Poster Sessions

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When does the chirality of NaClO$_3$ crystals arise in solution growth?

Hiromasa Niinomi, Katsuo Tsukamoto, Takahiro Kuribayashi, Hitoshi Miura, *Graduate School of Science, Tohoku University, (Japan).* E-mail: h_niinomi@s.tohoku.ac.jp

Chiral symmetry breaking in sodium chlorate (NaClO$_3$) crystallization from a solution was reported by Kondepudi et al. (1990) [1]. The chiral NaClO$_3$ crystal has cubic crystal system and space group of $P2_13$. When Kondepudi et al. evaporated NaClO$_3$ solution without any mechanical disturbance, they obtained equal numbers of L- and D-crystals in the solution. In contrast, from a stirred solution almost only one type of crystals was obtained. This significant bias in chirality is termed as chiral symmetry breaking. Some theoretical models have been proposed for the mechanism of the chiral symmetry breaking, however, the mechanism has not been elucidated yet. To obtain the direct evidence of chiral symmetry breaking, we carried out in-situ observation of the crystallization process by using a polarization microscope. As a result, we found that non-cubic metastable crystals appeared at first, and then, transformed to cubic crystals by a solid-solid phase transition or a solution-mediated phase transition [2].

On the assumption that the metastable crystal is achiral, we conclude that the chirality of NaClO$_3$ crystal arises when the phase transition occurs. However, it is unknown whether the metastable crystal is chiral or achiral because the crystal structure has not been analyzed in the literature till date. Thus, in the present paper, we reported the result of a single-crystal X-ray diffraction experiment for the metastable crystal.

The metastable crystal was prepared by drop evaporation method as follows. A drop (6 μl) of a NaClO$_3$ solution saturated at room temperature (293K) was put onto a cover glass. The metastable phase crystallized in the drop as the solution evaporated. After the crystal grew up to 200 μm in size, the drop were replaced with glycerin. Afterwards, the crystal and the drop of glycerin were frozen by liquid nitrogen. The frozen drop is the specimen for the X-ray diffraction experiment. X-ray diffraction data was collected in oscillation mode by imaging plate type single-crystal X-ray diffractometer (R-AXIS IV++, Rigaku). To keep specimen frozen during the experiment, we kept the temperature around the specimen at -266±1 K by Cryostream (Oxford).

From the X-ray diffraction, we determined the lattice constant, crystal system, and space group of the metastable phase as follows; a=8.42 (Å), b=5.26 (Å), c=6.70 (Å), β=109.71(°), monoclinic, and $P2_1/a$, respectively. These values are very similar to that of NaClO$_3$(I), which was reported as a high temperature phase of NaClO$_3$ crystal in melt growth (a=8.78 (Å), b=5.17 (Å), c=6.83 (Å), β=110 (°), monoclinic, and $P2_1/a$) [3]. Therefore, it is highly possible that the metastable phase we obtained from the solution is the same as the NaClO$_3$(I) phase. In addition, we found that the metastable crystal is achiral because a crystal having a space group of $P2_1/a$ is achiral. From these results, we concluded that chirality of the cubic NaClO$_3$ crystal arises when the phase transition occurs.

The achiral metastable crystals have not been considered in the NaClO$_3$ crystallization from the solution. The phase transition from the achiral phase to the chiral phase may lead to a new understanding for the chiral symmetry breaking.

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Functionalized ZnO nanostructures for gas sensing and photovoltaic applications

Andrea Zappettini,[a] Davide Calestani,[a] Laura Lazzarini,[a] Marco Villani,[a] Filippo Fabbri,[a] Lucio Zanotti,[a] Nicola Coppedè,[b] Marco Nardi,[b] Salvatore Iannotta,[a,b] *[a]IMEM-CNR, Parma (Italy). [b]IMEM-CNR, Trento (Italy).* E-mail: zapp@imem.cnr.it

Zinc oxide (ZnO) is an incredibly versatile material that in its nanostructured form is studied for a large number of applications in optoelectronics, photovoltaics, gas and bio-sensing, piezoelectric devices, photocatalysis, spintronics, etc.

Recently this group has successfully reported the optimized not-catalyzed synthesis processes for producing single morphologies of ZnO nanostructures (i.e. nanowires [1], aligned nanorods [2], and nanotetrapods [3]) among the many different ones that are generally obtained in vapor phase reactions. The proper combination of metal thermal evaporation and controlled oxidation has produced good quality nanostructures, whose properties were not affected by contamination from catalysts or precursors.

The great potential of these nanostructures, however, can be fully explored only once they are functionalized with different organic or inorganic materials for tailoring their intrinsic properties towards the final application.

In this work authors report some meaningful examples of surface functionalization of their ZnO nanostructures by inorganic (calcogenides) and organic (phthalocyanines and porphyrins) semiconductors for applications in gas sensing, photovoltaics and photocatalitic degradation of water and gas pollutants. Although different techniques were used (an optimized chemical bath deposition – CBD – process and a supersonic molecular beam deposition – SuMBD – apparatus), in both cases particular attention has been devoted to the interface formation in the coupled compounds, in order to obtain working heterostructures where charge carriers can be efficiently separated and transferred.

The obtained functionalized ZnO nanotructures have been characterized accurately by electron microscopy (SEM and TEM), x-ray diffraction (XRD) and optical measurements (optical absorption, photoluminescence, and cathodoluminescence). The heterostructures properties have been also studied by functional characterizations such as chemoresistive gas sensing tests, photocurrent and photocatalytic activity measurements. The correlation between structural and functional properties has then been discussed.

