# Magnetic field effects on crystallization by LLIP method

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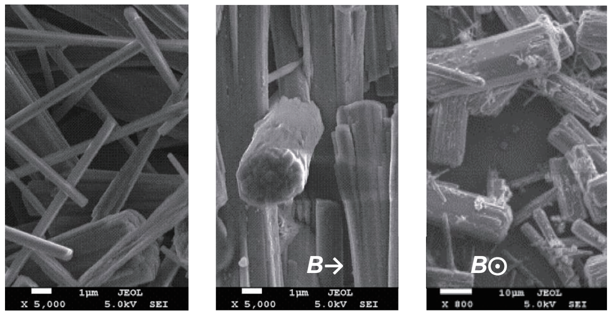
Application of magnetic fields to crystallization have been studied in order to make a high quality and large crystal.[1-3) Liquid-liquid interfacial precipitation (LLIP) method is one of technique of crystallization from solution. Two kinds of solvent are stacked to make their interface. One is a poor solvent for desired material, and the other is a good solvent saturated with the material. In general, right solvent is stacked on heavy one to prevent the convection owing to gravity. The seed crystal is born and grown at around the two-dimensional interface because the supersaturated layer is generated due to mutual diffusion of the two liquid. The sedimentation speed is low for small crystal and accelerated with increasing size of crystal according to Stroke's low. When the grown crystal is leaved from the interface and sunk to the bottom then the growth reaction is completed. Magnetic field and its gradient are thought to be influenced the crystallization processes as follows. The generation of seed crystal and the growth rate are controlled by the magnetic field because the degree of the super-saturation depended on the diffusion of solution is controlled by Lorentz force under the influence of magnetic field. The growth direction is also controllable magnetically because the posture of crystal is controllable against the two-dimensional interface if the crystal has anisotropic magnetic susceptibility. In addition, the crystal size is controllable because the staying period at around the super-saturated layer, which corresponds the reaction period, is controllable according to apply of magnetic force parallel or antiparallel to gravity.

In the experiments, some kinds of crystal were crystallized and the magnetic field effects of the size, morphology, magnetic orientation, and quality of crystal were estimated for C60-fullerene nano-rod (FNR), NaCl salt, ice, glycine, taurine, lysozyme, thaumatin, etc. as listed in Table 1.[4) For example, the long axis of FNR was oriented perpendicular to the magnetic flux as shown in Fig. 1(b). The volume of FNR was enlarged by 10 times in the homogeneous horizontal magnetic field of 13 T. Under the influence of the gradient vertical magnetic field, the volume was enlarged 100 times in the reduced gravity environment as shown in Fig. 2. The size effects were also recognized for other crystals as listed in Table 1. Moreover, changes of crystal hobbit and morphology were found as a magnetic field effect.

The magnetic field effect on size must be applicable to crystallization of protein for drag discovery, since crystallization for many unknown proteins is hard to make a good large crystal. If huge crystal is precipitated then the protein is analyzed easily by XRD structure analysis. A hen egg white lysozyme was crystalized by the LLIP method under the influence of magnetic field of up to 13 T. Ten times huge protein crystal was observed and its XRD structure analysis showed that the crystal kept high quality with the maximum resolution of 1.22 Å and R-merge of 4.6% (Fig. 3). The high mosaicity was




(a) $B$ = 0 T　(b) Horizontal $B$ = 9.6 T　(c) Vertical $B$ = 7.2 T

Fig. 1　SEM images of FNRs crystalized in (a) zero magnetic fields, (b) horizontal homogeneous field of 9.6 T, and (c) vertical field of $B$ = 7.2 T with gradient of d$B$/d$z$ = −58 T/m. The directions of magnetic flux were shown as allow in images (b) and (c). The scale bars indicated 1 μm for (a) and (b), and 10 μm for (c).

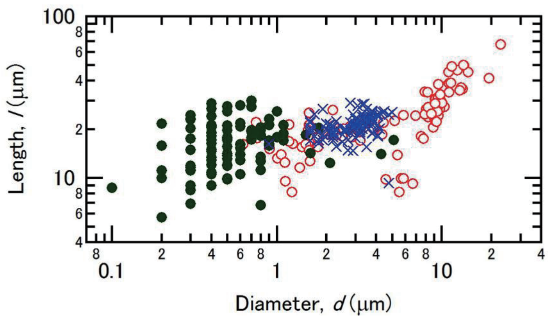



Fig. 2　Scatter plot for fullerene nano rod crystallized under the influence of magnetic fields. The symbols ●, ×, and ○, corresponded to the size for Fig. 1(a), (b) and (c), respectively.

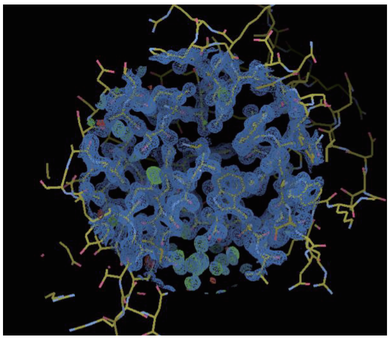


Fig. 3. The structure of lysozyme crystal precipitated under magnetic field with $BdB/dz = -587$ $T^2$/m.

Fig. 4 Side view of the vertical interface under horizontal gradient magnetic field. the interface was indicated as broken line.

expected because the crystal aligned perfectly to magnetic flux.

In addition, a new one-dimensional reaction field was developed among a paramagnetic liquid and two kinds of diamagnetic liquid under the influence of horizontal gradient magnetic field as shown in Fig. 4. The paramagnetic liquid was forced toward the magnetic center (the left-hand direction in Fig. 4) due to horizontal magnetic force. The horizontal two-dimensional interface was changed vertical by the high magnetic field and the coexistent line among three liquids was appeared. We except the new reaction field is available to make new low dimensional products.

Table 1. Typical experimental condition of LLIP method and the magnetic field effect

| Raw material / Good solvent | Poor solvent (precipitant) | Diameter of reactor, $d$ / mm | Reaction duration | Magnetic field effect | Remarks |
|---|---|---|---|---|---|
| C60 fullerene / Toluene | 2-propanol | 14.5 | 48 hr | Size x100, Orientation | rod crystal |
| Ice (water) / 1-BuOH | Toluene | 5.0 | 3 hr | Root position, Orientation, Growth rate x6 | ~20 °C |
| Glycine / Water | EtOH | 14 | 2 hr | Polymorph, Orientation | 0 °C |
| Taurine / Water | EtOH | 14 | 2 hr | Crystal habit, Orientation | |
| Thaumatin / Acid | (Rochelle salt) | 6.8 | 20 day | Orientation | pH = 5.0 |
| Lysozyme / TAE | PEG4000, ($CoCl_2$, etc.) | 6.8 | 5 day ~ 2 month | Size x10, Orientation | negative $g$ |

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