

JANE-2012

Japan-Netherlands Symposium on Crystal Growth

-Theory and in situ Measurements-

*Sunday 22 – Wednesday 25 July 2012*

*at*

*Akiu Spa Hotel Sakan*

*Sendai Japan*

*<http://www.sakan-net.co.jp/en/>*

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*Japan Society for the Promotion of Science (JSPS)*

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*Japan Association for Crystal Growth*

*Organizers:*

*J. ter Horst (Delft University of Technology, the Netherlands)*

*K. Tsukamoto (Tohoku University, Japan)*

*G. Sasaki (Hokkaido University, Japan)*

## Programme JANE 2008

### Sunday 22 July 2012

- 12:00            *Start of registration*  
Chairperson: J. ter Horst
- 13:50            Welcome by G. Sazaki
- 14:00    (O1)    **In situ observation of ice crystal surfaces by advanced optical microscopy**  
G. Sazaki (Hokkaido University)
- 14:45    (O2)    **Nanoscopy: from single molecule transport to playing pinball with atoms**  
Harold Zandvliet (University of Twente)
- 15:30            *Break*  
Chairperson: G. Sazaki
- 16:00    (O3)    **Atomic-scale 3D Visualization of Solid-Liquid Interfaces by FM-AFM**  
Hirofumi Yamada (Kyoto University)
- 16:45    (O4)    **Live STM observation of the growth of graphene and boron nitride monolayers**  
Joost Frenken (Leiden University)
- 17:30            *Break*  
Chairperson: B. McKenzie
- 18:00    (O5)    **In-situ TEM studies on the crystallographic and magnetic phase transformations in solids**  
Yasukazu Murakami (Tohoku University)
- 18:45    (O6)    **Crystallization 4.6 billion years ago**  
Katsuo Tsukamoto (Tohoku University)
- 19:30            *Dinner*

**Monday 23 July 2012**

Chairperson: K. Tsukamoto

- 9:00 (O7) **Opportunities for process intensification of solution crystallization**  
Richard Lakerveld (Delft University of Technology)
- 9:45 (O8) **Enlargement and annealing of a single colloidal crystal grain**  
Yoshihisa Suzuki (The University of Tokushima)
- 10:30 *Break*
- Chairperson: R. Lakerveld
- 11:00 (O9) **Crystal Nucleation**  
Joop ter Horst (Delft University of Technology)
- 11:45 (O10) **Growth and application of quantum dot superlattice for high-efficiency intermediate band solar cells**  
Yoshitaka Okada (Tokyo Univeristy)
- 12:30 *Lunch*
- Chairperson: K. Tsukamoto
- 14:00 (O11) **Preparation of nanostructured polymer particles by self-organization process**  
Hiroshi Yabu (Tohoku University)
- 14:45 (O12) **3D cryoTEM analysis of internally structured block copolymer nanospheres and their application as biomimetic mineralization templates**  
Beulah McKenzie (Eindhoven University of Technology)
- 15:30 *Break*
- Chairperson: H. Meekes
- 16:00 (O13) **Morphology and Growth Mechanism of Polymer Crystals in Thin and Ultrathin Films**  
Ken Taguchi (Hiroshima University)
- 16:45 (O14) **Computer simulation of crystal growth control by impurity molecule**  
Hiroki Nada (National Institute of Advanced Industrial Science and Technology)
- 17:30 *Break*
- 18:00 **Poster presentation (odd number)**
- 19:30 *Dinner*

**Tuesday 24 July 2012**

Chairperson: H. Zandvliet

- 9:00 (O15) **Polymorph selection by crystal nucleation simulations**  
Hugo Meekes (Radboud University Nijmegen)
- 9:45 (O16) **Photochemically-induced crystallization**  
Tesuo Okutsu (Gumma University)
- 10:30 *Break*
- Chairperson: M. Uwaha
- 11:00 (O17) **Polymorphism in industrial process development**  
Rob Geertman (DSM)
- 11:45 (O18) **Si nanoparticle motion on SiO<sub>2</sub>**  
Yukio Saito (Keio University)
- 12:30 *Lunch*
- Chairpoerson: Chaorong Lee
- 14:00 (O19) **DNA- covered nanoparticle assembly mediated by DNA nanostructures**  
Miho Tagawa (Nagoya University)
- 14:45 (O20) **Reaction-diffusion controlled growth of complex structures**  
Wim Noorduyn (Radboud University Nijmegen)
- 15:30 *Break*
- Chairperson: T. Okutsu
- 16:00 (O21) **Functional materials based on hybrid organic/inorganic perovskite structure**  
Chaorong Li (Zhejiang Sci-Tech University)
- 16:45 *Break*
- 17:15 **Poster presentation (even number)**
- 18:45 *Dinner*
- 21:15 **Night session: Special lecture about Tohoku earthquake**  
Toru Matsuzawa (Tohoku University)

**Wednesday 25 July 2012**

Chairperson: Y. Saito

- 9:00 (O22) **Pattern Formation of a Step Induced by a Guiding Linear Source -- Fluctuation and Anisotropy --**  
Makio Uwaha (Nagoya University)
- 9:45 (O23) **Atomic-scale structure at growth interfaces**  
Elias Vlieg (Radboud University Nijmegen)
- 10:30 *Break*
- 11:00 Excursion to Tsunami Area (including lunch)
- 19:30 Dinner and Closing

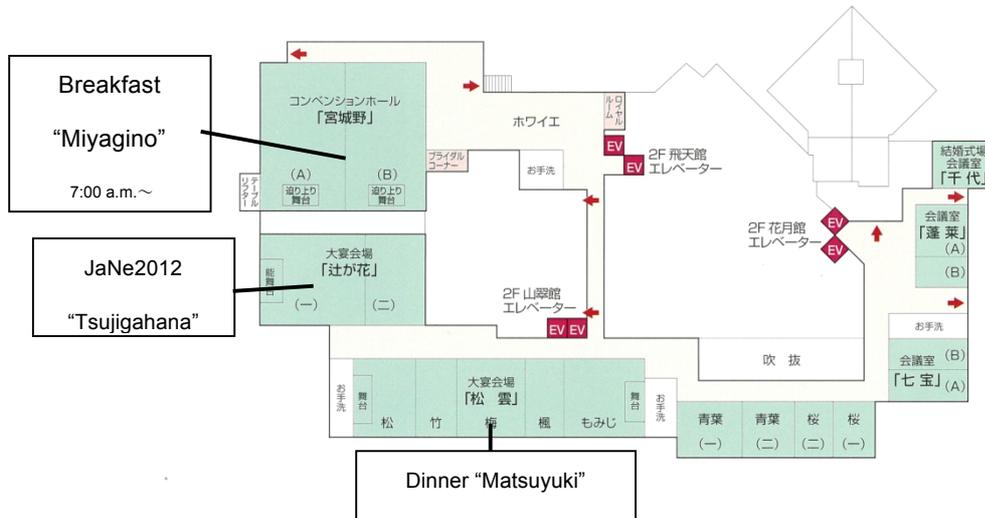
## List of posters

- (P1) **Crystallization of Colloidal Particles using Walls**  
Masahide Sato (Kanazawa University)
- (P2) **Temporal appearance of a homochiral state by random fluctuation in crystallization**  
Hiroyasu Katsuno (Gakushuin University)
- (P3) **Atomic Resolution Investigation in Liquid by Frequency-Modulation (Non-Contact) AFM**  
Ken Nagashima (Hokkaido University)
- (P4) **Crystallization of Isotactic Polypropylene from Mesomorphic Phase - A Constant Heating Rate Study -**  
Harutoshi Asakawa (Hokkaido University)
- (P5) **Effects of container shape on enlargement of grains of colloidal crystals by centrifugation**  
Kaori Hashimoto (The University of Tokushima)
- (P6) **A novel strategy of membrane protein crystallization in lipid**  
Hiroshi Ihira (Gunma University)
- (P7) **Light induced crystallization of protein from template molecules produced by photochemical reaction of aromatic molecules**  
Kazuhiro Tsubokawa (Gunma University)
- (P8) **Effect of shear and additive on crystallization of cocoa butter under the tempering process**  
Kazuya Moriyuki (Hiroshima University)
- (P9) **Crystallization inhibitory effect for crystallization of phytosterol in O/W emulsion droplets**  
Kenta Yamasaki (Hiroshima University)
- (P10) **Effect of tripalmitin on granular crystals formation in bulk model systems of W/O emulsion.**  
Aimi Nakaoka (Hiroshima University)
- (P11) **Crystallization of Triacylglycerols in O/W Emulsion Type Chocolate**  
Saya Izumikawa (Hiroshima University)
- (P12) **Atomic-scale observation of hydration structure on calcite**  
Yuki Araki (Tohoku University)
- (P13) **Morphology of Gypsum Crystals in Naica Mine**  
Soichiro Nozaki (Tohoku University)

# The venue map

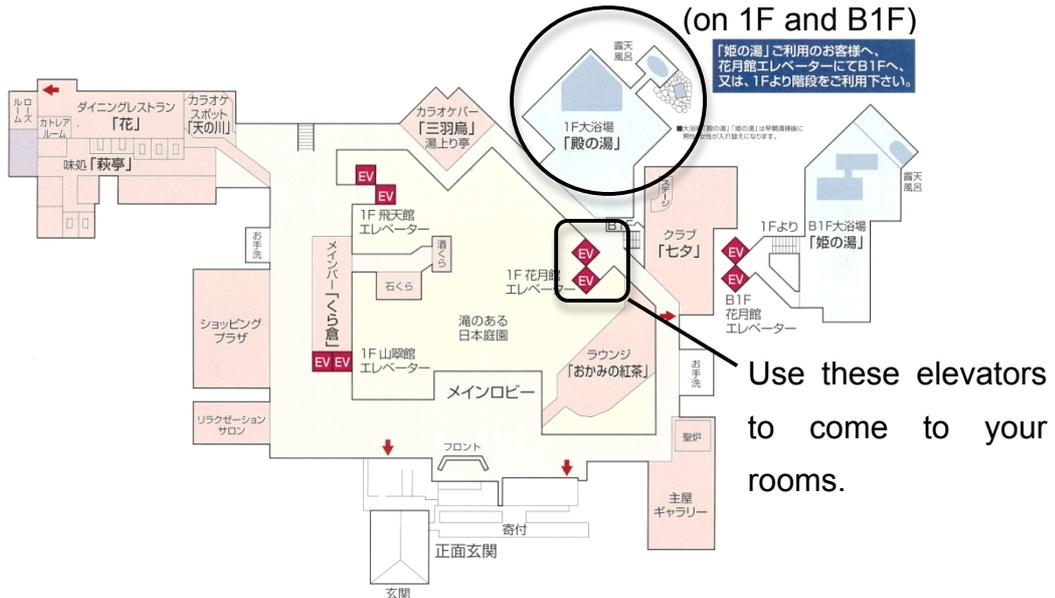
2nd floor: rooms for meeting, break fast, and dinner

非常口



1st floor: lobby, big common bath

Big common bath (on 1F and B1F)



Use these elevators to come to your rooms.

## Meals

### Breakfast

Every morning, you can eat breakfast at the breakfast room “Miyagino” on the 2nd floor from 7:00 a.m.

### Lunch

For a person who ordered a “lunch box set” *by the day before*, we will prepare a lunch box. For a person who does not have advance booking, please take your lunch at a restaurant on the 1st floor of the hotel. A convenience store, which is located in front of the hotel, is also available.

### Dinner

Every evening, you can eat dinner at the dinner room “Matsuyuki” on the 2nd floor.



