

Chiral Bias in Chiral Crystallization Induced by Circularly Polarized Laser Trapping of Silver Nanoparticles in Sodium Chlorate Solution

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Chiral crystallization, in which chirality emerges spontaneously in the course of crystallization, has been received attention from the viewpoint of emergence of chirality. Thus, the exploration of physical factors that induce a chiral bias in chiral crystallization provides implications for the origin of bihomochirality. Asymmetric interaction between circularly polarized light (CPL) and chiral compound, i.e. circular dichroism (CD), has been considered as a candidate for the origin of bihomochirality,[1]. Many previous studies on photosynthesis of chiral molecule have proven that asymmetric light-matter interaction induces slight chiral bias in enantiomeric ratio of reaction product, so far.[2] However, light-based chiral bias in chiral crystallization still remains unreported. Two conceivable reasons may exist: (1) CD is intrinsically small, (2) there is no investigation on chiral bias by CPL-induced chiral crystallization with a guarantee of optical field effect on nucleation. We overcome these difficulties by two strategies: (1) the plasmonic enhancement of CD [3] and (2) continuous-wave (CW) laser-induced nucleation [4]. In this presentation, we report the first demonstration of significant chiral bias in NaClO₃ chiral crystallization by irradiating a tightly-focused circularly polarized CW laser at the interface between air and a NaClO₃ solution containing plasmonic AgNPs.

A CW CPL green laser (532 nm, 940±5 mW, ellipticity >93%) was focused onto the air-liquid interface of the undersaturated NaClO₃ solution containing AgNPs by using a 60x objective lens (NA = 0.9) equipped on an inverted polarized light microscope. We repeated crystallization and chirality identification of the NaClO₃ crystal 100 times and 100 times by using *l*- and *r*-CPL, respectively. The number of the resulting enantiomorphs was counted.

As the result of the laser irradiation, crystallization occurred from the focal spot. The crystallization using *l*-CPL(*r*-CPL) yielded *l*-enantiomorph 42(65) times and *d*-enantiomorph 58(35) times, respectively, indicating that the *d*-(*l*-)enantiomorph was dominant over the *l*-(*d*-)enantiomorph. Namely, the "dominant" enantiomorph can be switchable by switching the handedness of incident CPL, i.e. the chiral bias is enantioselective. In total, the "dominant" enantiomorph crystallized 123 times out of 200 crystallization. This chiral bias is statistically significant because the number of the "dominant" enantiomorph deviates 99% interval of the binomial distribution $B(n,p) = B(200,0.5)$, where n is the number of trials and p is the probability that the "dominant" enantiomorph crystallizes out (Figure 1). This deviation demonstrates that the probability p is more than 0.5, i.e. the probability of the occurrence of each enantiomorph is no longer equal.

We found that the crystallization of NaClO₃ chiral crystal can be induced by the irradiation of tightly focused CPL laser (532 nm) at the interface between air and NaClO₃ solution containing AgNPs. We also found that this crystallization method can cause a statistically-significant chiral bias in the probability of crystallization of both of the enantiomorphs. Moreover, the "dominant" enantiomorph is found to be switchable by changing the handedness of CPL. Our results may provide implications for the origin of bihomochirality.

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