Chiral Crystallization from $NaClO_3$ Solution Containing Gold Nanoparticles Using Circularly Polarized Light

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Chiral crystallization, in which chirality spontaneously emerges in the course of crystallization, has been received attention from the viewpoint of the elucidation of the origin of homochirality. We recently succeeded in demonstrating the crystal enantiomeric excess (CEE) value of 25% upon chiral crystallization from sodium chlorate ($NaClO_3$) containing Ag nanoparticles (NPs) using circularly polarized light [1]. In this work, we performed a similar series of this experiment by adding AuNPs with various sizes into the solution instead of AgNPs, aiming to achieve higher CEE value and elucidate the mechanism of enantioselectivity.

A saturated $NaClO_3$ aqueous solution was used as a target solution. 15 μL of the solution was poured into a hand-made container to suppress the solvent evaporation. 0.3-0.5 μL of AuNPs with 10, 60, or 150 nm were added into the solution and the container was put on a stage of an inverted polarized light microscope. A continuous-wave 1064 nm laser with right- or left-handed circular polarization was tightly focused at the air/solution interface with a 60x objective lens (NA = 0.9) of the microscope. The handedness of the resultant chiral crystals was in-situ determined by an analyzer-rotation method under the microscope. The laser power throughout the objective lens was always fixed to be 1.0 W. The crystallization experiment was repeated 25 times for each experimental condition to evaluate the CEE value.

Before the laser irradiation, the aggregates of AuNPs were observed around the laser focus. After starting the irradiation, the aggregates were occasionally trapped at the laser focus, and then a single achiral metastable crystal showing birefringence was generated at the laser focus. The continuous laser irradiation to the achiral crystal resulted in the polymorphic transition from the achiral to the chiral crystal with a certain probability that became higher with the laser power and the size of AuNPs. We also found that there was a statistically significant difference in the generation probability of both enantiomorphs, and the CEE value achieved to 44%. Most intriguingly, we also found that the opposite trend of the CEE value can be observed upon the experiments using different size AuNPs. In the presentation, we will discuss the mechanism of this unique phenomenon from the viewpoint of chiral electromagnetic fields generated at the aggregates of AuNPs and the polymorphic transition process from achiral metastable to chiral stable phase under light irradiation.

References

[1] H. Niinomi *et al*., *CrystEngComm*, 18 (2016), 7441–7448.