Laser trapping dynamics of L-alanine depending on the laser polarization

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ABSTRACT

We successfully demonstrate crystallization and crystal rotation of L-alanine in D_2O solution using a focused laser beam of 1064 nm with right- or left-handed circularly polarization. Upon focusing each laser beam into a solution/air interface of the solution thin film, one single crystal is generally formed from the focal spot. The necessary time for the crystallization is systematically examined against polarization and power of the trapping laser. The significant difference in the average time is observed between two polarization directions at a relatively high laser power, where the left-handed circularly polarized laser takes 3 times longer than the right-handed one. On the other hand, the prepared crystal is stably trapped and rotated at the focal point by circularly polarized lasers after the crystallization, and the rotation direction is completely controlled by the polarization of the trapping laser. The mechanisms for the crystallization and the crystal rotation are discussed in terms of trapping force and rotation torque of circularly polarized lasers acting on the liquid-like clusters and its bulk crystal, respectively.

Keywords: laser trapping, circularly polarized laser, crystallization, crystal rotation, L-alanine

1. INTRODUCTION

The optical trapping of small particles was first demonstrated by Ashkin in 1970 using two laser beams propagating oppositely [1]. The simplest trapping technique using a tightly focused single laser beam was proposed, and the three-dimensional manipulation of the trapped particle was experimentally realized in 1986 [2]. Currently, this technique is well-known as "laser trapping" or "optical tweezers", and has been widely used for trapping and manipulating a single micrometer-sized object spatially in solution at room temperature without mechanical contact [3]. As with a micrometer-sized object, a focused laser beam can trap smaller objects with nanometer size such as nanoparticles, quantum dots, micelles, polymers, and molecular clusters at a focal spot [4–10]. They have much a smaller size compared to the focal spot with the volume of about $1\mu m^3$, so that plural particles, molecules, and clusters are simultaneously gathered, trapped, and confined in the focal volume, eventually forming their assemblies. When the target molecules or clusters have relatively strong mutual interactions, their assembling can be extended to the outside of the focal spot through nucleation and subsequent spontaneous growth, namely, the bulk phenomena of liquid-liquid phase separation and crystallization are achieved [11–13].

In 2007, we for the first time successfully demonstrated crystallization of glycine by applying this single laser trapping technique to its supersaturated D_2O solution, and have called this phenomenon "laser trapping crystallization" [14]. The crystallization is realized just by focusing a continuous wave (CW) near-infrared (NIR) laser beam into a solution/air interface and is not induced by the laser irradiation into solution or at a solution/glass interface. This result suggests that crystallization requires not only high molecular concentration due to laser trapping of the liquid-like clusters but also high-ordered molecular alignment at the surface layer. Recently, we also demonstrated the selective fabrication of glycine crystal polymorph by changing laser polarization (linear or circular polarization), power, and solution concentration, and discussed the mechanism of this polymorphism in view of local concentration increase, temperature

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elevation, and molecular rearrangement depending on these experimental parameters [15–17]. In that study, the most notable result is that radiation pressure working on the liquid-like clusters strongly depended on laser polarization [17]. The result prompted us to aim the selective crystallization of chiral compounds using a right- or left handed circular polarized laser as a future perspective.

In this work, for the crystallization study on a chiral amino acid under radiation pressure, we selected L-alanine as a target compound and demonstrated the laser trapping crystallization. As a result, we found that the necessary time for crystallization strongly depended on the laser polarization at a certain laser power. It was also confirmed that the formed crystal was rotated by a circularly polarized laser while being kept at the focal spot after crystallization, and that the rotation direction was completely controlled by tuning the laser polarization. These phenomena are discussed in terms of trapping force and rotation torque of circularly polarized lasers acting on the liquid-like clusters of L-alanine and its bulk crystal.

2. EXPERIMENTAL SECTION

L-alanine (>99.0 %, Wako) and D_2O (99.9 %, Cambridge Isotope Laboratories, Inc.) were used as a solute and a solvent, respectively, without further purification. We used D_2O, not H_2O, as a solvent in order to minimize the local temperature elevation due to light absorption by overtone vibration bands of OH. Actually, the temperature elevation was reported to be 22–24 and 2 K/W in H_2O and D_2O, respectively, upon focusing a 1064-nm laser beam by a high NA objective lens (NA=1.35, ×100) [18]. An L-alanine/D_2O supersaturated solution (110 %) used in this experiment was prepared by dissolving L-alanine (0.165 g) in D_2O (1.0 g) at 60 °C with vigorous shaking for 3 hours, and then it was slowly cooled down to room temperature (23 °C). A small amount (15 μL) of the solution was poured into a hand-made sample glass bottle with a highly hydrophilic surface, and the solution thin film with 120–160 μm thickness was prepared. The sample was immediately and completely sealed by a spigot to avoid solvent evaporation, and was set on the stage of an inverted microscope with a thermo-plate kept at 23 °C for the further laser trapping crystallization experiment.

