

Chiral asymmetry in NaClO₃ Chiral Crystallization Induced by Circularly Polarized Laser Trapping of Plasmonic Nanoparticles

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Chirality, the property that a certain 3D structure is not superimposable on its mirror image, is a fundamental characteristic prevailing in various natural hierarchies. Living organisms preferentially select only left-handed amino acids, despite the thermodynamic equality of mirror isomers. The significant chiral bias in living organisms is known as “homochirality”, and its origin is a great puzzle on the evolution of life. Among various hypothesizes which proposed to explain the origin of biohomochirality[1-3], the extraterrestrial scenario attributes the origin to enantioselective decomposition of chiral organic compounds on a meteorite by exposure to circularly polarized light (CPL), which asymmetrically interacts with chiral matters, emitted from a neutron star.[3] Therefore, asymmetric phenomena induced by CPL irradiation is of great interest from the viewpoint of earth science. Many previous studies on photosynthesis of chiral molecule have proven that asymmetric interaction between CPL and chiral matter, i.e. circular dichroism (CD), induces slight chiral bias in enantiomeric ratio of reaction products[4]. Chiral crystallization, in which chirality spontaneously emerges in the course of crystallization, has been received attention from the viewpoint of emergence of chirality. The exploration of physical factors that induce a significant chiral bias in chiral crystallization should provide implications for the origin of biohomochirality. However, light-based chiral bias in chiral crystallization still remains unreported. The conceivable reason is that CD is intrinsically small. Here, we provide the first demonstration of a statistically-significant chiral bias in sodium chlorate (NaClO₃) chiral crystallization induced by CPL irradiation with the help of CD enhancement by localized surface plasmon resonance (LSPR) of silver nanoparticles (AgNPs), which is caused by electronic state chiral materials coupled with the collective oscillation of free electron on the surface of metal nanoparticles.

A continuous-wave (CW) CPL green laser (wavelength is 532 nm, laser power is 940±5 mW, ellipticity is 93%) was focused onto the air-liquid interface of the undersaturated NaClO₃ solution (6 microliter) containing AgNPs by using a 60× objective lens (NA = 0.9) equipped on an inverted polarized light microscope. We repeated crystallization and chirality identification of the NaClO₃ crystal 150 times by using *l*-CPL and 150 times by using *r*-CPL, respectively. The number of the resulting enantiomorphs was counted. The crystallization dynamics was examined by *in-situ* microscopic observation of Raman scattering and polarized image.

Upon the laser irradiation, aggregates of the AgNPs occasionally floated on the air-liquid interface were trapped at the focal spot because of optical trapping. Crystallization was induced simultaneously with the optical trapping of AgNPs. The observation of Raman scattering showed that crystallization occurred at the moment when surface-enhanced Raman scattering (SERS) [5] active particle was optically trapped, showing that the excitation of LSPR plays significant role for nucleation [6]. As the result of counting the given enantiomorphs, the crystallization using *l*-CPL(*r*-CPL) yielded *l*-enantiomorph 55(93) times and *d*-enantiomorph 95(57) times, respectively[7]. These results indicate that the “dominant” enantiomorph can be switchable by changing the handedness of incident CPL, i.e. enantioselectivity. This chiral bias is statistically significant because the number of the “dominant” enantiomorph deviates 99% interval of

the binomial distribution $B(n,p) = B(150, 0.5)$, where n is the number of trials and p is the probability that the “dominant” enantiomorph crystallizes out. The chiral bias, which was approximately 25% in crystal enantiomeric excess, is much higher than that in typical enantiomeric excess in photosynthesis ranging from 0.5 to 2% [8].

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