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# 主 論 文 の 要 旨

論文題目　Rapid Fabrication of Metal Nanostructures by Laser Ablation under Supreme Condition
（超臨界中でのレーザーアブレーションによる金属ナノ粒子生成に関する研究）

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## 論 文 内 容 の 要 旨

Chapter 1: Introduction

The invention of laser apparatus in the early 1960 allows researchers to exploit its extraordinary characteristic to broad technological applications. One of the applications of laser is on the field of materials processing. It was made possible to evaporate and deposit materials utilizing a more advanced laser-specific irradiation technique, namely the pulsed laser ablation (PLA). In the early days of PLA processing on the solid material targets, the experiments were carried out under vacuum condition or in the diluted gas medium. On the process development of the material synthesis method employing the PLA, researchers began trying to change the medium to the liquid. In the beginning, the laser irradiation of the solid materials under the liquid media seemed to be less favorable than the application PLA on the gas-solid target. Owing the versatility of the material synthesis by the PLA technique, the author decided to further elaborate the synthesis of nanoparticles under supercritical media employing the PLA technique with different liquid media conditions. The works reported in this thesis aim at basic understanding of the mechanisms of PLA under liquid and supercritical $CO_2$, water and amino acid solvent.

Chapter 2: Nickel Nanoparticles Generated by Pulsed Laser Ablation in Liquid $CO_2$

Nickel nanoparticles with various structures were synthesized by a pulsed laser ablation (PLA) process in liquid $CO_2$ at 17°C and 5.2 MPa. A nickel plate immersed in liquid $CO_2$ was subjected as a target. This was irradiated by a laser beam with a fundamental wavelength of 1064 nm at 2.46 mJ for 15 min. The generated particles were deposited on a silicon wafer after natural evaporation of the liquid $CO_2$, and analyzed by field emission scanning electron microscopy (FE-SEM), scanning electron microscopy with energy-dispersive X-ray spectroscopy (SEM/EDS), and transmission electron microscopy (TEM). Nickel and carbon particles with sphere-like structures or apple-shaped structures were observed. Furthermore, characteristic nickel/carbon particles with core/shell structures were also produced. The generated particles ranged in size between 5–350 nm in diameter, with dominant sizes under 50 nm. Based on the results, it is proposed that this method is applicable as a medium for synthesized nanoparticles owing to the simple process by this technique.

Chapter 3: Formation of Au–Carbon Nanoparticles by Laser Ablation under Pressurized $CO_2$

Pulsed laser ablation (PLA) is known to be a promising method for synthesizing metal nanoparticles. Here, Au–carbon nanoparticles were synthesized by PLA under pressurized carbon dioxide ($CO_2$). Au plate was ablated using a Nd: YAG laser with a wavelength of 532 nm and energy of 0.83 mJ in a high-pressure chamber. The experiments were performed at temperatures and pressures of 21-25°C and 7-15 MPa, corresponding to $CO_2$ densities of 0.75-0.89 g/cm3, respectively. The synthesized products were collected on a silicon wafer and analyzed using field emission scanning electron microscopy (FE-SEM), transmission electron microscopy (TEM) and a scanning transmission electron microscopy (STEM) system equipped with energy dispersive X-ray spectroscopy (EDS). The results showed that the generated metal nanoparticles exhibited spherical and nanocluster structures. Au, C, and O were clearly found on the nanoparticle products. The results suggest that this method enables obtaining advanced nanostructured materials

Chapter 4: Consideration of Au–Carbon Nanoparticles by Laser Ablation under Supercritical $CO_2$

Au nanoparticles with carbon were successfully synthesized using the PLA method under supercritical $CO_2$. The PLA was carried out at temperatures of 40-80 °C, pressure of 8–15 MPa and an irradiation time 15 min. The generated nanoparticles were characterized using a STEM system equipped with EDS. SEM images exhibited generated metal nanoparticles with spherical and nanocluster morphologies. The network structure of smaller metal nanoclusters appears to surround the larger metal nanoparticles. Au, C, and O were found to be uniformly distributed on the generated nanoclusters. The smallest size of the generated nanoparticles is expected to be obtained at $CO_2$ medium under the condition of temperature and pressure of 60 °C and 12 MPa, respectively. The results suggest that this method enables obtaining advanced nanostructured materials.

Chapter 5: Preparation of Gold Nanoparticles by Pulsed Laser Ablation in Glycine and L-proline

By working with secondary harmony of pulsed laser ablation, we succeeded in producing small Au-NPs with narrow size distribution in Gly and Pro without any chemical agents. The effect of liquid medium on the size, optical properties and stability of Au-NPs were stuidied. Transmission electron microscope was used for characterization of the size and shape of generated particles. The generated Au-NPs was spherical shape in both solution, with an average size are 7 nm for Au-NPs in Gly and 11 nm for Au-NPs in Pro. Optical extinction spectra were also used to measure the optical properties of generated particles. A maximum optical extinction for generated Au-NPs in Gly and Pro are 528 and 524 nm, respectively. Dialysis was also performed in this work. After dialysis, generated Au-NPs was aggregated and formed chain-like structure. Optical extinction also shift and broadening with in all wavelength. Judging the results, high polar molecules like amino acid, provide strong surrounding electrical double layer, which can prevent nanoparticles to form aggregation.

Chapter 6: In Situ Synthesis of Composite Au/$TiO_2$ Nanoparticles by Pulsed Laser Ablation in Water

We have developed a facile and environmentally friendly method to synthesize Au/TiO2 using pulsed laser ablation (PLA). The generated nanoparticles has spherical morphology with Au particles attached into $TiO_2$ particles with the average size of 5-20 nm and 100-150 nm, respectively. The mechanism of the nanoparticle formation has also been explained that composite nanoparticles were synthesized by the difference of melting point. Based on the results, our method can be used as an alternative method to synthesize Au/$TiO_2$ nanoparticles along with the conventional methods.

Chapter 7: Summary

The merits of liquid phase laser ablation over other conventional methods for synthesizing nanoparticles attract the attention of many researchers in the field of nanotechnology. Understanding the synthesis dynamics of nanoparticles is very important to optimize and to control the size and the structure of nanoparticles. The fundamental investigations of growth processes of nanoparticle are seriously insufficient. Moreover, exploiting the liquid pressure to control the properties of nanoparticles in liquid–phase laser ablation is an absolutely new idea.

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