Figure 1 shows a schematic illustration of an optical setup in this experiment. A NIR laser beam from a CW Nd^{3+}:YVO_4 laser (Spectra Physics, J20-BL-106C, λ = 1064 nm) was used as a laser trapping light source. A He-Ne laser adjusted coaxially with the trapping laser was introduced to the inverted microscope in order to check the focal position. After confirming the focal point of the He-Ne laser at a solution/air interface of the thin film through an objective lens (60× magnification, NA 0.90), the laser was switched off, and then the NIR laser was switched on. The power of the NIR laser throughout the objective lens was tuned from 1.0 to 1.4 W by adjusting a half-wave plate (HWP) coupled with a polarizing beam splitter (PBS). A right- or left-handed circularly polarized laser beam was changed by adjusting a quarter-wave plate (QWP) and was irradiated into the sample of L-alanine/D_2O solution for 30 minutes. Crystallization and rotation behaviors were directly observed by an EMCCD video camera (Flovel, ADT-40C) under halogen lamp illumination.

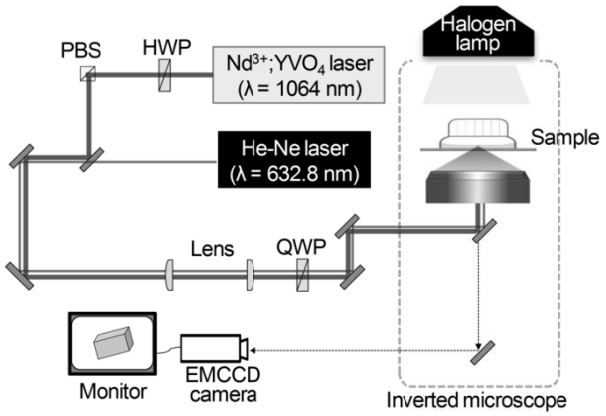

Figure 1: An experimental setup for the laser trapping system

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3. RESULTS AND DISCUSSION

3-1. Laser trapping crystallization of L-alanine

Figure 2a shows a representative example of L-alanine crystal generation and growth at the focal spot. Immediately after starting irradiation of a right-handed circularly polarized laser beam at 1.3 W, only a small spot ascribed to weak reflection of the trapping laser at the solution/air interface was observed (Fig. 2a (1)). After 216 sec-laser irradiation, the crystal with a visible size of a few μm was observed at the focal point (Fig. 2a (2)). The formed crystal was trapped by further laser irradiation at the surface, where it rapidly became larger under the irradiation (Fig. 2a (3), (4)). When the crystal grew up to the size of several tens μm at the focal spot, it could not be trapped anymore with this laser power and migrated from the spot. In general, no one can predict where and when crystallization takes place in conventional crystallization methods such as solvent evaporation and cooling of solution. On the other hand, the crystallization by this technique was always observed at the focal spot within 10 minutes, namely, crystallization is controlled spatiotemporally.

In most cases, only one single crystal was formed at the focal point (Fig. 2a), while polycrystallization was rarely observed at the focal spot (Fig 2b). This indicates that the formation of a single nucleus takes place dominantly in the focal spot, in spite that the size of the nucleus should be much smaller than that of the focal spot. This can be possibly explained by the assumption that the initially generated crystal nucleus rapidly grows due to the high concentration at the focal spot prior to the next nucleation.

