Size-Selected Submicron Gold Spheres: Controlled Assembly onto Metal, Carbon, and Plastic Substrates

Ken-ichi Saitow,†‡*, Yoshinori Okamoto,‡ and Hidemi Suemori‡

†Natural Science Center for Basic Research and Development (N-BARD), and ‡Department of Chemistry, Graduate School of Science, Hiroshima University, 1-3-1 Kagamiyama, Higashi-hiroshima 739-8526, Japan

Supporting Information

ABSTRACT: Size-selected submicron spheres become very useful building blocks if the spheres could be synthesized and integrated at any desired position. In particular, spheres having a similar size to visible-light wavelength have attracted much attention. Here, we show the synthesis and assembly of size-selected submicron gold spheres using pulsed laser ablation of a gold plate in a supercritical fluid. Four findings were obtained in the study. Submicron spheres with a narrow size distribution were generated, and the polydispersity was ≈6%. The average diameter was controlled from 600 to 1000 nm. A thermodynamic condition for scalable synthesis was found. The assembly of spheres onto a metal, carbon, or plastic substrate was accomplished.

1. INTRODUCTION

Nobody doubts that gold as a material has attracted considerable attention in chemical and material sciences and industrial applications. In particular, gold nanomaterials are utilized as substrates for single-molecule detection by surface-enhanced Raman scattering and enhanced fluorescence, as optomaterials for ultrasensitive biosensors and medical sensors, as catalysts for chemical reactions such as CO oxidation, and as photothermal materials for cancer therapy. All of these properties are accomplished by nanomaterials with a size < 50 nm, which are synthesized by a conventional chemical synthesis method: reduction of gold (Au) ions in HAuCl₄ aqueous solution. However, it has been difficult to produce a size-selected metal particle larger than 100 nm. Specifically, submicron particles could become very useful building block materials if submicron-sized particles with a homogeneous size could be synthesized and integrated at any desired position, for example, photonic crystals matching the visible and near-infrared (NIR) light, nanoplasmonic electrodes with special smooth surface, field enhancement driven by high scattering efficiency, and parts of a molecular circuit.

Pulsed laser ablation (PLA), a physical synthesis method, is a promising approach used to obtain stable nanoparticles. This method consists of a one-step process conducted at room temperature with a short duration, for example, a few minutes to an hour. In addition, scalable synthesis of nanoparticles, several grams/hour as products, has been recently realized. PLA of Au in solution has been extensively investigated in the last decade. Recently, submicron-sized spherical Au particles were synthesized by PLA. We have developed a novel method for nanoparticle synthesis by conducting PLA in a supercritical fluid, as shown in Figures 1 and S1. Specifically, thermal and dielectric properties of a surrounding medium can be easily tuned by changing the fluid density and pressure. Thus, light-emitting silicon nanocrystals were generated with photoluminescence color (RGB and white-light continuum) that can be controlled by fluid pressure and/or density during PLA. The morphology of Au nanoparticles was also changed by the cooling rate or permittivity of fluids during PLA. Furthermore, PLA in a supercritical fluid becomes a popular method to synthesize various nanomaterials, recently.

Here, we show submicron Au spheres with a narrow size distribution, that is, deviations of diameters ranging 5–8%, using PLA laser synthesis in a supercritical fluid. The average diameter of particles ranged from 600 to 1000 nm, whose size matches the light wavelength in the visible and NIR regions.

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addition, a thermodynamic condition for scalable synthesis was found. Furthermore, the integration of gold spheres onto a metal, carbon, or plastic film was accomplished and optimized.

2. RESULTS AND DISCUSSION

Figure 2 shows scanning electron microscopy (SEM) images of submicron-sized Au spherical particles generated by PLA at three reduced densities \( \rho_r = \rho / \rho_c \), where \( \rho_c \) is the critical density of supercritical trifluoromethane (CHF\(_3\)) (\( \rho_r = 0.7 \), 1.7, and 1.9). Diameter \( D \) ranged over 600–1200 nm: (a) \( D(\rho_r = 0.7) = 890 \pm 55 \) nm, (b) \( D(\rho_r = 1.7) = 710 \pm 40 \) nm, and (c) \( D(\rho_r = 1.9) = 1050 \pm 80 \) nm. The plus–minus values denote the standard deviation, \( \sigma \), from the average diameters. The deviations of particle sizes are in the 5–8% range of the average diameters.

