	1.4 ± 0.17	0.35± 0.07	45 ± 14
PAA	1.8 ± 0.10	0.14 ± 0.022	25 ± 7.4
PEI	0.72 ± 0.10	0.28 ± 0.11	69 ± 12
PVA	-	0.52 ± 0.10	100 ± 8.4
PAH	0.78 ± 0.10	0.16 ± 0.026	69 ± 8.3
PVP	2.4 ± 0.39	0.15 ± 0.038	67 ± 18
PSS	4.6 ± 0.18	0.27 ± 0.039	95 ± 14
Asp	1.1 ± 0.17	0.12 ± 0.019	25 ± 9.5
Glu	1.1 ± 0.18	0.14 ± 0.051	27 ± 11

The additive organic molecules influenced on the sizes of the resultant platy guanine crystals.

XRD patterns of guanine crystals formed on the modified surface

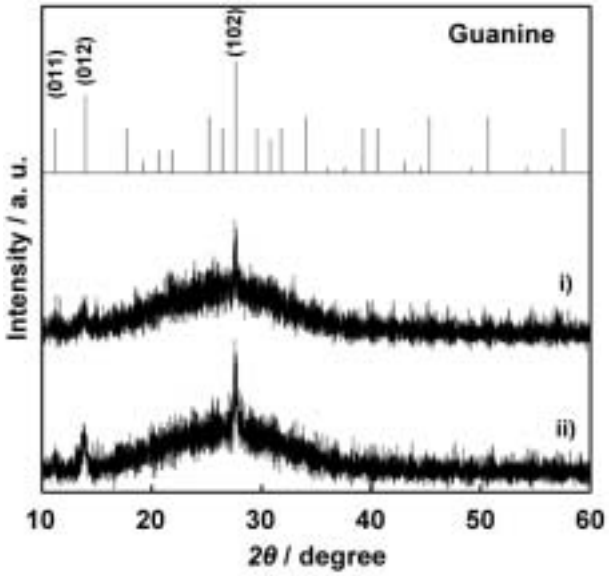

Figure S1. XRD patterns of guanine crystals formed on the substrate modified with amino groups (i) and the chitosan (ii) in the absence of additive organic molecules.

The changes of the orientation were observed on the FESEM images (Figure 2). The peak intensities of the pattern ii) were the stronger than those of the pattern i). However, the changes of the orientation were not clearly reflected to the peak intensity ratio of the XRD patterns, because the orientation is not perfectly controlled throughout the substrate.

XRD patterns of hypoxanthine and uric acid dihydrate crystals formed on the substrates

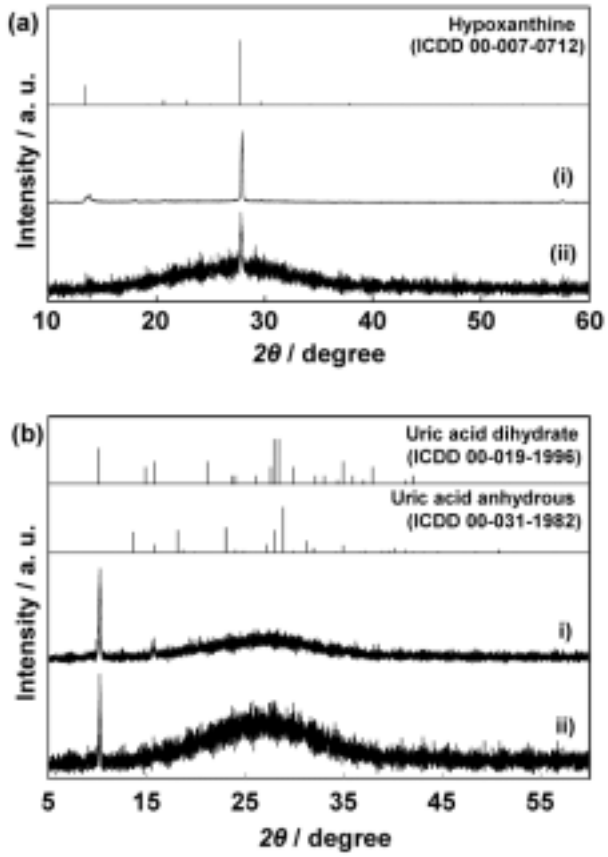

Figure S2. XRD patterns of the hypoxanthine (a) and uric acid dihydrate crystals (b). a) hypoxanthine crystals formed on a glass substrate in the absence of any additive organic molecules (i) and in the presence of PAA (ii), b) uric acid dihydrate crystals formed on a glass substrate in the absence of any additive organic molecules (i) and in the presence of PAA (ii). The bars in the panels a) and b) indicate the peak positions based on the ICDD cards.

When hypoxanthine was crystallized on the chitosan substrate, the intensified peak of the (10–2) plane was only observed on the XRD pattern (peak ii) in Figure S2a). The XRD pattern of uric acid dihydrate formed on chitosan only showed the intensified peak of the (200) plane (peak ii) in Figure S2b). The results imply the orientation of the crystals on the chitosan substrates.