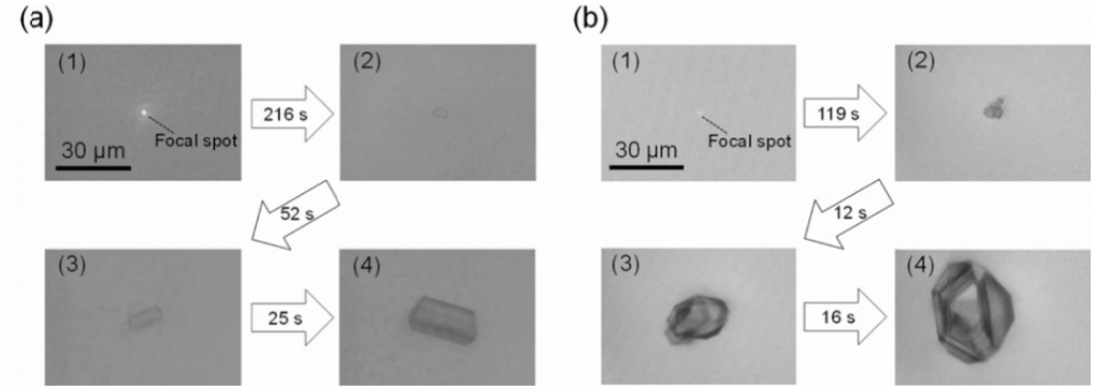

Figure 2: Formation behaviors of (a) single crystal and (b) polycrystal of L-alanine under laser irradiation.

Here we discuss the magnitude of the optical trapping force working on L-alanine molecule and the cluster. The force should be too small to trap individual L-alanine molecules, so that it is reasonable to consider that the liquid-like clusters are trapped similarly in the case of glycine [19]. The isoelectric point of alanine is reported to be 6.107 [20], where almost all of the molecules exist as zwitterions. The molecules are weakly linked with each other due to the electrostatic interactions of hydrogen bonds between the zwitterions, and the liquid-like clusters are formed in the solution. The clusters are trapped by radiation pressure in the focal volume, where they would be fused with each other. That is, their effective volume and polarizability increase, stronger trapping force is generated, and as a result the effective laser trapping is realized. Thus, the local concentration increases nonlinearly with time at the focal point, and the formation of a critical nucleus of L-alanine is eventually induced. Incidentally, this crystallization behavior could be observed even in the unsaturated solution. In such a solution, local supersaturated area is transiently formed at/around the focal spot, and the surrounding solution is still below the saturation condition. Actually, after the trapping laser is switched off, the formed crystal immediately and completely dissolves as with the case of glycine [16].

3-2. Crystallization time depending on laser power and polarization

Our laser trapping crystallization is spatially controlled and the crystal formation always takes place at the focal point unlike conventional crystallization methods such as solvent evaporation or solution cooling. Namely, we know where

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crystallization surely takes place. This feature enables us to examine the necessary time for crystallization (described as "crystallization time" in this paper) systematically through direct observation using an EMCCD camera. Crystallization time in this study was defined as the time when the crystal with a visible size was observed at the focal spot. A series of the experiments was repetitively carried out for 10 samples under each condition of laser polarization and power. The average crystallization time against laser power of each polarization is shown in Fig. 3, where a bar indicates the maximum and minimum time. The crystallization time at 1.0–1.2 W was scattered within 10 minutes as shown in the bar at each irradiation condition, which supports that crystal nucleation is stochastic process even under laser irradiation. Nevertheless, the right- and left-handed circularly polarized lasers at each laser power of 1.0–1.2 W showed almost the same average time independent of the laser polarization. We consider that, in this power range, there is almost no difference in the crystallization process between two polarization directions. On the other hand, a large difference in the time between the right- and left-handed circularly polarized lasers was found at 1.3 W, where the left-handed circularly polarized laser took about 3 times longer time on average for the crystallization compared to the right-handed one. The difference was confirmed to be statistically-meaningful through a Mann-Whitney's U test. However, no polarization dependence of the average time was again observed at 1.4 W. Thus, only the crystallization at 1.3 W showed a significant difference in the average time between two polarization directions.

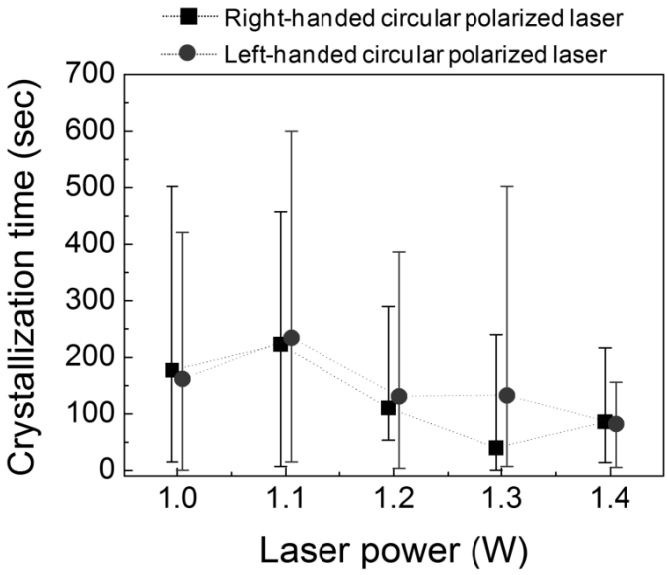

Figure 3: Average crystallization time against laser power of each polarization.

