Crystal Growth of Glycine Controlled by a Focused CW Near-infrared Laser Beam

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Crystal growth of glycine was accelerated just by focusing a CW 1064-nm laser beam at a position adjacent to a spontaneously generated glycine crystal in D_2O. Its rate depended on the distance between the crystal and the focal spot. Interesting crystal growth and dissolution were found, which is considered to be due to Ostwald ripening.

Photon pressure, which is a gradient force toward a focal spot generated by focusing a CW laser beam, has been widely studied in science and technological applications.[1,2] Over the past decade, we have expanded a series of molecular experiments on photon pressure effects by studying supramolecule-aggregates,[3] J-aggregates,[4] and nanoparticles[5] in solutions, and fabricating molecular assembling structures reflecting photon pressure.[6] Furthermore we have demonstrated that dye-doped polystyrene nanoparticles with 24-nm diameter were trapped by photon pressure and then formed aggregates at a focal point.[7] The results indicate that photon pressure generates a highly concentrated area of nm-sized objects at the focal spot, on which we considered that laser trapping and crystallization could be possible. Indeed, we have succeeded in glycine crystallization just by photon pressure of a focused near-infrared CW laser beam,[8] while Tsuboi et al. demonstrated the crystallization of hen egg-white lysozyme in heavy water based on its aggregation induced by photon pressure.[9] In our case this novel phenomenon is due to the enhancement of interactions among liquid-like clusters at a focal point. In this paper, we report another novel phenomenon of crystal growth of spontaneously prepared crystals by applying photon pressure of a focused CW 1064-nm laser beam.

Glycine (>99% pure; Wako) was used as a solute without any further purification. D_2O (>99.9% pure; Wako) was chosen as a solvent which does not absorb the 1064-nm photon appreciably. If H_2O is used, the temperature elevation cannot be ignored, since an intense laser beam was focused close to its diffraction limit by an objective lens[10] and can be absorbed by the overtone band of OH stretching mode. For the preparation of a supersaturated D_2O solution of glycine, 0.30 g of glycine was dissolved into 1.0 g of D_2O at 60 °C with vigorous shaking for 2 h. The solution was slowly cooled down to room temperature and kept standing for 2 days to confirm that no crystal nucleus existed in it. A 40-μL portion of the solution was dropped on a cover glass with a hydrophilic surface, which was set on a stage of an inverted microscope. The cover glass was immediately sealed with a small dish to suppress the solvent evaporation. No crystallization was observed at 20–30 min after setting it on the stage, but spontaneous crystallization occurred thereafter owing to slow solvent evaporation. Two samples A and B consisting of spontaneously generated glycine crystals were examined in this work. They had one and three crystals around a focal point, respectively. The laser irradiation was started at several min after completion of the spontaneous crystallization, when the crystal growth once stopped to the naked eye. The optical system for this experiment was the same as that described in the previous paper.[8] A CW Nd^{3+}:YVO_4 laser (Spectra Physics, J20-BL-106C, $\lambda = 1064$ nm) was used as an optical trapping light source. The laser beam was introduced into an inverted microscope and focused at a glass surface through an objective lens (40× magnification, NA 0.90). Crossed Nicols images of the crystal growth were observed by using a CCD video camera (Flovel, HCC-600). The laser power used during the whole experiment was fixed to be 1.1 W, which was measured through an objective lens.

Figure 1 shows crossed Nicole images of sample A, where a white arrow denotes a focal spot. After spontaneous crystal growth was stopped, laser beam irradiation was started by focusing the beam at a point of 18 μm away from the side of the crystal edge as shown in Figure 1a. Just after laser irradiation, a luminescence-like spot was observed, which could be ascribed to the reflection from the cover glass. Laser irradiation induced slow crystal growth, resulting in a slightly wider crystal as shown in Figure 1b. Note that no crystal growth toward the bottom was observed in Figure 1b.

Next, for the same sample, the laser beam was focused at 18 μm away from the bottom of the crystal as shown in Figure 1c. After irradiation, the crystallization started immediately with rapid crystal growth rate toward the focal spot. It is notable that crystal growth became faster as the growing crystal edge shifted closer to the focal spot, and in particular, the crystal grew very quickly up to the focal spot. Eventually, after 18-s laser irradiation, the crystal completely stopped growing as it reached the focal spot. The average growing rate is estimated

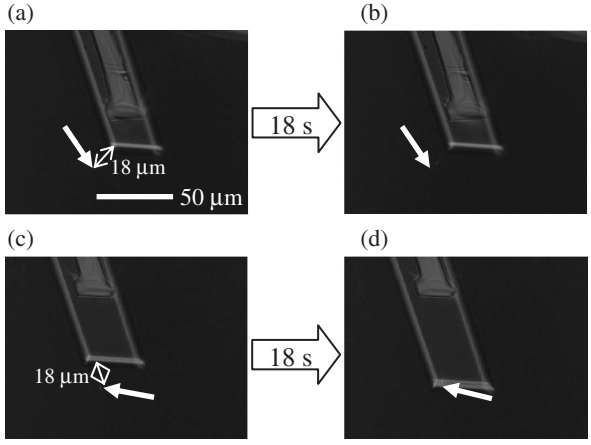

Figure 1. Crossed Nicole images of glycine crystal growth induced by focusing a laser beam.

