Crystallization and Polymorphic Transition of $NaClO_3$ via Plasmonic Trapping

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The localized surface plasmon resonances of metal nanostructures enable the excitation of hotspots beyond the diffraction limit of the light that can be used to optically trap various nanomaterials with high precision. Previously we demonstrated enantioselective control in chiral crystallization of sodium chlorate ($NaClO_3$) by plasmonic trapping and successfully achieved significant crystal enantiomeric excess (CEE) of more than 50 % [1]. In that work, we used triangular trimer gold nanostructures with side length of 230 nm as a plasmonic structure. The finite element method revealed that the enhanced electric field was not generated at the nanogap in the center of the trimer but at the outside of each triangle upon the 1064-nm excitation (Figure 1a). Here, we design and fabricate triangular trimer gold nanostructures with side lengths of 170 nm that confine and enhance the electric field at the nanogap of the trimer upon circularly polarized 1064-nm light excitation (Figure 1b). We investigate the possibility for both the metastable crystallization and the polymorphic transition of $NaClO_3$ to occur depending on the type of trimer gold nanostructure.

The 1064-nm continuous-wave laser with circular polarization at 1.0 MW/cm^2 was focused on a single triangular trimer structure. Crystallization was induced with almost 100% probability using both types of plasmonic structures, and the precipitated crystals were attributed to be the metastable achiral phase because of their birefringence. Noted, when 170 nm gold nanostructures were used, the crystallization time was much longer, and the crystal size was smaller than when 230 nm gold nanostructures were used. With further laser irradiation on 230 nm gold trimers, the birefringence of the crystals disappeared, indicating a polymorphic transition from the metastable achiral phase to the stable chiral phase. Intriguingly, this phenomenon has never been observed in the case of 170 nm gold nanostructures. These results will contribute to the understanding of the crystallization mechanism of $NaClO_3$ by plasmonic trapping and the elucidation of the mechanism of subsequent chirality control.

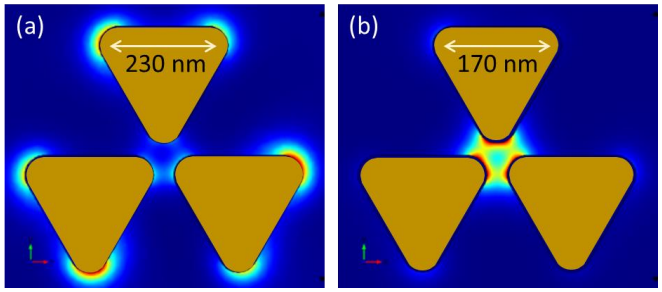

Figure 1. Simulated electric field distributions of the near field of triangular trimer gold nanostructures with side lengths of (a) 230 nm and (b) 170 nm excited by a circularly polarized 1064 nm light.

Reference

[1] Cheng, A.-C., Niinomi, H., Omatsu, T., Ishida, S., Sasaki, K. and Sugiyama, T., *J. Phys. Chem. Lett.* **11**, 4422–4426 (2020).