Femtosecond Laser-Induced Chiral Crystallization of Sodium Chlorate

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For the past decade, we have succeeded in demonstrating the crystallization of amino acids, proteins, saccharides, and inorganic compounds using optical trapping with continuous-wave (cw) lasers [1]. In addition, we demonstrated crystallization also by applying focused femtosecond (fs) laser pulses with a low repetition rate into a glycine supersaturated solution [2]. However, the crystallization mechanisms are totally different from each other. On the other hand, optical trapping is also made possible by a femtosecond laser with a high repetition rate. Such ultrashort-pulsed lasers exhibit high trapping efficiency due to the high intense photon density and nonlinear effects, comparing to optical trapping using cw lasers [2]. Here, we present the crystallization of sodium chlorate ($NaClO_3$) with a fs laser with a high repetition rate and discuss the dynamics and mechanism of crystallization and polymorphic transition from the viewpoints of laser trapping and laser ablation with fs laser pulses.

An aqueous solution of $NaClO_3$ with a low supersaturation was prepared and poured into a glass substrate with a hydrophilic surface. Fs pulse laser pulses (800 nm, 120 fs, 80 MHz) were focused at the air/glass/solution interface through an objective lens (60×, NA = 0.9). The laser fluence throughout the lens was tunned, ranging from 0.14-0.67 J/cm^2.

Figure 1 shows a representative crystallization behavior of $NaClO_3$ upon fs laser irradiation at 0.20 J/cm^2. Before the irradiation, no crystal was observed all over the sample solution (Fig. 1a). At about 4 min after the irradiation, cavitation bubbles started to be generated from the laser focus (Fig. 1b). We consider that fs laser trapping achieves an increase in the local concentration at the laser focus, forming cavitation bubbles due to the multiphoton absorption enhanced by the high solute concentration. Following the bubble generation, the achiral crystal was firstly formed (Fig. 1c), and further irradiation caused the polymorphic transition from the achiral to the chiral crystal from the laser focus (Fig. 1d). The polymorphic transition was not always observed, and the probability of the transition increased with the laser power. Comparing to the case of cw lasers, fs laser irradiation tremendously enhances the possibilities of crystallization and polymorphic transition even at the much lower intensity. In the presentation, we also discuss the handedness of the resultant chiral crystals.

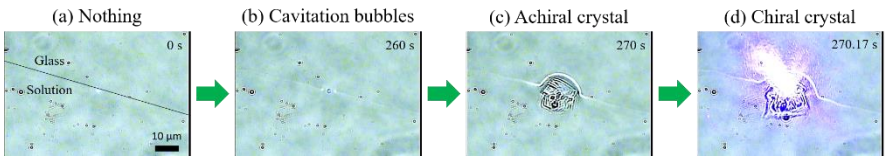

Figure 1. Bright images of crystallization behavior of $NaClO_3$ during fs pulse laser irradiation.

References

[1] T. Sugiyama et al., *Acc. Chem. Soc.*, 45, 1946 (2012).

[2] T.-H. Liu *et al., J. Cryst. Growth,* 366, 101 (2013).