Figure 2. SEM images of submicron spherical Au particles generated by PLA in supercritical CHF\(_3\) at a reduced temperature \( T_r = T / T_c = 1.02 \). The Au particles are generated at a reduced density \( \rho_r = \rho / \rho_c \) of (a) 0.7, (b) 1.7, and (c) 1.9. Diameter \( D \) ranges over 600–1200 nm: (a) \( D(\rho_r = 0.7) = 890 \pm 55 \) nm, (b) \( D(\rho_r = 1.7) = 710 \pm 40 \) nm, and (c) \( D(\rho_r = 1.9) = 1050 \pm 80 \) nm. The plus–minus values denote the standard deviation, \( \sigma \), from the average diameters. The deviations of particle sizes are in the 5–8% range of the average diameters.

The amounts of particles produced as a function of fluid pressure/density during PLA were investigated. Figure 3a–d shows the typical SEM images of Au spherical particles fabricated with four representative densities. A significant dependence on the fluid density is observed; a large amount of gold nanospheres was generated by PLA at a high fluid density, whereas that generated at a fluid density lower than \( \rho_r = 0.7 \) in a supercritical fluid submicron-sized Au particles are generated within the time shorter than 300 ns after laser irradiation. Thermodynamic calculations indicated that the generation process is attributed to the solidification of hot liquid droplets, by which the lowest surface free energy is obtained with a spherical shape, within a few 100 ns. A cavitation bubble, in which nanoparticles are generated, emerges within submicroseconds on the irradiated surface of the target in liquids and high-pressure liquids, according to time-resolved shadowgraph and light scattering measurements. On the basis of these experimental evidences in a supercritical fluid and the observations by in situ time-resolved spectroscopy, it was considered that a concerted process of evaporation and cooling of Au liquid droplets are responsible for the particle size. Specifically, the evaporation and cooling rates of the gold liquid droplet in which the cavitation bubble adiabatically expands and shrinks in the high-pressure fluid are key factors for the characterization of the particle size by PLA at high pressures.

Figure 3. SEM images of submicron spherical Au particles generated by PLA in supercritical CHF\(_3\) at a reduced temperature, \( T_r = T / T_c = 1.02 \). Particles were fabricated at a reduced density \( \rho_r = \rho / \rho_c \) of (a) 0.3, (b) 0.7, (c) 0.9, and (d) 1.9. Corresponding pressures are denoted in the upper axis. The particles were integrated into the micropores. The number of particles increases with the fluid density during PLA. (e) Numbers of Au particles produced at various \( \rho_r \).
was significantly decreased. To quantify the dependence of the amount of particles on the fluid density, the number of particles was estimated both for the number density of particles and the particle-deposited area in the SEM image. Figure 3e shows the number of particles as a function of reduced densities during PLA. Many particles were generated by PLA at \( \rho_f \gtrsim 0.7 \), whereas few particles were generated at \( \rho_f < 0.7 \). Thus, Figure 3e reveals that the thresholds of fluid density and pressure for the generation of particles are \( \rho_f = 0.7 \) and \( P = 5.3 \) MPa, respectively. From the Supporting Information, it is noted that many gold nanonetworks, composed of smaller nanospheres with 30 nm diameter, are generated by PLA at a lower density of supercritical \( \text{CHF}_3 \) but disappear at a higher density of \( \rho_f = 0.7 \) (Figures S3 and S4). The density for the emergence of submicron particles is in good agreement with that for the disappearance of the nanonetworks, that is, liquid gold droplets as precursors are fragmented to form smaller nanospheres at lower densities giving the gold nanonetwork, whereas at higher densities, the solidification of liquid droplets produces submicron-sized particles. This precursor model of gold liquid droplets has been confirmed by measuring the amounts/laser pulse of both spherical particles and nanonetworks generated by PLA in supercritical \( \text{CO}_2 \). Briefly, the amount of gold nanonetworks increased, whereas that of spherical particles with diameter \( \approx 800 \) nm simultaneously decreased, as the number of laser pulses for PLA was increased. The density dependence of the amount of spherical particles is attributed to the branching ratio, which determines whether the liquid gold droplet solidifies or fragments to the nanonetwork. Thus, the threshold density for solidification via cooling was \( \rho_f = 0.7 \).

