

プラズモン光ピンセットによる有機分子の結晶化操作と二段階溶解過程の発見

“Manipulated” Organic Crystallization and Two-step Dissolution Process Attained by Plasmonic Optical Tweezers

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Spatiotemporal control of crystallization from a solution is often required for detailed exploration on mechanism of early stage of crystallization because the stochastic nature of nucleation process hinders us to chase its early stage. Recently, laser trapping-induced crystallization technique has received increasing attention as a possible candidate to realize spatiotemporally controllable crystallization.[1] In the technique, the crystallization is induced by trapping molecular clusters in a solution with optical tweezers, in which dielectric tiny particles are captured by electrical field gradient force generated by tightly focusing laser light by optical lens. This technique has actually demonstrated forced nucleation of various organic molecules from an unsaturated mother solution at the focal spot. Although recent progress of nanoscience including research on nucleation dynamics demands precise manipulation of nanoscopic objects, the conventional optical tweezers, electrical field gradient force of which relies on the focusing the laser by optical lens, has a limitation of diffraction limit on focusing the light. To overcome the limit, the use of near-field generated by localized surface plasmon resonance, which is collective oscillation of free electrons on surfaces of metal nanoparticles when light impinges on the nanoparticle, has been proposed. [2] Because the near-field is confined in nanoscale, the light focusing beyond the diffraction limit can be achieved consequently, allowing us to capture the smaller particles much tightly than the conventional method. However, the plasmonic optical tweezers has never been applied to crystallization. Here we applied plasmonic optical tweezers to crystallization of acetaminophen molecule from an aqueous solution.

Figure 1 shows schematic illustration of experimental setup. Periodic Au nanolattice the unit structure of which is gammadion with the size of 500 nm was fabricated on a cover glass by electron beam lithography. An aqueous solution of acetaminophen saturated at room temperature (24°C) was dropped on the Au nanolattice, and then solution thin layer supported by the nanolattice was formed by capillarity. Near-infrared continuous-wave left-handed circularly polarized laser (1064 nm, 6.4×10^9 W/m²) was focused to the nanolattice supporting the solution thin layer by passing through an objective lens equipped on an inverted polarized-light optical microscope. In-situ microscopic observation for the vicinity of the focal spot was also performed simultaneous with the laser irradiation.

Figure 2 shows time-lapse micrographs of the in-situ observation in the vicinity of the focal spot. After the laser irradiation, crystals with the size of 1000 ~ 2000 nm were precipitated 19 mm away from the focal spot in annular pattern. The position of the annular pattern moved while following the change of in-plane position of the focal spot via dissolution/precipitation process, indicating that position of the crystal is manipulatable. When the plasmon excitation by laser irradiation was stopped, the crystals were disappeared via two-step dissolution process; the crystals first transformed to dense liquid droplets, and then the dense droplet disappeared through molecular diffusion.

Generally, large temperature gradient generates in the vicinity of the focal spot when localized surface plasmon resonance was excited, because of the heat generation through electron-phonon scattering. Thus, the large temperature gradient exerts thermophoretic force outward from the focal spot on acetaminophen molecules. Since the electrical field gradient force attracts the molecules towards the focal spot, the annular-patterned precipitation can be interpreted as the consequence of the balancing the electrical field gradient force as attractive force and the thermophoretic force as repulsive force. Therefore, our observation strongly suggested that plasmonic optical tweezers can precisely control crystallization.

[1] T. Sugiyama *et al.*, *Acc. Chem. Res.* **2012**, 45(11), 1946-1954.

[2] T. Shoji *et al.*, *J. Phys. Chem. Lett.* **2014**, 5(17), 2957-2967.

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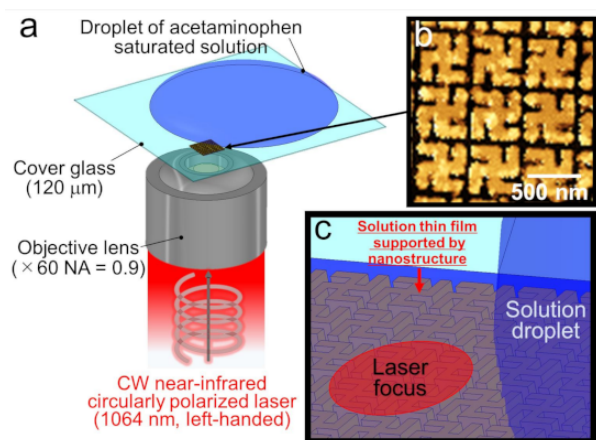


Figure 1 a Schematic illustration of the experimental setup b Atomic force microscopic image of the plasmonic Au nanolattice c Position of the laser focus.

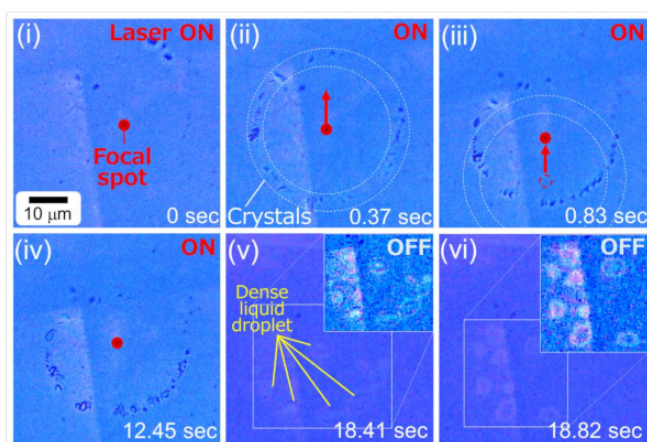


Figure 2 Time-lapse micrographs showing the dynamics of the plasmonic trapping-induced crystallization and the two-step dissolution process.