[O1]

## In situ observation of ice crystal surfaces by advanced optical microscopy

G. Sazaki<sup>1,2</sup>, S. Zepeda<sup>1</sup>, S. Nakatsubo<sup>1</sup>, Y. Furukawa<sup>1</sup>

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Due to the abundance of ice on earth, the phase transition of ice plays crucially important roles in various phenomena in nature. Hence, the molecular-level understanding of ice crystal surfaces holds the key to unlocking the secrets of a number of fields. However, it has been generally acknowledged that molecular-level observation of ice crystal surfaces is very difficult even using scanning probe microscopes.

Then first, we tried to improve laser confocal microscopy combined with differential interference contrast microscopy, and then tried to visualize elementary steps of ice crystals and their dynamic behavior at air-ice interface [1]. As shown in Fig. 1, we could observe the appearance and lateral growth of two-dimensional islands with elementary height (0.37 nm) by our optical microscopy.

Next, we tried to observe surface melting processes in situ at air-ice interface [2]. Then we found that two types of quasi-liquid layer (QLL) phases appear that exhibit different morphologies and dynamics (Fig. 2). The two immiscible QLL phases appeared heterogeneously, moved around and coalesced dynamically on ice crystal surfaces. This picture of surface melting is quite different from the conventional picture.

[1] G. Sazaki, et al., *Proc. Nat. Acad. Sci. USA.*, **107**, 19702-19707 (2010).

[2] G. Sazaki, et al., *Proc. Nat. Acad. Sci. USA*, **109**, 1052-1055 (2012).

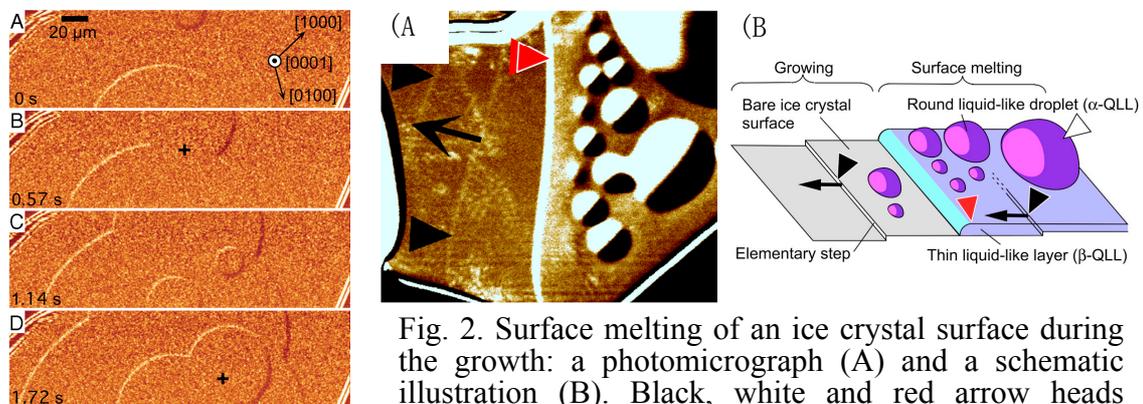


Fig. 1. Elementary steps on an ice crystal surface.

Fig. 2. Surface melting of an ice crystal surface during the growth: a photomicrograph (A) and a schematic illustration (B). Black, white and red arrow heads respectively show elementary steps, round liquid-like drops ( $\alpha$ -QLL), and thin liquid-like layer ( $\beta$ -QLL).

[O2]

## **Nanoscopy: from single molecule transport to playing pinball with atoms**

Harold J.W. Zandvliet

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The structural and electronic properties of self-lacing atomic chains on Pt modified Ge(001) surfaces have been studied using low-temperature scanning tunnelling microscopy and spectroscopy. The self-lacing chains have a cross section of only one atom, are perfectly straight, thousands of atoms long and virtually defect free. At low temperatures the atomic chains undergo a Peierls transition: the periodicity of the chains doubles from a 2x to 4x periodicity and an energy gap opens up [1].

Subsequently I will show the feasibility of controlling an atomic scale mechanical device by an external electrical signal. On a germanium substrate, a switching motion of pairs of atoms is induced by electrons that are directly injected into the atoms with a Scanning Tunneling Microscope tip [2]. By precisely controlling the tip current and distance we make two atom pairs behave like the flippers of an atomic sized pinball machine. This atomic scale mechanical device exhibits six different configurations.

Finally, I will present an *electrode-molecule-electrode* junction that can be controllably opened and closed by careful tuning of the contact's interspace and voltage [3,4]. The molecule, an octanethiol, flips to bridge a ~1 nm interspace between substrate and scanning tunnelling microscope tip when an electric field exceeds a threshold (switch "on"). Reducing the field below this threshold value leads to the reproducible detachment of the octanethiol (switch "off"). Once contacted, a further reduction of the contact's interspace leads to an increase of the conductance of the molecule.

[1]. N. Oncel et al., *Physical Review Letters* **95**, 116801 (2005).

[2]. A. Saedi et al., *Nano Letters* **9**, 1733-1736 (2009),

[3]. D. Kockman et al. , *Nano Letters* **9**, 1147-1151 (2009).

[4]. A. Kumar et al. , *Journal of Physics: Condensed Matter*, **24**, 082201 (2012).

[O3]

## Atomic-scale 3D Visualization of Solid-Liquid Interfaces by FM-AFM

H. Yamada<sup>1</sup>, K. Suzuki<sup>1</sup>, K. Umeda<sup>1</sup> and K. Kobayashi<sup>2</sup>

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2) Office of Society-Academia Collaboration for Innovation, Kyoto University

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Force mapping method based on frequency modulation atomic force microscopy (FM-AFM) is a remarkable technique for atomic-scale investigations of interaction forces on a specific site of crystal surfaces. The technique has been used mainly in vacuum environments, where highly sensitive force detection can be performed due to the high Q-factor in the cantilever oscillation. However, since significant progress has been made in FM-AFM in liquids over the past few years [1, 2], the force mapping method can be used for atomic or molecular scale investigations of interaction forces at solid-liquid interfaces, such as solvation forces (Fig. 1).

Hydration structures are related to various physical, chemical and biological phenomena so that it is essentially important to have molecular-scale understanding of them. We applied the force mapping technique to 3D atomic/molecular-scale visualization of various solid-liquid interfaces. Figure 2 shows one of 3D frequency shift ( $\Delta f$ ) data, obtained on a muscovite mica surface in aqueous solution, which basically reflects 3D interfacial force data. The result was compared with water density distributions calculated using the 3D reference interaction site model (3D-RISM) theory. Furthermore, latest results on 3D visualization of hydration structures around biomolecules such as DNA molecules are also discussed.

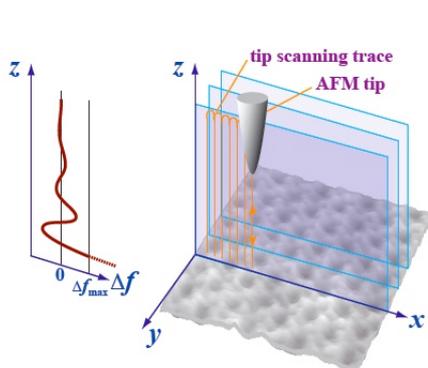


Fig. 1. Schematic of 3D force mapping method.

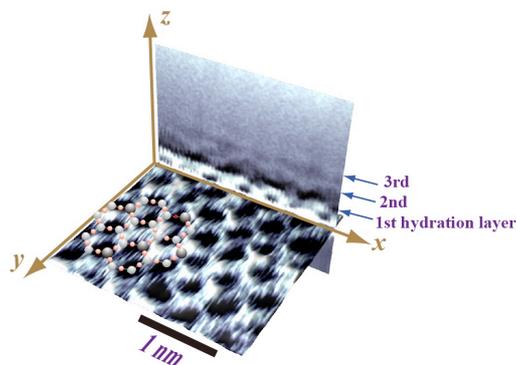


Fig. 2. Atomic-scale 3D hydration structure at a mica-water interface, obtained by 3D force mapping method.

[O4]

## Live STM observation of the growth of graphene and boron nitride monolayers

J.W.M. Frenken<sup>1</sup>, G. Dong<sup>1</sup>, D.W. van Baarle<sup>1</sup>, R. van Rijn<sup>1,2</sup>

1) Kamerlingh Onnes Laboratory, Leiden University, Leiden, The Netherlands,

2) Applied NanoLayers BV, Leiden, The Netherlands

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Graphene is drawing much attention because of its special properties and potential applications. Achieving high-quality graphene reproducibly remains a challenge. Small quantities can be obtained for research purposes by the so-called “Scotch-tape” method. Most other methods, in particular those based on the direct growth of graphene, suffer from high defect densities, caused by multilayer growth, chemical contamination, dislocations, etc. These imperfections may seriously influence the properties and the stability of the graphene.

We report an investigation of the CVD growth of graphene and its ‘lookalike’ hexagonal boron nitride (*h*-BN) on Rh(111). Both form nearly perfectly regular films with a thickness of precisely one atom on this and several other metal surfaces. Using a variable-temperature scanning tunneling microscope, specialized for the live observation of processes at high temperatures and even *during* substantial temperature variations [1,2], we follow the formation of single-layer graphene from ethylene and the growth of single-layer *h*-BN from borazine on Rh(111) under realistic growth conditions, up to 1200 K. Our STM movies demonstrate in detail how both structures grow and how defects are introduced. In particular, we distinguish the nucleation of the overlayer, the direct growth from gas-phase deposited material and the indirect growth via the segregation from a dissolved phase. Based on these observations we arrive at optimized recipes for high-quality overlayers of both materials [3,4].

[1] M. S. Hoogeman *et al.*, *Rev. Sci. Instrum.* **69**, 2072 (1998).

[2] M. J. Rost *et al.*, *Rev. Sci. Instrum.* **76**, 053710 (2005).

[3] G. Dong *et al.*, *Phys. Rev. Lett.* **104**, 096102 (2010).

[4] G. Dong *et al.*, *New J. Phys.* **14**, 05303 (2012).

[O5]

## In-situ TEM studies on the crystallographic and magnetic phase transformations in solids

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murakami@tagen.tohoku.ac.jp

This paper reports on our transmission electron microscopy (TEM) studies about structural phase transformations observed in crystalline solids. The targets of research include “nucleation and growth process” of the ferromagnetic phase in perovskite-type manganite,  $\text{La}_{0.25}\text{Pr}_{0.375}\text{Ca}_{0.375}\text{MnO}_3$ , which has attracted considerable attentions of researchers due to the effect of colossal magnetoresistance [1]. Cryogenic Lorentz microscopy reveals that the ferromagnetic phase is produced as a droplet (in a form of magnetic single-domain: Fig.1(a)), although it changes to a form of multiple domains by further cooling, as demonstrated in Figs. 1(b) and 1(c). Within a specific temperature range near Curie temperature, in which the ferromagnetic phase coexists with the nonmagnetic mother phase, the magnetic domain structure is extremely sensitive to an applied magnetic field and/or temperature fluctuation; it appears that this delicate nature of magnetic microstructure is responsible for the achievement of significant conduction paths made of the ferromagnetic (*i.e.*, metallic) portions. The observations in Fig. 1 determine the critical radius at which the single magnetic domain transforms to the state of multiple domains. In addition, electron holography studies revealed the width of magnetic domain walls. Based on these TEM observations, we have determined the principal magnetic parameters of nanometer-scale regions, such as the magnetocrystalline anisotropy constant ( $3.6 \times 10^4 \text{ J/m}^3$ ) and exchange stiffness constant ( $5.6 \times 10^{-12} \text{ J/m}$ ), without bulk magnetization results.

