Chiral Crystallization Directed by Superchiral Plasmonic Near-field Force

Hiromasa Niinomi[1*], An-Chieh Cheng[2], Teruki Sugiyama[3], Miho Tagawa[4], Toru Ujihara[4], Hiroshi Yoshikawa[5], Ryuzo Kawamura[6], Jun Nozawa[7], Junpei T. Okada[7], Satoshi Uda[8], Tomoya Oshikiri[1], and Masaru Nakagawa[1]
* hiromasa.niinomi.b2@tohoku.ac.jp
1 IMRAM, Tohoku Univ., Japan, 2 RIES, Hokkaido Univ., Japan, 3 National Yang Ming Chiao Tung Univ., Taiwan, 4 IMaSS, Nagoya University, Japan, 5 Osaka Univ., Japan, 6 Saitama Univ., 7 IMR, Tohoku Univ. Japan, 8 NICHe, Tohoku Univ., Japan

Control of handedness of chiral materials by circularly polarized light (CPL) has received attention from the viewpoint of the origin of biohomochirality, pharmaceutical industry, and spintronics. Although CPL laser-induced chiral crystallization has been performed so far, no significant chiral bias has been reported [1]. This is because the large-scale difference between helical pitch of CPL and chirality unit results in weak asymmetric interaction between CPL and chiral matter. Recent studies on plasmonics have shown that chiral plasmonic near-field can boost the weak interaction because the enhancement of a degree of chirality in electromagnetic field (EM-field), known as optical chirality (OC) [2], can shorten the helical pith of EM-field relative to incident CPL for plasmon excitation. Here, we show that large chiral imbalances in sodium chlorate ($NaClO_3$) chiral crystallization from a solution can be obtained by inducing nucleation from plasmonic nanoparticles as a nucleation site [3,4]. Numerical analysis suggested that the origin of the chiral imbalance can be chiral optical force generated by the interaction between the superchiral plasmonic near-field and chiral crystalline clusters.

Triangle-trimer plasmonic nanostructures consisting of gold triangular nanoparticles with sides of 230 nm were fabricated on a cover glass by electron beam lithography. A saturated solution of $NaClO_3$ was dropped on the nanostructure (10 mL). Crystallization was induced by irradiating a focused continuous-wave near-infrared (λ = 1064 nm) CPL laser using an inverted polarizing microscope to the nanostructures (1.0 MW/cm^2). The handedness of the resulting crystals was identified by the rotating analyzer method. OC enhancement in near-field and chiral optical force was analyzed by finite-difference time-domain (FDTD) method.

50 crystallizations using *l*- (*r*-) CPL yielded 37 (11) *l*-crystals and 13 (39) *d*-crystals. The resulting crystal enantiomeric excess (CEE) was 52 %, which is about 10-fold of a typical imbalance in chiral photosynthesis using CPL. The numerical analyses showed that OC enhancement beyond 30-fold was locally observed in the nano-gap with 20 nm width at the center of the nanostructure. Several tens of fN of chiral optical force was found to be exerted on $NaClO_3$ pre-critical chiral crystalline clusters [5]. Comparable magnitudes of achiral optical force have been found to be sufficient to induce crystallization even from an unsaturated solution by locally concentrating solute molecules using laser tweezers [6]. This suggests that the chiral near-field force can be responsible for the large CEE.

References

[1] Murphy NC et al. Effect of Chiral and Achiral Perturbations on the Crystallization of 4,4‘-Dimethylchalcone from Ethyl Acetate. Cryst. Growth Des. 2007;7(2):449-452.
[2] Tang Y et al. Optical Chirality and Its Interaction with Matter. Phys. Rev. Lett. 2010;104:163901.
[3] Niinomi H et al. Enantioselective amplification on circularly polarized laser-induced chiral nucleation from a $NaClO_3$ solution containing Ag nanoparticles. CrystEngComm. 2016;18:7441-7448.
[4] Cheng AC et al. Plasmonic Manipulation-Controlled Chiral Crystallization of Sodium Chlorate. J. Phys. Chem. Lett. 2020;11(11):4422-4426.
[5] Niinomi H et al. Chiral Optical Force Generated by a Superchiral Near-Field of a Plasmonic Triangle Trimer as Origin of Giant Bias in Chiral Nucleation: A Simulation Study. J. Phys. Chem. C. 2021;125(11):6209-6221.
[6] Cheng AC et al. Evolving Crystal Morphology of Potassium Chloride Controlled by Optical Trapping. J. Phys. Chem. C. 2020;124(12):6913-6921.