Crystallization of Glycine by Photon Pressure of a Focused CW Laser Beam

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An intense CW-YVO_4 laser beam of 1064 nm was focused into a supersaturated D_2O solution of glycine, leading to its crystallization. At the focal point on an air–solution interface, a small single glycine crystal was trapped and grew quickly. The crystallization mechanism is considered in view of gathering and organization of large solute clusters of glycine by photon pressure.

Laser-induced crystallization has attracted increasing attention, as can be applied to various organic compounds and proteins in their low supersaturated solutions. The quality of the crystal in low supersaturated solution is much higher than that in highly supersaturated solution, which is recognized in the conventional crystallization methods. Until now, the laser-induced crystallization can be achieved through chemical and nonchemical processes. In the former chemical process, laser irradiation generates a photoproduct, whose solubility is lower than that of mother compound, and subsequently the crystal growth originates from the photoproduct which works as a nucleus.[1,2] As for the latter nonchemical process, we have recently reported femtosecond laser-induced crystallization for low molecular organic compounds[3,4] and some proteins.[5,6] Garetz et al. reported another example of nonchemical process; nanosecond pulsed laser irradiation have induced glycine crystallization through light field assisted molecular orientation,[7] and also its polymorphism could be controlled by changing polarization of the laser beam.[8] All experiments used intense laser pulses as a light source for the nucleus generation of crystals.

On the other hand, we have extended a series of experiments on the photon pressure effects induced by an interaction of a focused CW near-infrared (NIR) laser beam with polymers,[9] dye-aggregates,[10] and nanoparticles[11] in solutions at ambient temperature. As an example, we have succeeded in preparing molecular assembling structures reflecting the photon pressure and clarified its formation dynamics and mechanism. As a matter of course, it is difficult to trap a single molecule including a small nanoparticle stably in a focal spot, because these polarizabilities on which the optical gradient force depends are considerably low. However, we have recently demonstrated that small plural nanoparticles were simultaneously trapped by an intense CW laser beam and formed their assemblies, namely, photon pressure-assisted association.[12,13] During the studies, we consider that an optical trapping force by a focused CW NIR laser beam may induce crystallization in a low supersaturated solution.

Glycine (Wako, >99% pure) and D_2O (Wako, >99.9% pure) were used without any purification. As descried below, D_2O was used as a solvent to avoid temperature elevation by laser irradiation. A supersaturated glycine/D_2O solution was prepared as follows; 0.30 g of glycine was dissolved in 1 g of D_2O at 60 °C with vigorous shaking for 2–3 h. Then, the solution was slowly cooled down to room temperature and aged for 2 days, and the sample for which no crystallization was observed was selected to use further crystallization experiments. The optical trapping system was almost the same as that described in the references.[9–11] A NIR laser beam ($\lambda = 1064$ nm) from a CW Nd^{3+}:YVO_4 laser (Spectra Physics, J20-BL-106C) was used as an optical trapping light source. This beam was introduced into an inverted microscope and focused at the air–solution interface via an objective lens (40× magnification, NA 0.90). Bright field and crossed Nicols images were observed by a CCD video camera (Flovel, HCC-600). A 40-µL portion of supersaturated glycine/D_2O solution was dropped on a cover glass with a hydrophilic surface, which was installed on the stage of an inverted microscope, as shown in Figure 1. The thickness of the solution layer was about 120 µm. Then, the stage was covered with a dish to slow down the evaporation of D_2O. Glycine crystals spontaneously appeared after about 15 min, owing to increasing the saturation with slow evaporation. It should be noted that the NIR laser beam irradiation started far before spontaneous crystallization. The laser power used here, measured after an objective lens, was 1.1 W.

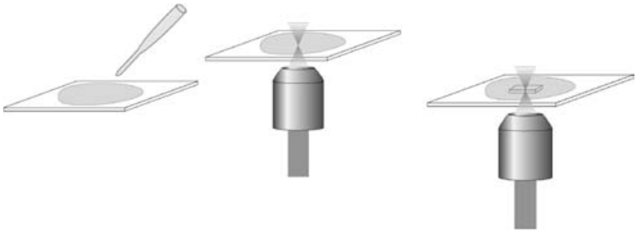
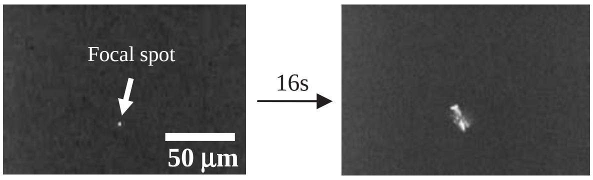


Figure 1. A schematic representation of glycine crystallization in a D_2O solution induced by a focused intense CW-YVO_4 laser beam.