[1] Y. Murakami, H. Kasai, J.J. Kim, S. Mamishin, D. Shindo, S. Mori, A. Tonomura, *Nature Nanotech*, **5**, 37-41, 2010.

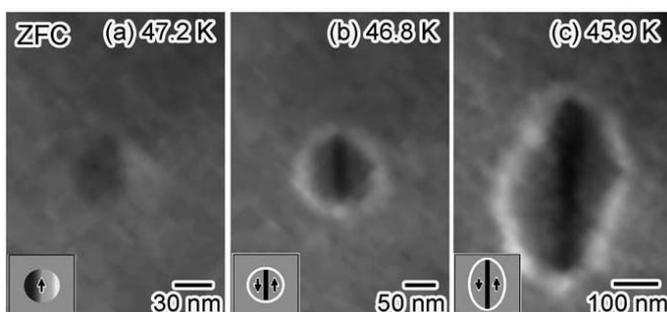


Fig.1 Nucleation and growth of the ferromagnetic phase in a perovskite-type manganese oxide  $\text{La}_{0.25}\text{Pr}_{0.375}\text{Ca}_{0.375}\text{MnO}_3$ . (a) A pair of black and white dots indicates the formation of magnetic single domain. (b), (c) The ferromagnetic phase (framed by white lines) shows a form of magnetic multiple-domains.

[O6]

## Crystallization 4.6 Billion Years Ago

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[ktsuka@m.tohoku.ac.jp](mailto:ktsuka@m.tohoku.ac.jp)

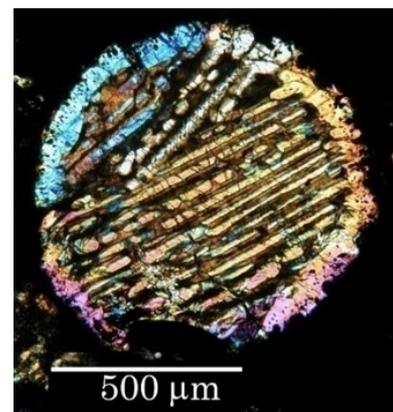
Crystallization in space is one of the interesting subjects in crystal growth because the crystallization takes place in real open and levitated environments and thus, for instance, homogenous nucleation is possibly be of importance. We will discuss the two



crystallizations in the early solar nebula, 4.6 billion years ago, (1) cosmic dusts, fig.1, which are mainly silicate crystals, crystallized far below the equilibrium concentration and (2) chondrules, fig.2, which are the result of crystallization from a silicate melt droplets with a few mm in diameter show unique which never found in an earth environment. There still a long discussion about the formation mechanisms of (1) and (2) because of almost no good experiments in space environments.

The formation of (1) could theoretically be interpreted due to the sharp increase of gas concentration and temperature followed by sharp drop of these parameters around shock waves formed at rapidly moving cosmic material or asteroid in space environment, Miura et al, 2009.

The formation of (2) is largely related to crystallization mechanism which we want to discuss in the symposium. Homogeneous nucleation, pattern formation in a hypercooled melt and levitation are the key word in the topics.



[O7]

## Opportunities for Process Intensification of Solution Crystallization

R. Lakerveld, A. Soare, H.J.M. Kramer, A.I. Stankiewicz

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The design of current industrial crystallizers is strongly focused on optimization of known types of crystallization equipment. These crystallizers harbor various physical phenomena, which are strongly entangled. The application of generic principles of process intensification to crystallization processes requires individual control over physical phenomena<sup>1</sup>. This talk will discuss the experimental investigation of several novel technologies that have the potential to specifically manipulate individual physical phenomena of crystallization processes. These technologies include, a) ultrasound<sup>2</sup> for improved control over nucleation, b) membrane-assisted crystallization<sup>3,4</sup> for improved control over supersaturation generation, and c) air-mixed devices to provide mixing with low shear forces for improved control over crystal growth. The results show that the investigated technologies can individually contribute to an improved crystallizer design. However, the true strength lies in the integration. Dynamic model-based optimization of an integrated system results in a surprising flexibility to produce different grades of product. This flexibility is the result of the ability to manipulate physical phenomena independently from each other, which is poorly possible in conventional crystallization equipment.

[1] R. Lakerveld, et al., *Chem. Eng. Process.*, **49**, 979-991 (2010).

[2] R. Lakerveld, et al., *AIChE J.*, **57**, 3367-3377 (2011).

[3] J. Kuhn, et al., *Ind. Eng. Chem. Res.*, **48**, 5360-5369 (2009).

[4] R. Lakerveld, et al., *Chem. Eng. Sci.*, **65**, 2689-2699 (2010).

[O8]

## Enlargement and annealing of a single colloidal crystal grain

Yoshihisa Suzuki<sup>1</sup> and Yuuki Uehara<sup>2</sup>

- 1) Institute of Technology and Science, The University of Tokushima, 2) Graduate School of Advanced Technology and Science, The University of Tokushima  
suzuki@chem.tokushima-u.ac.jp

A three-dimensionally large and close-packed face-centered cubic colloidal crystal is useful as a template for inverse opals with perfect three-dimensional photonic bandgap [1]. The crystal is easily fabricated by drying highly-concentrated colloidal crystals [2]. However, controlled fabrication of the crystal with sufficiently large and high quality grains for device applications is still difficult.

We developed effective enlargement and annealing methods to obtain such a colloidal crystal grain by applying two kinds of external fields. One is a gravitational field [3], and the other is an optical trapping field.

Fig. 1 shows merged transmission and reflection microscope images of large grains in a tilted optical cell. The grains were obtained by centrifugation. The size of the largest grain is  $\sim 6.1 \text{ mm}^3$ . We will also show the results on gravitational annealing of a colloidal crystal. Fig. 2 shows a condensation and colloidal crystallization process of silica particles in an optical trapping field. We will also show the results on annealing of

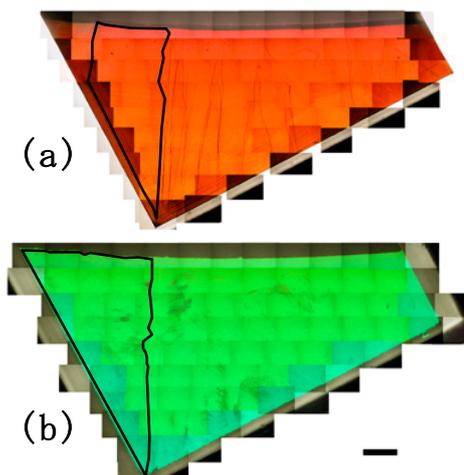


Fig. 1. Merged (a) transmission and (b) reflection images of a polystyrene colloidal crystal in an optical cell. Solid black lines show the largest grain in the crystal. Scale bar represents 1 mm.

the crystal in the optical trapping field.

[1] A. Blanco, et al., *Nature*, **405**, 437-440 (2001).

[2] Y. Suzuki, et al., *J. Cryst. Growth*, **322**, 109-113 (2011).

[3] Y. Suzuki, et al., *J. Cryst. Growth*, **318**, 780-783 (2011).

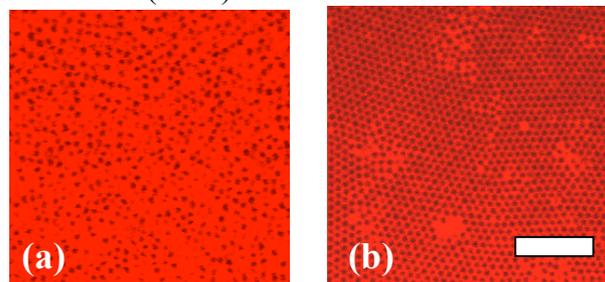


Fig. 2. Fluorescent confocal microscopic images of silica particles. (a):  $t = 0 \text{ s}$ , and (b):  $t = 100 \text{ s}$  after starting application of an optical trapping field. Scale bar represents  $5 \mu\text{m}$ .

## [O9] Crystal Nucleation, Polymorphism & Self-Association

*Joop H. ter Horst*

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Crystal nucleation is a stochastic process in which building units attach to and detach from a cluster forming a nucleus. By controlling the self-association of the solute in solution, the solvent can have a large impact on which building unit is present in solution and thus on the crystal nucleation process. This impact in turn is reflected in the nucleation rates measured and the polymorphic form crystallized.

Nucleation rates can be determined by measuring induction time distributions [1]. These measurements show that the kinetic pre-exponential factor of the nucleation rate equation is lower than theoretically expected which would indicate that either the concentration of heterogeneous particles or the attachment frequency of building units is lower than expected. They further indicate that apparently a single nucleus mechanism is occurring, which was confirmed visually [2,3]. A general occurrence of such a mechanism would have large implications for product quality control of industrial crystallizers.

We demonstrate the reproducible effect of solvents on the formation of for instance isonicotinamide polymorphs [4]. In solvents with strong hydrogen bond acceptors, the dominant self-association of the isonicotinamide molecules is by amide-pyridine heterosynthons (head-to-tail chains). Contrarily, solvents with strong hydrogen bond donors lead to a self-association by amide-amide homosynthons (head-to-head dimers). Using these strongly hydrogen bonding solvents leads to the formation of polymorphs containing the structural motif reflecting the self-association in solution. Based on these results we are now working to establish a systematic method for the discovery and reproducible preparation of new polymorphs.

1. S. Jiang, J.H. ter Horst, Crystal Nucleation Rates from Probability Distributions of Induction Times, *Crystal Growth Design* **11** (2011) 256-261.
2. S.S. Kadam, H.J.M. Kramer, J.H. ter Horst, Combination of a Single Primary Nucleation Event and Secondary Nucleation in Crystallization Processes, *Crystal Growth Design* **11** (2011) 1271–1277.
3. 5. S.S. Kadam, S.A. Kulkarni, R. Coloma Ribera, A.I. Stankiewicz, J.H. ter Horst, Herman J.M. Kramer, A new view on the metastable zone width during cooling crystallization, *Chem. Eng. Sci.* **72** (2012) 10–19.
4. S.A. Kulkarni, E. S. McGarrity, H. Meekes, J.H. ter Horst, Isonicotinamide self-association: the link between solvent and polymorph nucleation, *ChemCommun.* **48** (2012) 4983-4985.

[O10]

## Growth and application of quantum dot superlattice for high-efficiency intermediate band solar cells

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Efficiency enhancements exceeding the Shockley-Queisser limit of a single junction solar cell is possible with an intermediate band solar cell (IBSC) [1], which incorporates a quantum dot (QD) superlattice in the active region of a *p-i-n* cell structure. The presence of IB leads to generation of a net electron-hole pair when 2 below-bandgap photons are absorbed, *i.e.* one photon pumps an electron from the valence band (VB) to IB, while a second photon pumps an electron from the IB to conduction band (CB). These electron-hole pairs add to those produced by band-to-band transitions with photons above the bandgap energy  $E_G$  that excite electrons directly from VB to CB.

Experimental challenges to demonstrate IBSCs require fabrication of a close-packed QD superlattice. We have demonstrated the first QD solar cell with 30 multi-stacked InAs/AlGaInAs QD layers fabricated on InP (311)B substrate by using *strain compensation technique* [2]. Recently, strain-compensation technique has been applied to demonstrate multi-stacked QDSCs with InAs/GaNAs on GaAs substrates [3,4].

[1] A. Luque and A. Martí, *Phy. Rev. Lett.* **78** (1997) 5014.

[2] Y. Okada *et al*, *Proc. of 20th European PVSEC* (Barcelona, June 2005) 1AO.7.6.

[3] R. Oshima, A. Takata, and Y. Okada, *Appl. Phys. Lett.* **93** (2008) 083111.

[4] Y. Okada *et al*, *J. Appl. Phys.* **109** (2011) 024301.

