CONSIDERATION OF AU–CARBON NANOPARTICLES BY LASER ABLATION UNDER SUPERCritical CO\textsubscript{2}

Mardiansyah Mardis\textsuperscript{1}, Wahyudiono\textsuperscript{2}, Noriharu Takada\textsuperscript{2}, Hideki Kanda\textsuperscript{2} and Motonobu Goto

\textsuperscript{1}Department of Chemical Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya, Japan
\textsuperscript{2}Department of Materials Process Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya, Japan

E-Mail: goto.motonobu@material.nagoya-u.ac.jp

ABSTRACT

In our previous works, we observed the formation of Au-carbon nanoparticles via pulsed laser ablation (PLA) under pressurized CO\textsubscript{2}. We showed that the size of the generated nanoparticles depend strongly on the pressure and the temperature of the CO\textsubscript{2} medium. Here, we further elaborate this finding by applying more extreme conditions for the CO\textsubscript{2} medium. The experiments were performed at temperatures and pressures of 31-80 °C and 5-15 MPa, corresponding to the supercritical phase of CO\textsubscript{2}. We observed that the generated Au-carbon nanoparticles has the average size of 11 nm with spherical and nanocluster structures. The effects of the medium temperature and pressure will be discussed thoroughly.

Keywords: gold nanoparticles, gold-carbon particles; supercritical CO\textsubscript{2}, laser ablation.

INTRODUCTION

Gold nanoparticles show promising technological applications in the field of chemistry, physics and biology. For instance, the unique chemical properties of gold nanoparticles, which are believed due to the relativistic effects, enable their application as catalysts [1] where depending on the size, larger gold particles show less catalytic activity compared to the smaller gold nanoparticles. For such a metal, bulk gold is usually considered as inactive catalyst. One of the remarkable properties of gold nanoparticles is their optical property due to localized surface plasmon resonance (LSPR). The main application of LSPR in gold nanoparticles is in the field of biophysics where they can be used as biomolecule sensors, bio-imaging for cancer treatment and photothermal cancer therapy [2]. Therefore, an efficient way to synthesize gold nanoparticles is one of the main issues to efficiently utilize the gold nanoparticles for the aforementioned technological applications.

The simplest technique to synthesize gold nanoparticles is probably an arc discharge plasma technique [3]. In this technique, as an example, two titanium electrodes in HAuCl\textsubscript{4} solution are connected to an electric power source to produce high-temperature plasma. The HAuCl\textsubscript{4} is directly reduced into Au due to the electron transfer from the plasma zones. The electrode enables producing the desired metal nanoparticles due to the high temperature of the plasma.

Pulse laser ablation (PLA) in liquid or compressed fluid is one of the alternative methods to synthesize nanoparticles. This method has been considered as a clean, facile and rapid way to synthesize the nanoparticles since it requires minimal amount of chemicals and also gives less by products and residues. Since laser has the strong ability to ablate many types of material, it can be used to produce almost any inorganic type nanomaterials including metals, oxides, sulfides and among others. New phases of nanomaterials can be attained using this method where the other conventional methods usually fail [4].

Recently, there have been plenty of reports on the laser ablation method to produce Au nanoparticles from Au plate immersed in pure liquid media such as water [5-10], n-decane [11], dimethylsulfoxide (DMSO), tetrahydrofuran (THF), acetonitrile (ACN) [12], chloroform [13], ethanol [13] and toluene [13,14]. The Au nanoparticles generated in those media have the size of 1.8-18 nm, depending on the laser wavelength, duration and the fluence.

In the previous gold nanoparticles synthesis using PLA method, we discovered that the Au nanoparticles generated in liquid (pressurized) CO\textsubscript{2} are not pristine Au nanoparticles [15]. Instead, the Au nanoparticles are coated by the carbon nanostructure, which was generated due to the dissociation of the CO\textsubscript{2} molecules by the incoming photons. Hence, the new class of nanomaterials might be discovered as the side reaction due to the laser irradiation.

Motivated by these findings, we further elaborate this finding by applying more extreme conditions for the CO\textsubscript{2} medium. The experiments were performed at temperatures and pressures of 31-80 °C and 8-15 MPa, corresponding to the supercritical phase of CO\textsubscript{2}. We observed that the generated Au-carbon nanoparticles has the average size of 11 nm with spherical and nanocluster structures.

