How Laser-Generated Surfactant-Free Particles Evolve in Presence of and in Absence of SU-8 Photoresist Molecules

Dongshi Zhang[1], Wonsuk Choi [1, 2], Koji Sugioka [1,*]

[1] RIKEN Center for Advanced Photonics, RIKEN, Japan
[2] Korea University of Science and Technology (UST), Republic of Korea
E-mail: ksugioka@riken.jp

1. Introduction

The technique of laser ablation in liquids (LAL) has already demonstrated its flexibility and capability for the synthesis of a large variety of surfactant-free nanomaterials with high purity [1]. However, high purity can cause trouble for nanomaterial synthesis because active high-purity particles can spontaneously grow into different nanocrystals [2], which makes it difficult to accurately tailor the size and shape of the synthesized nanomaterials. Therefore, a series of questions arise in regard to whether particle growth occurs during colloid storage, how large the particle size increases to, and which shape the particles evolve into.

Two options of laser modulation and surface chemistry manipulation are available for size control [1]. The former strategy is mainly implemented by changing laser parameters such as the laser power, pulse duration, repetition rate and beam shape to fragment particles into smaller particles or to melt the particles into submicrospheres. The latter strategy relies on either the conjugation of the particles by polymers or biomolecules or the inhibition of particle growth by salts, surfactants or carbon clusters while implementing LAL in organic solvents. As easily deduced, even though the particle sizes are tailored, the particles obtained by laser modulation are still surfactant-free, which inevitably induces particle growth. Hence, tailoring the colloidal surface chemistry by ex situ functionalization would be a better solution to accurately control the particle size.

2. Results and conclusions

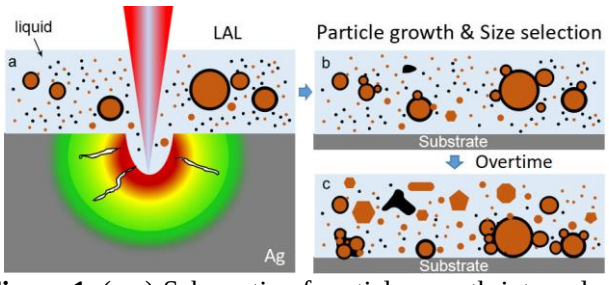

Figure 1. (a-c) Schematic of particle growth into polygonal nanocrystals followed by size separation of ultrasmall particles by large particle precipitation due to carbon encapsulation. In the liquids, Ag and carbon are denoted by orange and black colored spheres, respectively [3].

Recently, we observed that ultrasmall Ag nanoparticles (NPs) which are generated by femtosecond laser ablation in acetone (457 fs, 1045 nm, 100 kHz, 300 mW and 600 mW) grow into polygonal nanocrystals accompanied by an increase in the particle size during storage of the colloid for 6 months [3]. However, the aged Ag NPs still have a broad size distribution between 1 nm and 200 nm with an average size of ca. 5.9 nm and polydispersity (σ) of 127-207%, suffering from large polydispersity. After SU-8 functionalization and 6 month storage, most particles larger than 10 nm become aggregates and precipitate, which makes the distribution narrower with an average diameter of 4-5 nm and σ of 48-78% [4]. Morphology analysis indicates that ex situ SU-8 functionalization inhibits the particle growth into polygonal nanocrystals. Radical polymerization of SU-8 on Ag NPs is considered to be the reason for the gradual colloidal aggregation and precipitation. Benefiting from Ag NPs embedment, the glass transition temperature of SU-8 photoresist is increased from 314 ℃ to 331 ℃ according to thermogravimetric analysis (TGA).

This work is expected to provide a new route to better size control of LAL-synthesized colloids via ex situ photoresist functionalization at the expense of the 50 wt % of colloidal mass loss due to precipitation.

References

[1] Dongshi Zhang, Bilal Gökce, Stephan, Barcikowski, Chem. Rev. 2017, 117, 3990-4103
[2] Dongshi Zhang, Jun Liu, Changhao Liang, Sci. China Phys. Mech. Astron. 2017, 60, 074201
[3] Dongshi Zhang, Wonsuk Choi, …, Koji Sugioka, Nanomaterials, Submitted
[4] Dongshi Zhang, Wonsuk Choi, …, Koji Sugioka, ACS Omega, Submitted.

Appendix

Secretariat of the JSAP-OSA Joint Symposia
E-mail: joint_osa@jsap.or.jp