In spite of their low absorption coefficients of H_2O and D_2O at 1064-nm wavelength, temperature elevation by laser irradiation cannot be ignored when the high-intensity laser beam is focused close to its diffraction limit. Ito et al. recently estimated the temperature elevation at the focal spot in some solutions by applying fluorescence correlation spectroscopy.[14] They reported that the local temperature elevation is by 22–24 T/W in H_2O and 2 T/W in D_2O, where T is temperature in Kelvin, with a high NA objective lens (NA = 1.35). When using water as a solvent, temperature elevation drastically increases the solubility of glycine; therefore, it is preferable to use D_2O in this study in order to simplify the experimental conditions.

Figure 2 shows crossed Nicols images of glycine crystal generation at the focal point of the air–solution interface in the D_2O solution. Just after laser irradiation, we observed the small spot in Figure 2a, which can be ascribed to weak reflection due to the difference in refractive index between solution and air. After 16-s laser irradiation, the glycine crystal generation was observed at the focal point as shown in Figure 2b. When the laser beam was focused on the glass–solution interface or in solution, such crystal generation at the focal point could not be observed.



(a) (b)

Figure 2. Crossed Nicols images of crystal generation of glycine in a D_2O solution at the focal point.

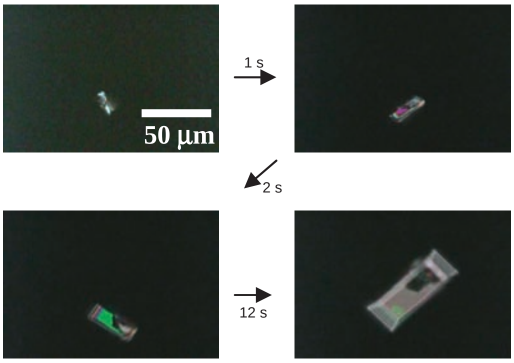


Figure 3. Crossed Nicols images of crystal growth of glycine in a D_2O solution trapped at the focal point.

The laser intensity at the focal point was estimated to be approximately 0.4 $\mathrm{GW/cm^2}$ in this work. The magnitude of the optical trapping potential energy is estimated to be too small to trap one glycine molecule, since optical gradient force must be much lower than the energy of thermal molecular motion, kT, where k is the Boltzmann constant. We consider that glycine molecules may form large solute clusters, due to the large dipole moments of a glycine molecule, and some of the clusters evolved to a critical nucleus by reorganization of clustering glycine molecules. An intense focused laser beam efficiently trapped the large solute clusters and slowed down their diffusion in the focal spot. Consequently, in the focal spot the interaction between the clusters was enhanced, and critical nucleation of glycine might be induced.

Note that further laser irradiation kept the generated glycine crystal trapped at the air–solution interface, and it rapidly grew as shown in Figure 3. Thus, the crystal generation and its subsequent crystal growth proceeded at a focal point. When growing proceeded, a large crystal was formed. It could not be trapped anymore with this laser power, and the formed crystal started to migrate. Furthermore, when the growing crystal was trapped, second harmonic generation (SHG) was sometimes observed. As a matter of course, no SHG signal was observed from the solution containing the solute clusters. It is known that γ-glycine is the most stable polymorph when recrystallized from D_2O, whereas α-glycine is the most stable from H_2O.[15] Considering the space groups of α- and γ-glycine are $P2_1/n$ (achiral space group) and $P3_1$ or $P3_2$ (chiral space group), respectively, the glycine crystal induced by a focused laser beam might have a γ-form since chiral space group is a requirement for SHG. Garetz et al. reported that when glycine solutions were exposed to intense pulsed laser beam for several min, no quick change has happened.[7] In contrast, in this work the generation of glycine crystal was immediately observed after about 20-s laser irradiation.

In summary, we have demonstrated crystal generation of glycine by an intense focused CW-YVO_4 laser beam. It is amazing that photon pressure by a focused intense CW laser beam can enhance the interaction between solute clusters and induce the nucleation of organic molecules. The crystallization was induced simply by CW laser irradiation, which is the first report as far as we know. Moreover, the growing crystal was trapped at a focal point, which will make it possible to elucidate the mechanism of crystal nucleation and growth by molecular spectroscopy in future. We consider that a new door is being opened by applying CW laser-induced crystallization to supramolecules, pharmacologic agents, and protein molecules.

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