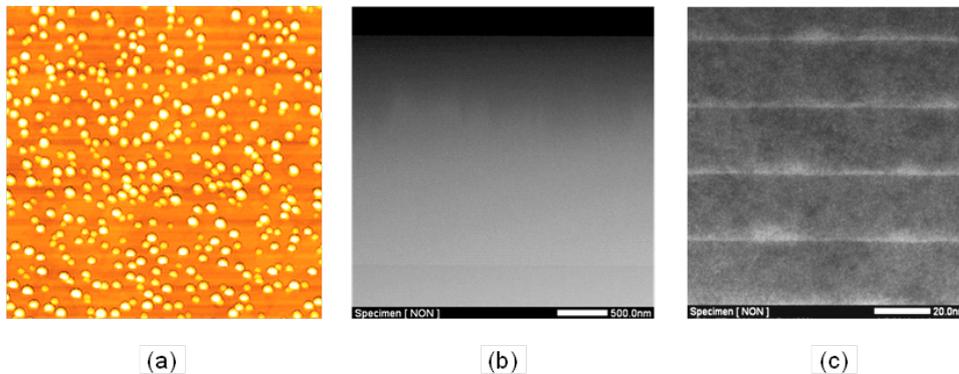


Fig. 1 (a) AFM image of topmost QD surface, (b) cross-sectional STEM image, and (c) magnified view, measured for 100 layer-stacked InAs/GaNAs strain-compensated QDs on GaAs, respectively. The structure is integrated into a *p-i-n* junction to form an IBSC.

[O11]

## Preparation of Nanostructured Polymer Particles by Self-Organization Process

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The development of nano-structured polymer particles and their applications constitute an emerging field in nanotechnology. We have discovered a simple and versatile particle preparation method termed “Self-ORganized Precipitation (SORP)” [1]. First, polymer is dissolved in a good solvent, and then a poor solvent is mixed into the solution (Fig. 1). After complete evaporation of the good solvent, the polymer precipitates as micro- or nano-particles in the poor solvent. The boiling point of the good solvent should be lower than that of the poor solvent to remove the good solvent selectively, and the solvents should be miscible. Under these conditions, particles of various polymer materials can be formed.

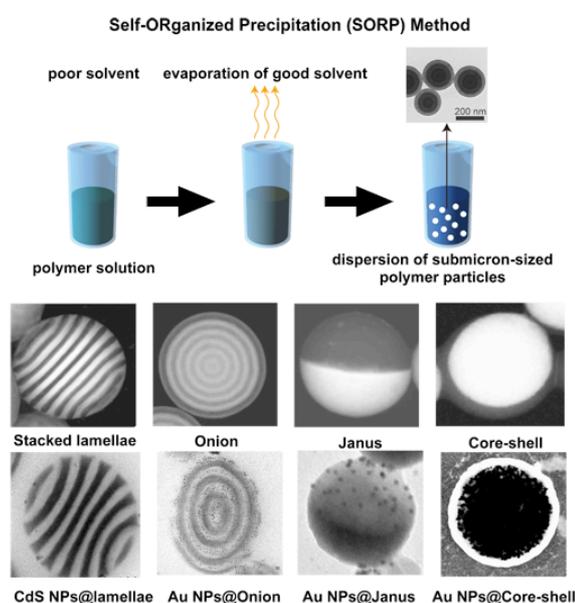


Fig. 1. Schematic illustration of the SORP method and various polymer particles prepared by using the SORP method.

One of the advantages of the SORP method is that mixtures of polymers and other functional materials including nanoparticles and pigments can be transformed into nanoparticles. Polymer blends that comprise mixtures of two or more homopolymers exhibit phase separation at greater than the micrometer scale. Block copolymers also form microphase-separated structures ranging from several nanometers to tens of nanometers. We found that unique phase-separated structures form in the polymer blend and block-copolymer particles. We discuss the morphological control of polymer particles based on the types of polymer materials used for particle preparation.

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[O12]

## 3D-CryoTEM Analysis of Internally-structured Block Copolymer Nanospheres and their Application as Biomimetic Mineralization Templates

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The self-assembly of amphiphilic block copolymers has been of increasing interest due to the encapsulation and solubilisation properties they possess. In addition to micelles, cylinders and vesicles, more complex structures are being observed, such as toroids, multi-compartment micelles, and nanospheres with internal morphology [1]. A new class of complex micelles has also been observed: amphiphilic block copolymer nanospheres with internal bicontinuous structure. CryoTEM has become an essential tool for the visualization of such structures. Following initial reports on internally-structured micelles [2,3], we recently reported the formation of micelles with thermally-tunable bicontinuous internal structure from semi-crystalline amphiphilic block copolymers (Fig.1) [4]. Similar bicontinuous structures have been observed from a variety of block copolymer amphiphiles [5,6], although rarely. Intriguingly, there is no seemingly obvious unifying blueprint for their formation. Hence, the challenge is to understand the contributory factors for their formation, enabling the tailored synthesis of bicontinuous nanospheres from any block copolymer to target new and exciting applications. This talk will discuss the formation of these novel bicontinuous nanospheres and the elucidation of their internal morphology through extensive 2D and 3D cryoTEM studies, in addition to their possible application as a novel polymeric template for biomimetic mineralization.

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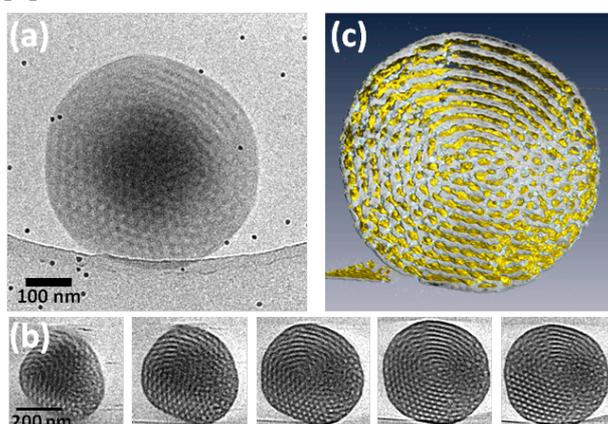


Fig. 1: **a)** cryoTEM image of a bicontinuous nanospheres from PEO<sub>39</sub>-PODMA<sub>17</sub>; **b)** z slices showing different cross-sections of a 3D SIRT reconstruction of a tomographic series recorded from the vitrified film in a); **c)** 3D visualization showing an inner section of the whole structure, where all the channels and compartments are visible.

[O13]

## Morphology and Growth Mechanism of Polymer Crystals in Thin and Ultrathin Films

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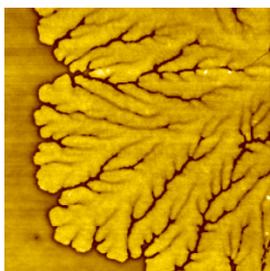
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Studies of growth and morphology of polymer crystals in thin films are of particular interest due to their intriguing features and of importance for technological applications such as microelectronics, coatings and so on. The polymer crystallization in thin films generally shows that the reduction in growth rate and morphological change with decreasing film thickness, which indicate the importance of the role of mobility or diffusion of polymer chains in thin films.

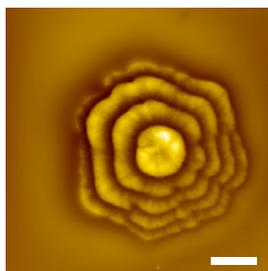
We have investigated the crystal growth of isotactic polystyrene (iPS) thin films ranging from several micro- down to nanometers in detail and found various growth patterns such as branching pattern (figure 1) in ultrathin film region [1-2] or concentric-ring pattern (figure 2) in submicron film region [3]. We have also examined the effect of molecular weight of samples on the growth rate and these patterns in order to elucidate the role of diffusion of polymer chains; for low molecular weight, less reduction in growth rates and larger branching patterns (figure 3). From the observed molecular weight dependences, we discuss the role of polymer diffusion or film instability on the crystal growth kinetics and pattern formation.

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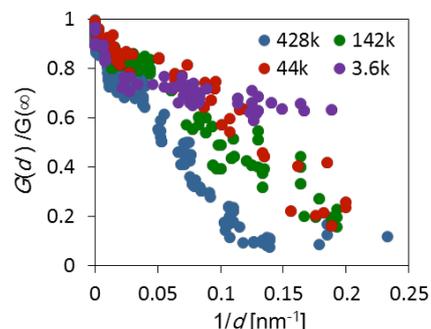
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**Fig. 1** AFM image ( $10\mu\text{m}^2$ ) of iPS crystal grown in 13nm thick films at 180C. Molecular weight is 428k.



**Fig.2** AFM image of iPS crystal grown in ca. 70nm films at 180C. Molecular weight is 44k. The scale bar is 10  $\mu\text{m}$



**Fig.3** Growth rates ( $G$ ) vs. inverse of film thickness ( $1/d$ ) for iPS thin films with four different molecular weights.

[O14]

## Computer simulation of crystal growth control by impurity molecules

H. Nada

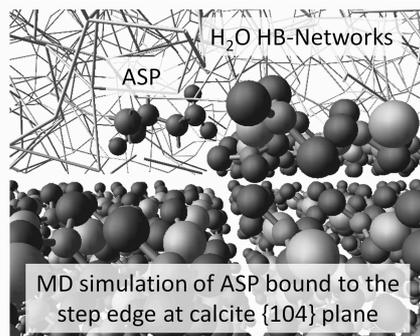
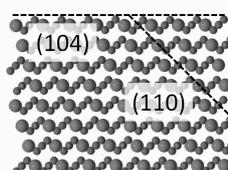
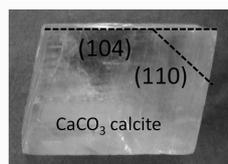
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Living organisms learn special “techniques” of crystal growth in their bodies. Using the techniques, they produce functional organic/inorganic hybrid materials (biominerals), such as teeth, bone, shells and exoskeletons. The essence of the techniques is skillful use of organic molecules, such as proteins and peptides, for precise controls of nucleation, growth and morphological changes of inorganic, mineral crystals. Such biological mineral crystallization is known as biomineralization.

Mineral crystals formed in biomineralization consist of ubiquitous elements on the Earth. Biomineralization needs neither lowering of temperature nor applying high pressure. Hence, biomineralization is an excellent “textbook” from which we learn how to develop energy-saving, environmentally-friendly technologies for crystal growth and material design. Thus, elucidating the mechanisms of crystal growth in biomineralization is of particular importance. However, it is quite difficult to elucidate them by experimental means. Elucidating the mechanisms requires analysis of complicated atomic-scale dynamics of organic molecules, water molecules, anions and cations on the surface of mineral crystals.

Recently we started a few fundamental studies on the growth control of mineral crystals by organic molecules using atomistic simulation. One of them is a molecular dynamics (MD) simulation study of the binding conformation and dynamics of aspartic acid (ASP) at the surface of a  $\text{CaCO}_3$  calcite crystal, which is a typical mineral crystal formed in biomineralization. Simulation results strongly suggested that “water” plays crucial roles in the stabilization of ASP’s binding at the surface, especially, at the {104} plane surface of the crystal. Details of the simulation results will be shown at the presentation.



[O15]

## Polymorph selection by crystal nucleation simulations

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Information on crystal structure is essential for understanding crystal nucleation, crystal morphology, and more general polymorphism. It is usually assumed that the appearance of (meta)stable polymorphic forms of a compound is determined in the nucleation stage of crystallization. Besides temperature and solvent, the supersaturation during nucleation is the key parameter for this. By measuring the stability of 3D clusters of the polymorphic forms of a compound, using Monte Carlo simulations, one can determine their relative nucleation rates as a function of the supersaturation.<sup>[1]</sup> In this way the experimental conditions for which polymorphic forms are expected to appear, can be determined once their crystal structures are available.