In our previous studies on laser trapping crystallization of glycine, the crystallization time and the polymorph control in supersaturated solution was well explained from the viewpoints of the increase in local concentration due to laser trapping of the liquid-like clusters and the accompanied temperature elevation [15–17]. In this work, we also consider that the difference in the crystallization time with each polarized laser beam depends on these two factors, and propose the prospective mechanism for the different crystallization time based on the obtained results, as schematically illustrated in Fig. 4. In our assumption, the laser trapping of the clusters increases the supersaturation value (SS) at the focal spot, which provides rapid crystallization time. Conversely, the laser heating decreases the SS, suppressing the crystallization.

The former laser trapping is based on the gradient dipole force of the non-uniform electromagnetic field, and the magnitude of the trapping force is determined by size and polarizability of targets in Rayleigh approximation [21]. L-alanine molecule and its precursor cluster possibly show the slight difference in the polarizability between right- and left-handed circularly polarization of the 1064 nm-trapping laser. The difference becomes prominent with the nonlinear increase in local concentration of the clusters, which would cause the polarization dependence of the SS increase at higher laser power. Considering that the right-handed circularly polarized laser beam showed the rapid crystallization time at 1.3 W, the laser with right-handed circularly polarization should generate stronger trapping force for the liquid-

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like clusters and increase the SS effectively by their efficient laser trapping (Fig. 4b-1). Next, we should consider local temperature elevation due to photon absorption of 1064 nm by overtone vibrational modes of L-alanine molecules themselves. The heating effect suddenly becomes prominent above a certain laser power where the thermal dissipation is overcome by input vibrational energy (Fig. 4b-2). The temperature elevation leads to vigorous molecular motion and rotation, resulting in the SS decrease.

The local SS in the focal volume is represented by the multiplication of these two conflicting factors. The difference in SS between the right- and left-handed circularly polarized lasers shows a bell-shaped curve against laser power (Fig. 4c). Namely, the efficient laser trapping of the clusters at 1.3 W generates the large difference in the local SS between two polarization directions, resulting in polarization dependence of the average crystallization time. However, the heating effect at 1.4 W effectively decreases the local SS, which compensates the SS difference between two polarization directions similarly in the case of laser irradiation at lower power. In addition to the above mechanism, we point out that laser irradiation with each circularly polarized laser beam may give the different temperature elevation. This viewpoint makes us remind the different absorption coefficient at 1064 nm of the trapping laser between right- and left circular polarization [22–24], since the photon absorption for the temperature elevation is ascribed to overtone bands of vibrational modes of L-alanine molecule. Thus, the crystallization time is well explained by two laser induced effects of concentration increase and temperature elevation and by their polarization dependence.