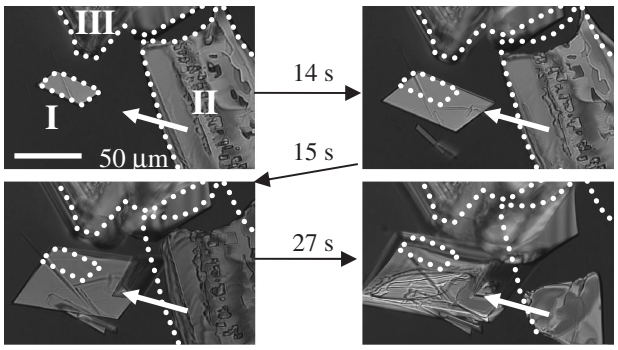

Figure 2. Crossed Nicole images of crystal growth and dissolution of glycine in a D_2O solution.

to be 1 μm/s. Furthermore, when the focal spot was moved away from the crystal by shifting the microscope stage, the crystal growth started again. This result indicates that the crystal growth is repetitively enhanced by laser irradiation and that its rate is accelerated near the focal point.

The apparent difference of growth behavior based on the position of the focal point is probably due to an anisotropic characteristic of crystal growth. In general, the crystal has a certain preferred direction for its growth, because molecules have directional preference of assembly due to inter- or intramolecular attractions and steric effects. The present result demonstrates that the crystal growth even toward an unpreferred direction can be attained by a focused laser beam.

Next, sample B had three glycine crystals (labeled I–III) generated spontaneously around a focal spot as shown in Figure 2. Before laser irradiation, all the crystals showed spontaneous and very slow growing. Then, the laser beam was focused between crystals I and II, as indicated by a white arrow. After irradiation, the growth rate of crystal I was extremely enhanced, and the two-dimensional growth was observed, which seems quite different from the directional growth of sample A. The difference could be explained by identifying the crystal face and polymorphology of glycine, which is being examined in our laboratory.

Here, laser irradiation made crystal I larger, while the crystal II started shrinking from its upper side as shown in Figure 2. Upon further irradiation, crystal II eventually disappeared, while crystal III also grew incidentally and slightly toward the focal spot by laser irradiation. This interesting behavior of crystal growth could be explained in terms of the enhancement of Ostwald ripening,[11] which is due to the difference of surface free energy among the plural faces of the crystals I–III. Namely, we consider that the local and temporal concentration distribution of glycine molecules and clusters in solution is manipulated by photon pressure. Thus laser irradiation restarts the crystal growth as well as the dissolution of a crystal.

The laser intensity in this work is estimated to be approximately 0.4 GW/cm^2 at the focal point. It is clear that it is too low to overcome Brownian motion of a single glycine molecule in D_2O. We believe that large liquid-like solute clusters,[12] which should be formed under the present concentration, are trapped forming an extremely high concentration region. The size of the cluster may be more than 14 nm estimated by an equation related to radiation force.[11]

The focal spot, about 1-μm diameter, was set relatively far from each crystal in all the experiments, while indeed the growth rate is accelerated close to the focal spot and becomes quite fast around the spot. Hence, it can be considered that a highly concentrated area of glycine molecules was formed not only at the focal spot but also its surrounding. This is due to trapping of large liquid-like clusters and the suppression of their diffusion at the focal point by photon pressure, where Marangoni convection based on slight temperature elevation should be coupled. It is reasonable to consider that glycine clusters at/around the focal point are efficiently transferred to the growing crystal by mass transfer based on convection. One may doubt that the exchange from D_2O to H_2O takes place to some extent and that laser-induced heating due to absorption of 1064 nm photon by H_2O enhances the convection. However, only dissolution of a glycine crystal was confirmed to occur in H_2O by a separate experiment, so we consider that such exchange is practically negligible.

In summary, we have succeeded for the first time in demonstrating crystal growth of glycine and its Ostwald ripening phenomenon by photon pressure due to a focused CW laser beam. Their dynamics and mechanism are now being studied, from which we will be able to grow a single crystal from polycrystalline sample. This approach will be useful for crystal growth, especially of protein whose single crystal formation is not always easy.

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