In case not all polymorphic forms are known, crystal structure prediction can be of help. In practice, however, the number of predicted structures is much larger than the number of observed polymorphic forms. Also here, selection of the predicted forms on the basis of their simulated nucleation rates might be of help.

On the other hand, the quality of the force fields used in crystal structure prediction are still of too low quality to come to a reliable ranking of the predicted structures on the basis of their energy.<sup>[2-4]</sup> In recent years it has been shown that additional information from an experimental XRPD-pattern, even if of limited quality, can improve the ranking of structures considerably.<sup>[5]</sup>

We will discuss the use of simulated crystal nucleation rates in polymorph selection and in polymorph prediction. Furthermore, we will present a novel tool for applying additional information like XRPD-patterns in crystal structure prediction.

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[O16]

## Photochemically-induced crystallization

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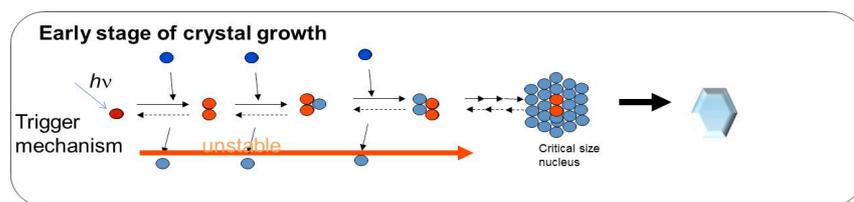
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Photochemically-induced crystal growth of protein was studied. We found phenomenon of light-induced crystallization of protein and have been revealed its mechanism.<sup>1)</sup> The mechanism is illustrated in Scheme 1. Covalent bonded photochemical product dimer plays a role instead of  $n = 2$  cluster.

The aim of this study is to obtain single protein crystal from one droplet with high efficiency without high throughput. We aim to know the instance of nucleation to prevent excess irradiation which brings about protein damage. For this purpose, we examined in situ observation of nucleation process.



Scheme 1. Mechanism of photochemically induced nucleation of lysozyme.

Figure 1 shows the representative result of light scatter experiment. Hen egg-white lysozyme was used as protein. UV LED (280 nm) was used for excitation and white LED was used as probe light source.

Scatter decreased in the beginning, and then turned to increase. After 100 s irradiation, the scatter did not increase which means products are not template of nucleus, after 600 s irradiation, the scatter increased in dark, which indicates nucleus formation.

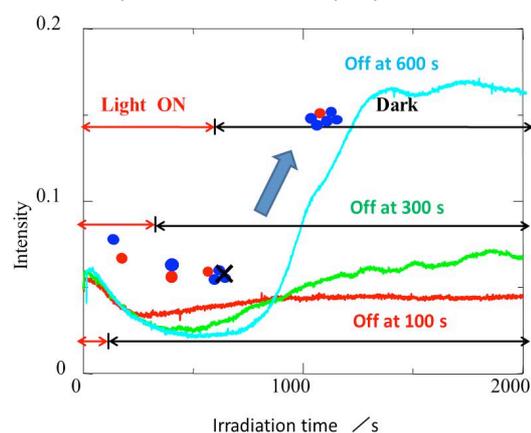


Figure 1 Light scatter intensity change against the irradiation time. Scatter intensity once decreased due to dimer formation. Once the dimer formed, the scatter

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[O17]

## Polymorphism in industrial development

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In industrial process development the initial focus of the polymorphic screening is finding a suitable polymorphic form for the product; it should be stable, have the desired properties (solubility, dissolution rate, handling characteristics etc.) and can be produced with a reasonable effort.

Often neglected is the fact that in a number of cases (highly) unstable solvates can occur. These solvates are in many cases not observed in the initial polymorphic screening as this is intended to find stable polymorphs. However, missing such unstable solvates can result in an erratic production process.

This is illustrated with two cases, one case where a thus far unobserved methanol solvate caused a rapid polymorphic transition. This transition had major impact on the dissolution properties of the product and the handling characteristics. Further research showed that not one but probably two to three polymorphic transitions occurred within a very short timeframe. This initiated a complete redesign of the crystallization process.

The other case highlights the importance of knowing the solvate system. A product with multiple anhydrous and hydrate forms is produced by cooling crystallization. During cooling the initial anhydrate is transformed to a dihydrate and later a tetrahydrate. If the production is started with the right anhydrous form the transformation to the hydrated forms can take place without complete recrystallization. If however the wrong anhydrous form initially nucleates a complete recrystallization will occur later on resulting in very poor filtration characteristics.

[O18]

## Si nanoparticle motion on SiO<sub>2</sub>

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Si thin film on SiO<sub>2</sub> dewets during annealing at high temperatures above 700C, and three-dimensional Si nanoislands are formed. On further elevating the temperature, these nanoislands react with substrate SiO<sub>2</sub> and evaporate. While nanoislands are evaporating, they migrate randomly and drill holes on substrate.

We theoretically study the motion of nanoparticles during evaporation by using a solid-on-solid lattice model with surface diffusion and chemical reactions. Si atoms diffuse on Si and SiO<sub>2</sub> surface. SiO<sub>2</sub> at interface decomposes into Si and two oxygens. The emitted oxygen diffuses along the interface. When oxygen atom meets the topmost Si atom, they combine to form a volatile SiO molecule and it evaporates irreversibly. We study the process for the one-dimensional system by means of kinetic Monte Carlo simulations. At small evaporation rate nanoparticles migrate diffusively, whereas they drill holes at large evaporation rate. These behaviors are in qualitative agreement with experimental findings.

[O19]

## DNA- covered nanoparticle assembly mediated by DNA nanostructures

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Due to the programmability and self-assembly characteristic, DNA is a powerful tool for guiding the assembly of nanometer-sized particles into large-scale ordered structures. Recently, DNA-guided nanoparticle crystallization has been demonstrated and many types of crystal structures have been created [1, 2, 3]. By changing particle size ratio, DNA length and complementarity, particles assemble into different types of crystals. However, by this method, it is difficult to control the number of connecting bonds and the coordination number (the number of nearest neighbors) and to make open, asymmetric and heterogeneous structure for further assembly and applications. Here, we demonstrate DNA-covered nanoparticle assembly mediated by DNA nanostructures, which are tetrahedra with four symmetrical connecting bonds. Tetrahedra play a role in limiting the number of connections between particles into four and particles assemble into diamond structure. Successful crystal structure shows that precise structure control of colloidal crystallization mediated by DNA nanostructures is possible and DNA nanostructures can control the number of connecting bonds between particles and determine the crystal structure.

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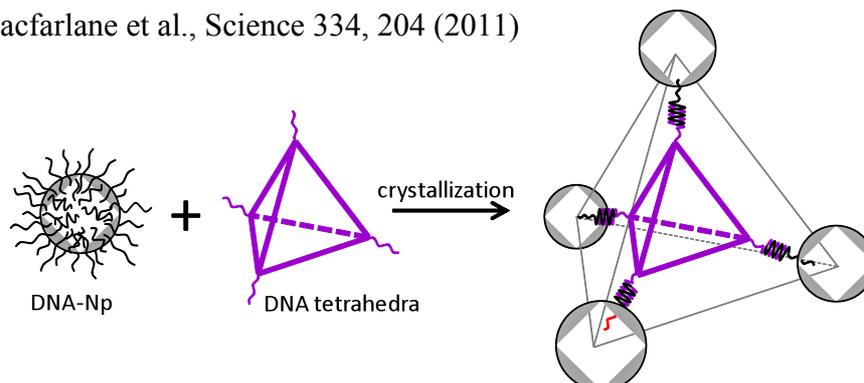


Fig. 1. DNA-covered nanoparticle assembly mediated by DNA tetrahedra

[O20]

## Reaction-diffusion controlled growth of complex structures

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Understanding how the emergence of complex forms and shapes in biominerals came about is of fundamental interest, and with practical ramifications for bio-inspired micro- and nano-fabrication strategies. Although biomineralization processes and organization strategies to give higher order architectures have been studied extensively, synthetic approaches to mimic these self-assembled structures are highly complex and have been difficult to emulate, let alone replicate. In the absence of additive molecules, the emergence of solution patterns has been found in reaction-diffusion systems such as Turing patterns and the BZ reaction. Intrigued by this spontaneous formation of complicity we explored if similar processes can lead to the emergence of patterns in the solid state. We here identify a reaction-diffusion system that exhibits an unprecedented level of morphological complexity that can be attributed to a delicate balance between the diffusion of compounds and their subsequent chemical reactions. The latter triggers a localized feedback reaction giving composite materials with a shape that is a direct readout of the environmental conditions. Based on the insights in the underlying reaction diffusion processes, we continuously adjusted the environment during the growth to finely sculpt patterns and shapes, and developed a toolbox of engineering strategies to deterministically stack different morphologies on top and inside each other to create a landscape of hierarchical multi scale-complex architectures with unprecedented levels of complexity and precision. These findings may hold profound implications for understanding, mimicking and ultimately expanding upon nature's morphogenesis strategies, allowing the synthesis of advanced highly complex microscale materials and devices.

[O21]

## Functional materials based on hybrid organic/inorganic perovskite structure

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Perovskite structure is a hot topic for long time, due to its continuous emerging of new performance, such as piezo, colossal magnetoresistance, ferroelectricity, superconductivity, charge ordering etc. The traditional perovskite is denoted as  $ABO_3$ , the octahedral  $BO_6$  forms in a layer and stacks layer by layer. If an organic chain is inset between the octahedral  $BO_6$  layers, a deformed new type of perovskite structure is formed. The new type of organic /inorganic hybrid perovskite material can be described as one or more inorganic octahedral layers separated by an organic chain. That structure is a kind of self-assembled molecular level of quantum well structure. Therefore, new properties emerged. We have focused on the hybrid material system of  $(C_nH_{2n+1}-NH_3)_2(CH_3NH_3)_{m-1}Pb_mI_{3m+1}$  (abbreviated as  $C_nPb_mI_{3m+1}$ ;  $n=4, 8, 12$ ;  $m=1, 2, 3$ ), where  $n$  represents the length of the organic chain, hence determines the width of barrier in the quantum well structure, while  $m$  relates to the thickness of the well and is the number of inorganic octahedral layers between the organic chain. Two-dimensional (2D) layered organic-inorganic hybrid perovskite with its unique self-assembly and photoelectric properties, has been proposed to functionalize for applications in photoconductive integrated devices. Special devices with the heterostructure of ITO/TiO<sub>2</sub>/TiO<sub>2</sub>: $C_nPb_mI_{3m+1}$ /Pt were fabricated through a facile physical-chemical process. The relationship of the photoconductive performance of the devices and device structures was systematically investigated. The photoconductivity could be optimized by adjusting the alkyl chain length ( $n$ ) or inorganic sheet thickness ( $m$ ) of the hybrid perovskite. The photocurrent of the device showed a negative and positive dependence with  $n$  and  $m$ , respectively. Particularly, a high ratio value of  $3.96 \times 10^4$  of the photocurrent and dark current ( $J_i/J_d$ ) was achieved for the ITO/TiO<sub>2</sub>/TiO<sub>2</sub>:(C<sub>4</sub>H<sub>9</sub>NH<sub>3</sub>)<sub>2</sub>Pb<sub>3</sub>I<sub>10</sub>/Pt device at the bias voltage of 1.0 V. That is due to that both the shortened alkyl chain and thickened inorganic sheet can facilitate the exciton dissociation at the donor-acceptor interface and enhanced the carrier transport.

