Particle Generation by Pulsed Excimer Laser Ablation in Liquid: Hollow Structures and Laser-Induced Reactions

by

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ABSTRACT

Pulsed laser ablation of solid targets in liquid media is a powerful method to fabricate micro-/nanoparticles, which has attracted much interest in the past decade. It represents a combinatorial library of constituents and interactions, and one can explore disparate regions of parameter space with outcomes that are impossible to envision *a priori*. In this work, a pulsed excimer laser (wavelength 248 nm, pulse width 30 ns) has been used to ablate targets in liquid media with varying laser fluences, frequencies, ablation times and surfactants. It is observed that hollow particles could be fabricated by excimer laser ablation of Al, Pt, Zn, Mg, Ag, Si, TiO_2, and Nb_2O_5 in water or aqueous solutions. The hollow particles, with sizes from tens of nanometers to micrometers, may have smooth and continuous shells or have morphologies demonstrating that they were assembled from nanoparticles. A new mechanism has been proposed to explain the formation of these novel particle geometries. They were formed on laser-produced bubbles through bubble interface pinning by laser-produced solid species. Considering the bubble dynamics, thermodynamic and kinetic requirements have been discussed in the mechanism that can explain some phenomena associated with the formation of hollow particles, especially (1) larger particles are more likely to be hollow particles; (2) Mg and Al targets have stronger tendency to generate hollow particles; and (3) the 248 nm excimer laser is more beneficial to fabricate hollow particles in water than other lasers with longer wavelengths.

The work has also demonstrated the possiblities to fabricate novel nanostructures through laser-induced reactions. $Zn(OH)_2$/dodecyl sulfate flower-like nanostructures, AgCl cubes, and Ag_2O cubes, pyramids, triangular plates, pentagonal rods and bars have been obtained via reactions between laser-produced species with water, electrolytes, or surfactant molecules. The underlying mechanisms of forming these structures have been discussed.

The experimental results and the associated mechanisms developed in my research, and described in this thesis, have enriched the current understanding of particle generation by pulsed laser ablation in liquid. In so doing, my research has expanded the mechanistic routes for novel, or designer, nanoparticle geometries. Within the combinatorial and non-equilibrium environment provided by the unique experimental

arrangement, the basic laws of material science still apply. Understanding and utilizing the laws will help researchers to fabricate new nanostructures by this and other methods providing similar environment.