In the case of functionalization with CdS, for example, a thickness dependent effect of charge transfer to the ZnO nanostructure has been demonstrated, together with an enhancement of the photocatalytic properties, and the modification of the gas sensing response mechanisms.

In the case of functionalization with organics, different emission spectra have been observed together with different morphologies of the obtained depositions. These phenomena have been discussed in terms of distinct molecular bonding of phthalocyanines and porphyrins at the interface with the oxide nanostructures.

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Principle of the unique adhesion mode in protein crystallization

Jindrich Hasek, *Institute of Macromolecular Chemistry, Academy of Sciences, 16206 Praha 6, (Czech Republic).* E-mail: hasek@imc.cas.cz

Analysis of crystal packing and of the role of ligands built into protein crystals [1,2] lead to very natural concepts helping in rational growth of high quality crystals:
1) The principle of a dominating protein-protein adhesion mode says that high diffraction quality protein crystals require a unique driving force of crystallization guaranted by a single dominating adhesion mode.
2) The protein surface shielding molecules block competitive adhesion modes leading thus to a unique deposition of protein molecules into the growing crystal.

Protein molecules in solution have always number of mutual adhesion modes because of their generally large surface areas. In the case, that crystallographicaly incompatible adhesion modes combine during crystallization, the growing crystals are full of stacking faults. In extreme cases it leads to so called phantom crystals – optically well looking crystals without diffraction. The protein surface shielding (PSS) molecules can temporarily block possibly incompatible adhesion modes lowering thus the probability of irregular stacking of molecules in the crystal lattice.

The good PSS molecules should bind only to very specific places on the protein surface, and only with low affinity so that they can leave the protein surface during deposition of other protein molecules into the growing crystal and the PSS molecules dissolve again in the crystal cavities filled by solvent. Due to low affinity, the PSSA molecules are experimentally observed on the protein surface rarely (often disordered and with lower occupancies). In few cases they are observed also trapped at the protein-protein interfaces contributing to stability of crystal.

Different PSS molecules have different binding characteristics, they bind to different places on protein surface and thus they can force protein to crystallize in different space groups. It is useful, because the structure determination of identical protein in different molecular environments provides more complete description of its hydration shell and also shows possible tiny changes of the surface structure induced by protein associations.

Even low concentration of PSS molecules can bring the desirable effect, so that their use generally does not change dramatically the existing crystallization screens.

The hypothesis presented above is supported by numerous experimental observations of polyethyleneglycol molecules selectively trapped on protein surfaces in structures deposited in the PDB. The classification of experimentally observed binding of the PEG-type polymers [1] is instructive for understanding the PSS effect of the hydrophilic polymers.

These concepts give also more natural and less conflict explanations of many mysterious methods including the "lysine methylation", "surface entropy reduction", "silver bullets". They offer several new alternative ways how to improve current crystallization methods.

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A Crystal Growth Approach for DNA Nano-Structure Formation

Hitoshi Miura,[a] Yuya Ueno,[a] Shogo Hamada,[b,c] Satoshi Murata,[c] Katsuo Tsukamoto,[a] *[a]Departament of Earth and Planetary Materials Science, Tohoku University (Japan). [b]Interdisciplinary Graduate School of Science and Engineering, Tokyo Institute of Technology (Japan). [c]Graduate School of Engineering, Tohoku University (Japan).* E-mail: miurah@m.tohoku.ac.jp

The DNA molecule is now attracting attention as a new self-assemble material. Many nano-structures have been produced using DNA, for example, DNA tile [1]. DNA tile is a complex molecule, which is composed of some single strand DNA (ssDNA). Each tile has some sticky ends (a part of some exposed bases). The DNA tile combines with another one via the complementary sticky end to form an ordered nano-structure. The formation of the nano-structure occurs in the solution just by cooling the temperature, like as crystal growth in solution. The self-assembly of the DNA tiles has a calculation capability, however, the misfit between the complementary sticky ends is not a negligible problem [2]. To reduce the assemble misfit, we carried out experimental study of the DNA tile self-assembly and analyzed the result based on crystal growth theory.

We chose T-motif as DNA tile, which is able to grow on the electrically-charged Mica surface like two dimensional crystal [3]. We synthesized the T-motif ordered nano-structure on the Mica surface under a constant temperature T, and observed it using atomic force microscope. We found that the nano-structure was formed when T is lower than about 41.5℃, not depending on the initial solute concentration significantly in a range of 2 – 10 nM. When T is relatively high, most of the nano-structures have polygonal shape. As T decreases, the dendrite-shaped nano-structure was observed. We also found that the number density of nano-structures observed on the Mica surface monotonically increased as T decreased.

We analyzed our experimental results based on the theory of crystal growth assuming that the T-motif self-assembly can be considered as melt growth. We calculated the step free energy β and the melting point T_m under the assumption that the number density of nano-structures is proportional to the two-dimensional nucleation rate. When the melting point was assumed to be $T_m = 50℃$, we obtained the step free energy of $\beta = 4.2 \times 10^{-13}$ J/m. Using the calculated step free energy, we derived the critical undercooling ΔT_{dend} above which the dendrite-shaped nano-structure was formed. For small undercooling, many T-motif units bind only at a site with two sticky ends. In contrast, for large undercooling, the T-motif unit can bind to anywhere. We calculated the difference of Gibbs free energy in two cases, one match bond of sticky end or two matches, and derived ΔT_{dend} as a function of β and T_m. The theoretical consideration matched the morphological change of the nano-structure qualitatively.

Our study indicated that the DNA self-assembly could be interpreted as the crystal growth. We could propose DNA self-assemble methods with fewer misfit based on the crystal growth approach.

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