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[O22]

## Pattern Formation of a Step Induced by a Guiding Linear Source —Fluctuation and Anisotropy—

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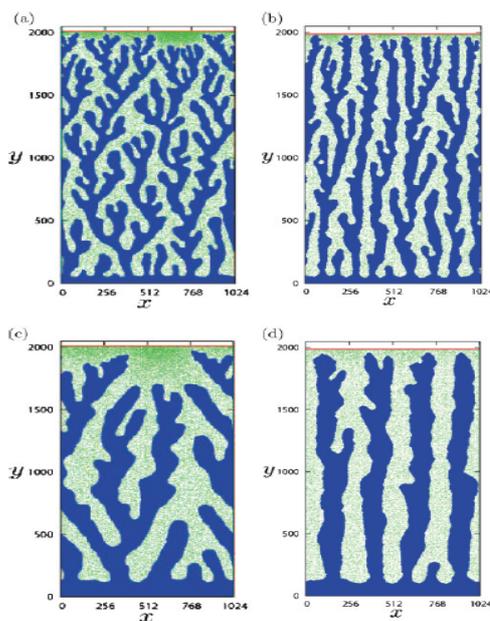
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Pattern formation of an atomic step induced by a moving linear source of adatoms is discussed. Our simple model explains the comb-like step pattern found on a Si(111) face during Ga-deposition[1] and a growth pattern of graphene sheets on a SiC surface[2].

If adatoms are supplied to a step from a straight source that is located in front of the step and moving at a constant velocity, the straight step is unstable during growth[3,4]. The balance between the destabilizing effect of diffusion and the stabilizing effect of the step stiffness selects a characteristic length. In contrast to the usual wandering pattern of steps, a tree-like step follows the source, and a steadily growing state is realized. The branching pattern depends on the crystal anisotropy. A comb-like pattern with few branches may be formed in the  $\langle 11 \rangle$  directions of a square lattice.

The pattern formation is studied with the use of a lattice model and a phase field model.

Fig.1 (01) and (11) steps.



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## [O23]

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One of the grant challenges is to achieve a sufficient and sustainable energy supply for mankind. Solar energy in the form of photovoltaics (PV) is playing an increasing role to partially meet this challenge. Silicon-based PV is the dominant technology used, owing to the availability of relatively cheap but good quality Si crystals. III-V (e.g. GaAs) solar cells achieve a much higher efficiency than Si, but are currently too expensive and are therefore used for special applications like space. Two developments promise to make this technology also economically attractive for terrestrial applications (1) the use of lenses to concentrate the solar light and (2) the use of epitaxial lift-off that allows the reuse of the expensive GaAs substrates.

Macromolecular crystallography is the most direct and accurate approach to determine the three-dimensional structure of biological macromolecules. The growth of high quality single crystals, yielding the highest X-ray resolution, remains a bottleneck in this methodology. It has long been realized that convection-free conditions hold promise to yield better protein crystals because diffusion-limited growth minimizes defects and impurity incorporation. The microgravity environment of space continues to be tested for this application. We developed a laboratory-based convection-free growth environment where crystals grow at the ‘ceiling’ of a cell that is completely filled with crystallizing solution. We tested three cases that all yield resolutions beyond the current best records, even while using growth solutions with moderate purity.

[P1]

## Crystallization of Colloidal Particles using Walls

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Crystallization of colloidal particles on walls has been studied by experiments and simulations. Recently, Suzuki and co-workers experimentally showed that large crystal with few defects is formed by controlling the inclination of wall to centrifugal force. In their proposed scenario, by choosing a suitable inclination of walls, the number of nucleus of colloidal crystal on walls decreases. Since each nucleus grows largely, the numbers of domain of crystal decrease and large crystal with few defects is formed.

In their scenario, ordering of colloidal particles on wall may be the most important in order to form good crystal. Thus, we carry out simulations and study how nucleation and ordering of colloidal particles on walls changes by the inclination of walls. Figures 1 and 2 show results of our simulation. In our model, colloidal particles are treated as particles on which both a uniform force and a random force act. We take account of a short-range repulsion between particles. The particles which are ordered well are expressed as dark particles. When the direction of uniform force is normal to the top face, there appear many small area formed by ordered particles, and many linear defects are observed on the face (Figure 1). When the uniform force acts on a side line with an angle, the area with ordered particles becomes large and the number of line defects decreases (Figure 2). In our talk, we intend to report how the ordering of particles on walls changes by the angle of uniform force.

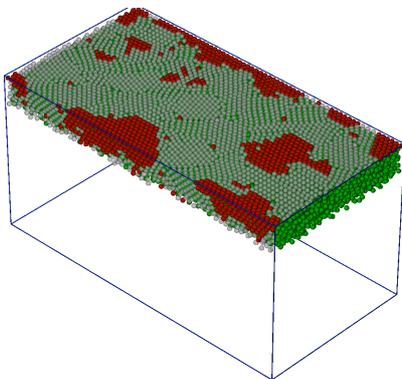


Figure 1

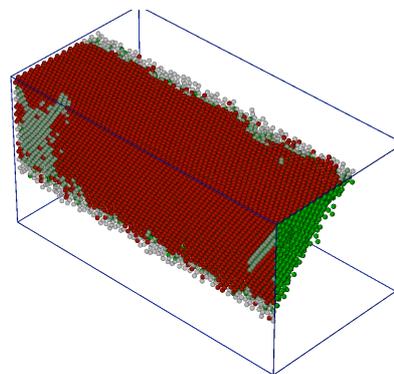


Figure 2

[P2]

## Temporal appearance of a homochiral state by random fluctuation in crystallization

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Viedma discovered that complete chirality conversion of crystals occurs in a solution of NaClO<sub>3</sub>[1]. Starting with powder crystals of both chiral types, grinding and stirring convert the crystals from the racemic state to a homochiral one, which implies that the crystals of minor chirality disappear (Viedma ripening). A similar phenomenon has been reported for an organic material[2].

For a chemical reaction, Sugimori et al.[3] showed that homochirality is realized by random fluctuation in a small system. Following their method, we study the effect of random fluctuation on the chirality conversion in crystallization. With the rate equation analysis of a simple model without nucleation, which neglects fluctuations, the homochiral state cannot appear. By integrating the master equation for a very small system, random fluctuation is shown to produce a homochiral state. The homochiral state, however, does not last forever because the present model is too simplistic.

In order to investigate the behavior of a larger system, we perform a Monte Carlo simulation of the master equation. Any initial state reaches a fixed line obtained from the rate equation, and it diffuses along the fixed line in the size space. The behavior of the system on the fixed line can be described by the diffusion equation with a position dependent diffusion coefficient. The estimation of the time necessary for homochirality is in good agreement with the simulation data.

As in the chemical reaction system[3], the homochiral state induced by random fluctuation in crystal growth may occur only in a microscopic system.

[1] C. Viedma, Phys. Rev. Lett., **94**, 065504 (2005).

[2] W.L. Noorduin et al., J. Am. Chem. Soc. **130** 1158 (2008).

[3] T. Sugimori, H. Hyuga, and Y. Saito, J. Phys. Soc. Jpn., **77**, 064606 (2008).

[P3]

## Atomic Resolution Investigation in Liquid by Frequency-Modulation (Non-Contact) AFM

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High resolution Frequency-Modulation AFM (FM-AFM) imaging had been limited to a vacuum environment. Fukuma et al. (2005) succeeded in obtaining true atomic resolution in a liquid by FM-AFM.<sup>1</sup> Subsequently, insoluble crystals have been mainly observed in liquid by FM-AFM. However, to observe the soluble crystals with atomic resolution is very important for discussing about mechanism of crystal growth process. We observed soluble crystals such as alkali halide or protein crystals.<sup>2</sup>

FM-AFM images were obtained using a modified commercial AFM (Shimadzu, SPM-9600) with open fluid cell. We intentionally observed the soluble crystals in undersaturated solution at first. However, the concentration of solution gradually increased because of evaporation of water. Therefore, dissolution, near equilibrium, or growth conditions could be observed depending on time. By using this method, crystal growth speed of vertical direction was suppressed and atomic resolution images could be obtained.

Figure 1 shows KCl(100) cleaved surface in solution. We could observe periodic structure, in which the wavelength is 6.29 Å. Therefore, only one kind of atom was considered to be imaged in liquid environment as well as ultrahigh vacuum environment.

Figure 2 shows the molecular resolution image of lysozyme (110) in solution. The surface unit cell (black rectangle in fig. 2b, 11.2 × 3.8 nm) involves four molecules with the four unique orientations, which make two kinds of zigzag structures (circles and triangles) along the [001] direction. Figure 2 shows the individual four molecules in the unit cell and the image have higher resolution than images obtained by conventional contact mode or amplitude-modulation (tapping) mode AFM[3].

[1] T. Fukuma et al., *Appl. Phys. Lett.* **87**, 034101 (2005).

[2] K. Nagashima et al., *J. Vac. Sci. Technol. B* **28**, C4C11 (2010).

[3] J. H. Konnert et al., *Acta Crystallogr. D* **50**, 603 (1994).

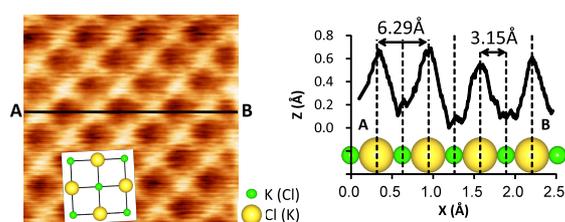


Fig.1 Atomic resolution image of KCl (100) surface in saturated solution. Crystal growth speed of vertical direction  $V < 0.005$  nm/s.

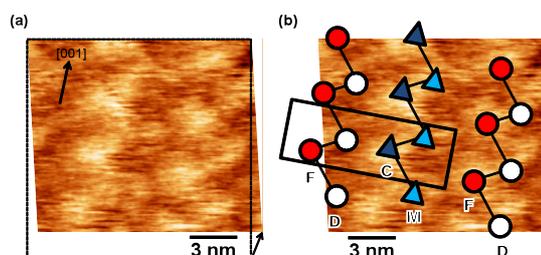


Fig.2 (a) Topographic image (13.0×13.0 nm). (b) theoretical molecular packing on (a).

[P4]

## Crystallization of Isotactic Polypropylene from Mesomorphic Phase - A Constant Heating Rate Study -

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We have studied crystallization behavior of isotactic polypropylene (iPP) from intermediate state, so-called “mesomorphic phase”. Mesomorphic iPP is obtained by quenching molten amorphous iPP; empirically, this is achieved by dropping a thin piece of a sample rapidly into ice water. The mesomorphic iPP is cellulated into the granular particles, so-called “nodules” with a diameter of Ca. 10 nm. The morphology of the crystal obtained from the mesomorphic phase is very different from that obtained from the melt. The mesomorphic phase of iPP is considered meta-stable state whose energy level is low comparable to that of crystal. Therefore, differential scanning calorimetry (DSC) would be a rather insensitive method to investigate the transition of iPP from mesomorphic phase to crystal. Instead of the thermal measurements, we have performed in-situ measurements of wide-angle X-ray diffraction (WAXD) and de-polarized light transmission (DPLT) with a constant heating rate as the same thermal trace of DSC measurement. Time-resolved in-situ WAXD measurements were conducted at a synchrotron radiation (SR) X-ray beam line of SPring-8 (Fig. 1). As the results, Time-resolved WAXD sensitively detected the crystallization and gave crystallinity as a function of temperature. DPLT also detected the crystallization but it gave a quantity weighted by the grain size of crystal. Taking the results of WAXD and DPLT into consideration, formation of micro crystallites proceeds extensively around 90 - 100 °C and the coarsening of the micro crystallites proceeds around 140 - 150 °C when mesomorphic iPP is crystallized by heating at a constant heating rate.