Another distinct feature evident in Figures 3 and S3 is that almost all the synthesized particles are not present on a flat region of the substrate but are selectively collected in a pore of size \( \approx 100 \) \( \mu \)m on the substrate. Briefly, let us describe the mechanism of collection of particles into the pore, and the details are given elsewhere (vide infra). As a first step, particles are synthesized in supercritical \( \text{CHF}_3 \). In this step, the particles disperse in the supercritical fluid. As a second step, the pressure of supercritical \( \text{CHF}_3 \) is decreased to retrieve the synthesized particles from the high-pressure vessel after the synthesis, during which the fluid temperature decreased from 305 to 285 K with the adiabatic expansion of the high-pressure fluid. Thus, the temperature \( T \) of \( \text{CHF}_3 \) became lower than the critical temperature \( T_c \) (\( T_c = 299.3 \) K), that is, tentative temperature \( \approx 10 \) °C, so that the supercritical \( \text{CHF}_3 \) became a liquid. Liquid \( \text{CHF}_3 \) was successively evaporated until its pressure was equal to the pressure of the atmosphere. These successive phase transition processes caused liquid \( \text{CHF}_3 \) to settle at the bottom of the vessel. The final liquid, including many Au particles, was collected in the pores of the substrate, and many particles were integrated in the bottom of the pores. Multiple concerted factors, such as viscosity and surface tension depending on the pressure and temperature of \( \text{CHF}_3 \), wettability of the substrate, mass transfer driven by capillary flow, and pinning and depinning at the interface between the liquid and the substrate can also govern the collection efficiency. Note that the integration into the pore was also established using the substrate made of other materials, such as stainless steel (SUS), copper, carbon, and polyethylene terephthalate (PET). The data are displayed in Figure 5. Thus, the pores in these substrates can also collect many submicron particles.

3. CONCLUSIONS
In summary, nanosecond PLA of an Au plate was conducted in supercritical \( \text{CHF}_3 \). Many spherical Au particles with diameters from 600 to 1000 nm were synthesized over the threshold density and/or pressure, that is, \( \rho_f = 0.7 \) and \( P = 5.3 \) MPa. The particle diameter was controlled according to the density and/or pressure used during PLA, and the polydispersity was as low.
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\( \eta \) is irradiated with the laser for 10 min at the isotherm where the examined using a equipment of which is illustrated in Figures 1 and S1. A high-performance liquid chromatography (HPLC) pump, the Nd:YAG laser serves as the PLA light source and was operated at an excitation wavelength of 532 nm, an energy of 19 mJ/pulse, a repetition rate of 20 Hz, a double Nd:YAG laser were used to conduct PLA. The pressure of heaters, a proportional–integral–derivative controller, and a thermocouple. The pressure of the fluid was increased with the HPLC pump. The Nd:YAG laser serves as the PLA light source and was operated at an excitation wavelength of 532 nm, an energy of 19 mJ/pulse, a repetition rate of 20 Hz, a fluence of 0.8 J cm\(^{-2}\), and a pulse width of 8 ns. A gold plate (99.95%, Tanaka Co.) immersed in supercritical fluid (CHF\(_3\), 99.995%) is irradiated with the laser for 10 min at the isotherm corresponding to a reduced temperature \( T_r = T/T_c = 1.02 \), where \( T_c \) is the critical temperature. The pressure for PLA ranged from 3.81 to 14.9 MPa. The fluid density was calculated from the empirical equations of state, using the measured values of \( P \) and \( T \). The density ranged from 0.158 to 1.00 g cm\(^{-3}\) and is expressed as \( \rho = \rho_c/\rho \), where \( \rho_c \) and \( \rho \) are the reduced and critical densities, respectively, as shown in Figure S5. The Au particles generated were deposited on a substrate immersed in supercritical CHF\(_3\), SUS, copper, and PET. The scale bar in (d) is 50 \( \mu \)m.

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**Associated Content**

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.9b01999.

Instrument of supercritical vessel, size analysis of Au particles, SEM images of particles and their amount analysis, and phase diagram of supercritical CHF\(_3\) (PDF)

**Author Information**

ORCID®

Ken-ichi Saitow: 0000-0003-2405-222X

Notes

The authors declare no competing financial interest.
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(18) After the synthesis of Au particles, the ambient around the particles drastically changes by reducing the fluid pressure. Under this situation, the depth of pore becomes deeper, the repeatability of collection of particles becomes higher, as shown in Figure 4c,d. This is because the spherical particles at the bottom of the deep pore are insensitive to the ambient such as strong convection caused by decreasing fluid pressure, whereas those at shallow pore can detract from the pore by that convection, as shown Figure 4c,d.

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