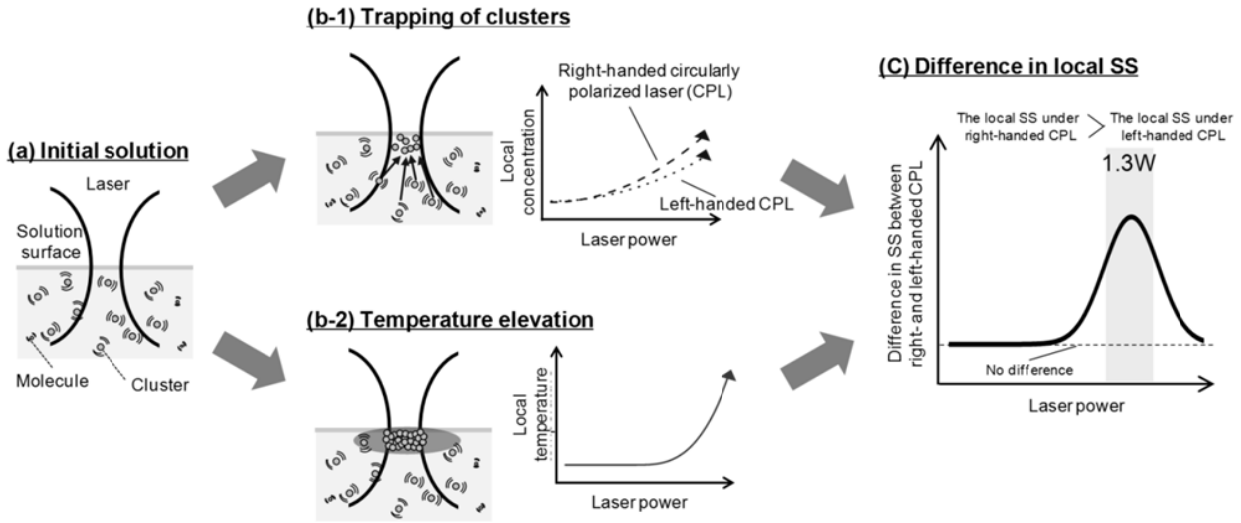

Figure 4: The mechanism of L-alanine crystallization depending on laser power and polarization.

3-3. Rotation of crystal by laser polarization

Another amazing result in this experiment is that the grown crystal was rotated by further irradiation, and the rotation direction was completely controllable by laser polarization. Figure 5 shows the rotation behavior under the irradiation of the right- and left-handed polarized laser beams at 1.0 W. The formed crystal was rotated clockwise under the irradiation of the right-handed circularly polarized laser (Fig. 5a), while the left-handed one provided counterclockwise rotation of the crystal (Fig. 5b). Incidentally, the rotation stopped under the irradiation of the linearly polarized laser beam, and the further irradiation kept the crystal at a certain position without rotating. Such a crystal rotation depending on the laser polarization can be explained on the basis of angular momentum of light. When circularly polarized light carrying angular momentum passes through a birefringent object, the polarization of light is changed, and the angular momentum of the transmitted light is different from the initial one. Namely, rotating torque is given to the object due to the law of conservation of angular momentum [25–27]. Since the direction of the rotation torque depends on angular momentum of circular polarization of the incident light, the rotation direction of the object is controllable by tuning the polarization.

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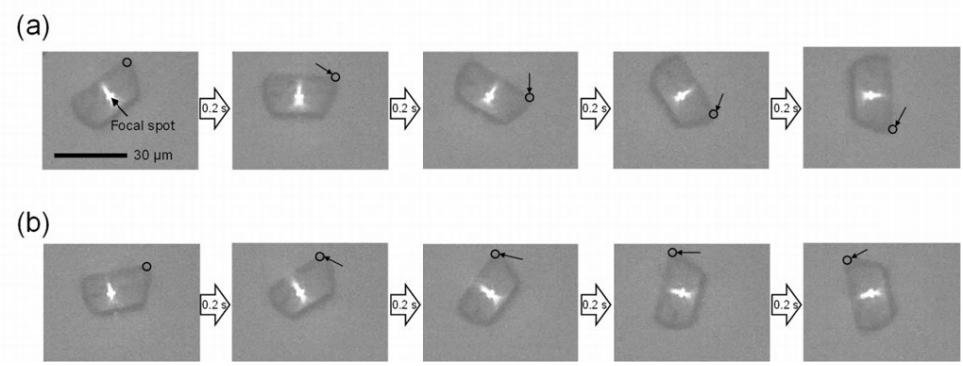

Figure 5: CCD images of crystal rotation under the irradiation of (a) the right-handed and (b) the left-handed polarized laser beams.

4. SUMMARY

We successfully demonstrated crystallization and crystal rotation of L-alanine in D_2O solution by a focused CW NIR laser beam with right- or left-handed circularly polarization. We examined the average time necessary for the crystallization between two polarization directions and found a significant difference of the time only at 1.3 W. We also found the interesting result of the crystal rotation under the further irradiation. The formed crystal was stably trapped and rotated at the focal spot by further irradiation, and the direction of rotation was completely controllable by tuning the polarization of the trapping laser. These two phenomena of the crystallization and the crystal rotation were discussed in terms of trapping force and rotation torque of circularly polarized lasers acting on the liquid-like clusters and the bulk crystal, respectively.

Finally, we try to suggest a new perspective on optical rotation torque for the crystallization process by laser trapping. The L-alanine crystal gradually grows with rotation under circular polarized laser irradiation. We imply that, on the crystallization process from the nm-sized liquid-like clusters to the μm-sized bulk crystal, the rotation of the small clusters possibly always takes place or the rotation torque is at least given to the clusters. The rotation of the liquid-like clusters by laser irradiation possibly affects the association rate before nucleation, leading to the different crystallization time under circular polarized laser irradiation. In future, laser trapping crystallization for racemic compounds showing spontaneous resolution will be done, and the achievement of optical resolution using laser trapping is expected.

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