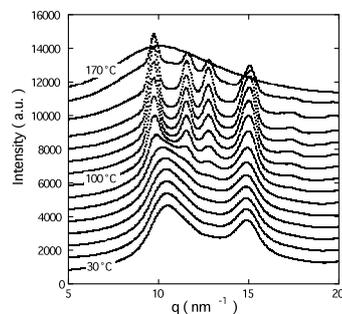


Fig. 1. Time-resolved WAXD profiles during heating process from 30 to 170 °C displayed at every 10 °C from bottom to top. The profiles were shifted vertically for clarification.

[P5]

## Effects of container shape on enlargement of grains of colloidal crystals by centrifugation

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Three dimensionally (3D) large close-packed face-centered cubic colloidal crystals of silica particles can be used successfully as templates for the fabrication of a 3D large silicon inverse opal with a complete three dimensional photonic band gap [1], and the crystals are easily fabricated simply by drying almost closed-packed (with high particle concentration) 3D large columnar-shaped grains of colloidal crystals which are prepared by centrifugation [2]. Although enlargement of the columnar grains is also well achieved by centrifugation, further enlargement requires additional developments of growth methods.

An inverted-triangle internal-shaped container (inverted-triangle container) will be useful for the enlargement, since the nucleation of grains is eliminated at an edged bottom, and the grains are widened due to a broadened shape of the container.

Inverted-triangle (edge angle  $\alpha = 90^\circ$  (Fig. 1(a)) and  $60^\circ$  (Fig. 1(b))) and normal rectangle (Fig. 1(c)) containers were used in this study. Dispersion of silica particles (particle diameter = 110 nm) in water was injected into 0.2 mm thick inner spaces of the containers. Almost close-packed colloidal crystals were fabricated in the containers by centrifugation at 2.2 g (at the bottoms of the containers) for 30 days.

The largest grain in an inverted-triangle container (width = 2.65 mm, Fig. 1(a)) was much larger than that in a normal container (width = 0.66 mm, Fig. 1(c)). An edged bottom of the inverted-triangle container eliminated the number of the grains, and then a broadened shape of the container effectively widened the grains.

[1] A. Blanco, et al., *Nature.*, **405**, 437-440 (2000)

[2] Y. Suzuki, et al., *Journal of Crystal Growth.*, **318**, 780-785 (2011).

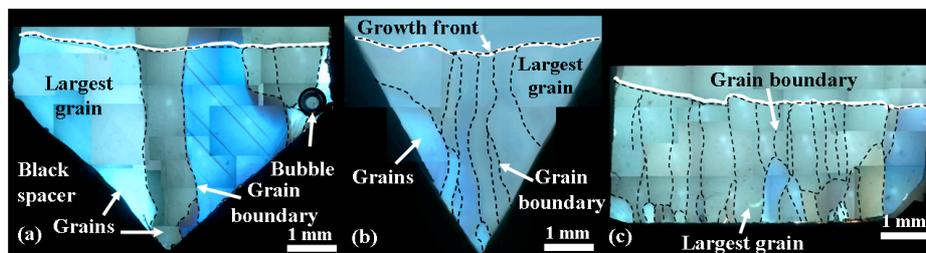


Fig. 1. Cross-polarized images of the crystal in inverted-triangle containers ((a)  $\alpha = 90^\circ$  and (b)  $\alpha = 60^\circ$ ) and a normal container (c).

## [P6]

### A novel strategy of membrane protein crystallization in lipid

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We studied phase transition of lipidic cubic phase induced by photoisomerization of the structural change of additive molecules.

Recently, membrane protein crystallization in lipid has been reported (Fig. 1) [1].

Membrane protein crystallize when medium lipid phase change from cubic to lamellar phase. The driving force of crystallization is thought to be brought about lipidic phase transition.

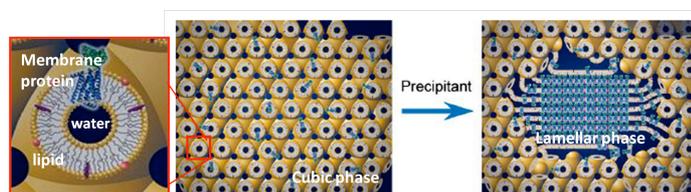


Fig. 1 Membrane protein crystallization using lipid as medium

In this thesis, we try to induce phase transition of lipid by photochemical reaction that changes in packing parameter. Photofunctional detergent of azobenzene derivative (AZTMA) was synthesized [2]. Monoolein lipidic cubic phase containing ca. 7 mol% all-trans AZTMA was prepared, and then the sample was exposed by 320 nm light which occurs trans-cis photoisomerization. Fig. 2 shows the result. Polarization changed from non-polarized property to polarized one, which indicates phase transition happened. Next, the sample was exposed by 520 nm light which induces cis-trans isomerization. The polarization property change again from polarized to non-polarized, reversibly. The phase transition is thought to be caused by change of packing parameter of AZTMA. We will try to apply this strategy to membrane protein crystallization.

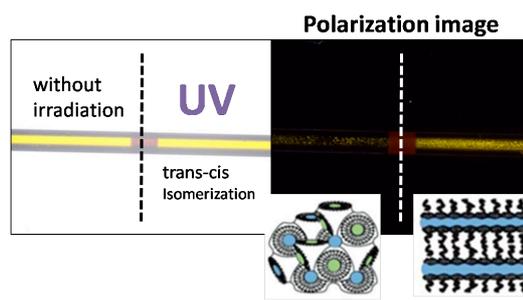


Fig. 2 Lipidic phase transition by photoisomerization

[1] G. Rummel, A. Hardmeyer, C. Widmer, M. L. Chiu, P. Nollert, K. P. Locher, I. Pedruzzi, E. M. Landau, J. P. Rosenbusch, *J. Struct. Biol.*, **121**(1998) 82.

[2] T. Hayashita, T. Kurosawa, T. Miyata, K. Tanaka, M. Igawa, *Colloid Polym. Sci.*, **272**(1994) 1611.

[P7]

## Light induced crystallization of protein from template molecules produced by photochemical reaction of aromatic molecules

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We have studied photochemically-induced crystallization of Proteins. The photoreaction of proteins formed covalent bonded dimer. [1] The dimers behave as stable template molecules in nucleation process, and crystallization is promoted. Photochemical intermediate Trp· and Tyr·radical protein would react with another protein with several amino acids to produce dimers. However, photochemically produced crystals are limited at arrangement of amino acid of protein. [2]

To overcome these problems, we used photochemical reaction of quinones. Excited state of quinone is known to abstract hydrogen atom from substrate to produce quinone ketyl radical and counter substrate radical. In this study, phenanthrenequinone (PHQ) was used to produce residual radical proteins from variety of amino acid. In transient absorption measurement, <sup>3</sup>PHQ· reacts with 12 amino acids. Dimers are produced by photochemical reaction of PHQ.

As a result, dimer was confirmed by SDS experiment (Fig.1). And photochemical dimers enhance crystallization in lysozyme, RNaseA and ConA systems.

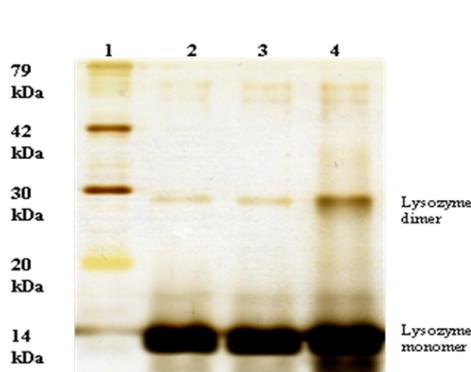


Fig. 1 Photograph of SDS-PAGE gel image of lysozyme. Lane 1 shows without irradiation. Lane 2 shows with irradiation and without presence of PHQ. Lane 3 shows irradiation and with presence of PHQ.

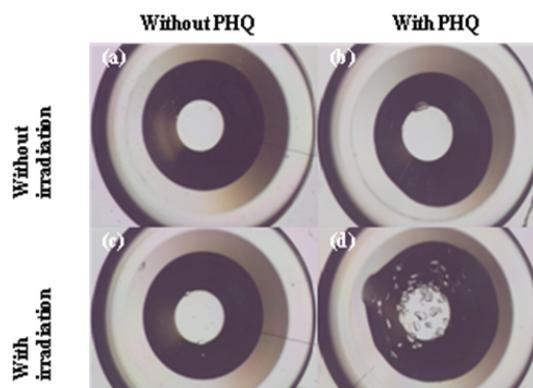


Fig. 2 Lysozyme droplets on the batch plate, (a) without irradiation and without PHQ, (b) without irradiation and with PHQ (c) with irradiation and without irradiation (d) with irradiation and with PHO.

[1] T. Okutsu, et al., *Chem. Lett.*, **36**, 6, (2007).

[2] T. Okutsu, et al., *Cryst. Growth Des.* **6**, 1631, (2006).

## [P8]

### **Effect of shear and additive on crystallization of cocoa butter under the tempering process**

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Atsushi Suzuki<sup>2</sup>, Keiichi Nagashima<sup>2</sup>, Tetsuo Koyano<sup>2</sup>,

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Cocoa butter is the major ingredients in chocolate. Six different polymorphic forms (form I - VI) are well known in crystalline cocoa butter. For chocolate production, controlling the crystallization to form V is critically important for optimal melting and textural properties. To obtain the form V, tempering and shear stress are applied on cocoa butter. In general, chocolate contains particles, such as cacao and sugar, and they affect significantly on the shear stress under the tempering process. Therefore, many researchers have been studied on the effect of shear stress and solid particles separately. However, the effect of shear stress and solid particles under tempering is still obscure. Elucidation of crystallization behavior of CB in the manufacturing process of chocolate, not only leads to the elucidation of the crystallization mechanism to form V but also brings significant information to chocolate makers. In this study, we observed the crystallization behavior of chocolate under shear and tempering in the system near the actual chocolate manufacture by using synchrotron radiation X-ray diffraction. We performed two different experiments, focusing on the effect of shear and particles as follows; tempering 1 and tempering 2. Shear rate was fixed at  $400\text{s}^{-1}$  during all experiments.

Tempering 1: CB (cocoa butter 100%) was applied to the temperature of cooling–heating–cooling program ( $50^{\circ}\text{C}$  for 15 min→ $15^{\circ}\text{C}$  for 10 min→ $27.5^{\circ}\text{C}$  for 5 min→ $15^{\circ}\text{C}$  for 5 min) under shear or without shear. CB was crystallized form II or III in first cooling process, then form V was observed after heating to  $27.5^{\circ}\text{C}$  with the shear. On the other hand, without shear CB was crystallized form II or III.

Tempering 2 : CB, with cocoa and/or sugar particles were applied to the tempering process of cooling-heating-cooling program ( $50^{\circ}\text{C}$  for 15 min→ $17.5^{\circ}\text{C}$  for 5 min→ $27.5^{\circ}\text{C}$  for 5 min→ $17.5^{\circ}\text{C}$  for 10 min) with or without shear. CB with solid particles was crystallized form V under shear. In contrast, CB without solid particles did not form any crystals. The form V was not obtained without shear.

These results indicate that shear stress promotes polymorphic transition to form V of CB. Additionally, not only cocoa particles but sugar promotes crystallization of form V.

[P9]

## Crystallization inhibitory effect for crystallization of phytosterol in O/W emulsion droplets

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### Experiment background and purpose

Functional lipids, such as carotenoids, lipid soluble vitamins, phytosterols, and numerous other substances, are widely used as active ingredients in various food products. However, because of the low solubility of functional lipids against water and oil, they could not be absorbed well in body. Functional lipids are absorbed through a small intestine. First, they are taken into bile acid micelle, and then they are absorbed inside of the body through a small intestinal epithelial cell. However, if functional lipids are transferred to a small intestine as crystals, they could neither be dissolved into bile acid micelle, nor be absorbed in body. Therefore, we attempt to improve bioabsorbable property, by dissolving functional lipids in the oil droplet of o/w emulsions, and controlling crystallization. In this study, we studied the effect of the types of emulsifier and emulsion droplet diameter on the crystallization of  $\beta$ -sitosterol in oil droplet of o/w emulsion.

### Experimental method

$\beta$ -sitosterol was dissolved in medium chain triacylglycerol oil phase of O/W emulsion. The emulsifiers we applied which consisted of polyglyceryl or Polyoxyethylene sorbitan fatty acid ester as a hydrophilic group, and of lauric acid, stearic acid or oleic acid as hydrophobic group (10G1L, 10G1S, 10G1O, Tween20, Tween60, Tween80). Emulsion droplets having the diameter of 3  $\mu$ m and 500 nm were prepared by homogenizer and high-pressure emulsification, then stored at 5°C. We examined whether crystallization occurred or not by using synchrotron X-ray diffractometer.

### Experimental result

The crystallization inhibitory effect for particle diameter 500 nm is higher than the case of 3  $\mu$ m. The small particle diameter made decrease the number of impurities contained in one oil droplet, and then crystallization was inhibited. The difference of crystallization inhibitory effect also depended on the type of emulsifiers. The crystallization inhibitory effect was higher in order of 10G1L > Tween60 > 10G1O, 10G1S, Tween20 > Tween80. This result implies that the size of hydrophilic group, unsaturated fatty acid, fatty acid chain length of the hydrophobic group related to the order of easy to crystallization.

**[P10]**

**Effect of tripalmitin on granular crystals formation  
in bulk model systems of W/O emulsion.**

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2 Megmilk Snow Brand Co, Tokyo, Japan

W/O emulsion consist of the dispersal water phase and of the continuous oil phase. Observation of the granular crystals during storage becomes a trouble for palm oil based on W/O emulsion. Granular crystals will be cause of coarse and grainy texture. A number of researches have been performed to clarify the mechanism of the formation of granular crystals since it is important to control appearing granular crystal. These researches have revealed that the granular crystals have and tripalmitin (PPP) exists in a center of the granular crystals. However, the mechanism of the granular crystals formation with PPP is still obscure. The purpose of this study is to elucidate to how PPP effects on the formation of granular crystals in early stage of ripening of fat spread.

We used only palm and soybean oils as bulk phase for the experiments. Three types of samples contained different state of PPP were prepared; bulk oil containing 2 wt% of PPP crystal powder, bulk oil containing 2 wt% of melting PPP, and bulk oil without additional PPP. The samples added PPP under and over the melting point of PPP are named as bulk oil with PPP crystal powder and bulk oil with melt PPP, respectively. All of samples were stored at the cyclic temperature program, 7 °C for 12 h and 15 °C for 12h. The polymorphic form of crystals in the bulk oil was determined by X-ray diffraction (XRD). The number of granular crystals was counted by naked eyes. By the XRD results, it shows polymorphs of fat crystals. Each different polymorph has characteristics with a form characterized as  $\beta$  form stable, highest melting point.

The diffraction peaks showing  $\beta$  form appeared within 1 day in the bulk oil with melt PPP and the bulk oil without PPP. In contrast, with PPP crystal powder, the same diffraction peaks appeared after 1 week. For the number of the granular crystal confirmed by eyes from the bulk oil with melt PPP was the largest among them. The number of granular crystals confirmed by eyes from the oil with melt PPP was the largest among them. These results illustrate that the crystallization of PPP plays an important role in the formation of granular crystals. If PPP was added in to the bulk oil with melt, PPP could be crystallized and form a lot of nuclei in the bulk oil. Those PPP nuclei would promote the formation of the granular crystals.

[P11]

## Crystallization of Triacylglycerols in O/W Emulsion Type Chocolate

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Tetsuo Koyano<sup>2</sup>, Hironori Hondoh<sup>1</sup>, Kiyotaka Sato<sup>1</sup>, Satoru Ueno<sup>1</sup>

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Ganache is a O/W emulsion type chocolate, which is made by mixing dark chocolate and fresh cream. Ganache has a unique character of smooth melting in mouth. This character is originated from the structure and physical properties of fat crystals in dark chocolate and milk fat in fresh cream. Dark chocolate has various polymorphism, which defined as forms I through to VI. The confectionary industry uses only one form V, as the optimal polymorphic phase. Dark chocolate, in general, requires the temperature control for the formation of the form V cocoa butter crystals. In contrast, it is well known that O/W emulsion type chocolates could be crystallized in form V without tempering process. The reason why form V are crystallized without tempering are pointed out two possibilities. One is the template effect between cocoa butter and emulsifier from milk, and another is a shear effect. However, the detail mechanism of the nucleation of the form V crystals in O/W emulsion type chocolate is still unclear. In this study, we observed the effect of shear and the ingredients put as additives of O/W emulsion type chocolates on the polymorphism of cocoa butter in emulsion type chocolates. Furthermore, we observed complex internal structure of O/W emulsion type chocolate which has not been found.

Non-emulsion and emulsion type chocolates were prepared by mixing cocoa butter, milk fat and emulsifiers with and without water. Polymorphism of cocoa butter crystals in these chocolates was determined by X-ray diffraction. Melting temperatures of the chocolates were also measured by DSC. Shear stress was loaded on the chocolate surface with a slide glass manually. Sample used in the observation of the internal structure of the o/w emulsion type chocolate were observed polarizing microscopy. All chocolates were kept at room temperature.

Form IV crystals were formed in the non-emulsion type chocolate at first. Then form V crystals appeared after 5 hrs. In contrast, if shear stress was loaded, the formation of form V crystal was promoted within 30 min. This promotion of form V crystal was also observed with emulsion type chocolate with loading of shear stress. These results simply suggest that the induction of shear stress promotes the formation of form V crystals but the addition effect of ingredients template effect is not significant. Using polarizing microscopy, we observed spherocrystal and developed a network of crystallized oil droplets. Crystallized oil droplets oriented parallel to the interface.

## [P12]

### Atomic-scale observation of hydration structure on calcite

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Dehydration is the growth rate-determining process in solution growth [1]. Recently it was suggested that dehydration was induced by organics [2]. We focused on the influence of the peptide on the hydration of the calcite surface. The synthetic polypeptide was adopted as organic material. The peptide was designed to imitate the periodic sequence of aspartic acid of a protein which was contained in pearl oyster shell [3]. The cleaved surface of calcite was observed by a recently developed frequency modulation AFM (FM-AFM) [4]. The supersaturated solution of calcium carbonate ( $\text{CaCO}_3$ ) was prepared so that supersaturation rate was  $\sigma = 0.8$  at pH 8.1 and  $T = 22^\circ\text{C}$ . First we obtained the layered structure in pure  $\text{CaCO}_3$  supersaturated solution (Fig. 1a). After the addition of the synthetic polypeptide ( $10^{-5}$  M), we obtained the clear FM-AFM image of lacy network of water clusters as shown in Fig. 1(b). These results suggest that the hydration structure of calcite was changed by the synthetic polypeptide.

[1] P. Bennema, P., *J. Cryst. Growth*, **1**, 287 - 292. (1967)

[2] S. Elhadj *et al.*, *Cryst. Growth Des.*, **6**, 197 – 201. (2006)

[3] R. Takagi and T. Miyashita, *Zoological Science*, **27**, 416-426. (2010)

[4] T. Fukuma *et al.*, *Appl. Phys. Lett.*, **87**(3), 034101. (2005)

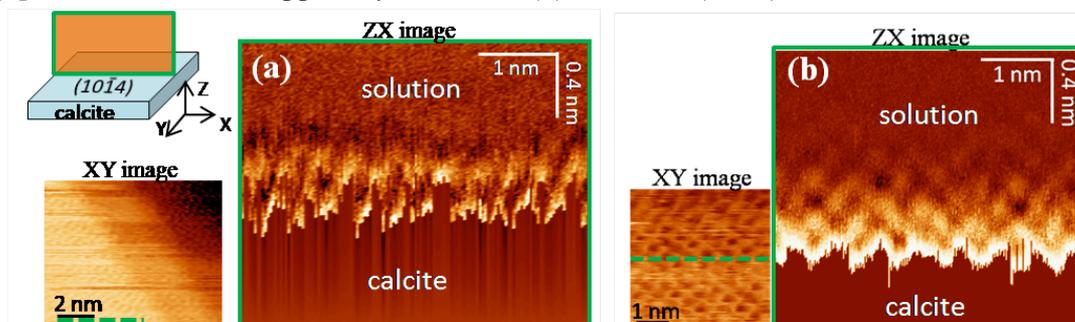


Fig. 1 (a) The 2D hydration structure on calcite surface in  $\text{CaCO}_3$  supersaturated solution and (b) in the solution containing the synthetic polypeptide.

[P13]

## Morphology of Gypsum Crystals in Naica Mine

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Sulfate minerals plays crucially important roles to make giant gypsum crystals (1~12 m) in Naica, Mexico [1]. Morphology of gypsum crystal holds the key to reveal natural history of Naica gypsum. We have a question of Naica gypsum: why two different crystal shapes (columnar type and platelet type) are there in same condition This study approach that question by morphological observation.

First, we measured of inter-facial angles on gypsum crystal faces with stereo microscope, and visualized crystal form with VESTA 3 [2].

Next, we observed surface morphological topography with differential interference contrast microscopy (DIM). As shown in Fig. 1, we could observe many bunching macro steps on (010) face and a few spiral steps on vicinal surface by DIM. Our spiral step is not same shape of synthesized [3]'s spiral steps. These differences show us some important implications for growth condition of Naica gypsum.

[1] J. M. García-Ruiz, R. Villasuso, C. Ayora, A. Canals and F. Otálora, Formation of natural gypsum megacrystals in Naica, Mexico, *Geology.*, **35-4**, 327-330 (2007).

[2] K. Monma and F. Izumi, VESTA 3 for three-dimensional visualization of crystal, volumetric and morphology data. [\*J. Appl. Cryst.\*, \*\*44\*\*, 1272-1276, \(2011\)](#).

[3] A. E. S. Van Driessche, J. M. Garcia-Ruiz, J. M. Delgado-Lopez, and G. Sazaki, In Situ Observation of Step Dynamics on Gypsum Crystals, *Crystal Growth & Design*, **10**, 3909-3916, (2010).

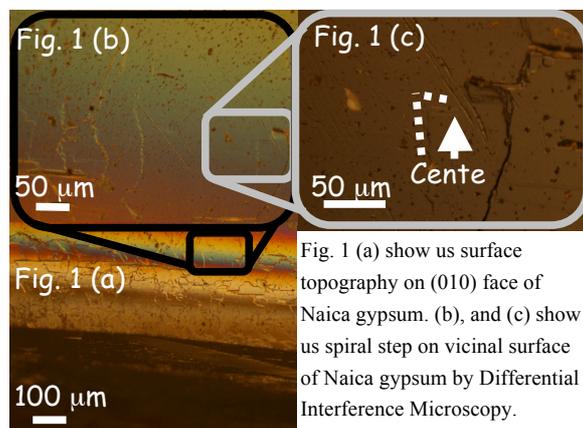


Fig. 1 (a) show us surface topography on (010) face of Naica gypsum. (b), and (c) show us spiral step on vicinal surface of Naica gypsum by Differential Interference Microscopy.