EXPERIMENTAL SECTION

Materials

Gold plates with each area of 10 × 10 mm and a thickness of 1 mm(99.95%; Nilaco Co., Japan) were prepared as the target material filled with CO\textsubscript{2} (99.95%; Sogo Co., Japan) as the PLA medium. A micro grid was purchased from Okenshoji Co., Ltd Japan, was employed as the collector for the generated particles.
**Methods**

![Experimental apparatus of PLA](image)

The experimental setup to generate nanoparticles has been developed by our groups and described in our previous works [15-21]. Briefly, the instruments consist of a 110 mL with 6.5 cm diameter high-pressure chamber constructed from SUS 316 stainless steel, a high-power Q-switched pulsed Nd:YAG laser (Spectra-Physics Quanta-Ray INDI-40-10), a lens with a aperture of a 1 mm hole and mirrors. CO$_2$ was pressurized and pumped into the chamber using a high-performance liquid chromatography (HPLC) pump (PU-1586, Jasco Co., Japan). The chamber temperature was regulated with a temperature controller, and the pressure was controlled with a backpressure regulator. The gold target was placed at the center of a high-pressure chamber, approximately 1 m from the laser and irradiated with the Nd:YAG laser operated with a wavelength of 532 nm, pulse energy of 0.83 mJ, a pulse rate of 10 Hz, and pulse duration of approximately 8 ns. The silicon wafer was placed beneath the Au target in order to collect the generated nanoparticles.

The temperature and pressure ranges for the experiments were 31-80 °C and 8-15 MPa corresponding to the supercritical phase of CO$_2$. A thermocouple for monitoring the experimental temperature was inserted into the chamber. K-type thermocouples were also inserted into the chamber’s walls to measure the radial temperature distribution. After the desired pressure and temperature were attained, PLA was performed for 15 min. After the CO$_2$ medium naturally evaporated, the particles deposited on the silicon wafer were collected and then characterized by field emission scanning electron microscopy (FE-SEM, Model JSM-6330F, JEOL, Japan).

Particle size characterization was also performed using (scanning) transmission electron microscopy, (S)TEM, with a JEM-2100F HK model operating at 200 kV and equipped with CCD camera. (S)TEM samples were prepared by placing carbon microgrid below the target material in the same position as that of the Si wafer to collect the particles. In order to examine the products elemental composition, scanning transmission electron microscopy with energy dispersive X-ray spectroscopy (STEM-EDS) (Model JEM-2100F HK, JEOL, Japan) was also performed.

**RESULTS AND DISCUSSIONS**

**Effect of pressure**

The effect of the pressure on the average size of the gold nanoparticle was examined at 40 °C. The TEM images and the particle size distribution are displayed in Figure-2. The results show that increasing the pressure generally decrease the size of the gold nanoparticles [22]. Therefore, the smallest average nanoparticles were obtained at 12 MPa with 9.0 nm. Previous studies report that the average size of several nanoparticles synthesized in the pressurized liquid medium via PLA has smaller size with increasing medium pressure. Zirconia nanoparticles synthesized in water [22, 23] decreased from 50 - 100 nm to below 20 nm at the ambient condition of 31 MPa and a constant temperature. Tin nanoparticles synthesized in pressurized CO$_2$ exhibits similar phenomenon [24]. We presume that similar effect applies also on the generated gold nanoparticles in supercritical CO$_2$.

![Figure-2. TEM images and size distribution of generated Au particles at 40 °C with different pressures (a) 8 MPa; (b) 9 MPa; (c) 10 MPa; (d) 12 MPa; (e) 15 MPa.](image)

**Effect of temperature**

The effect of the temperature on the average size of the gold nanoparticle was determined at 8MPa. The TEM images and the particle size distribution are displayed in Figure-3. The results show that increasing the temperature generally decrease the size of the gold nanoparticles with the smallest average nanoparticles were obtained at 60 °C with 11.0 nm.
Figure-3. TEM images and size distribution of generated Au particles at 8 MPa different temperatures (a) 40 °C; (b) 60 °C; (c) 80 °C.

As can be seen in the Figures 2 and 3, in the supercritical phase of CO$_2$, increasing pressure at constant temperature will yield smaller nanoparticles with the minimum at 12 MPa. Similarly, increasing the temperature at constant pressure will yield smaller nanoparticles with the minimum at 60 °C. It can thus be extrapolated that the smallest Au nanoparticle will be generated under the condition of temperature and pressure of 60 °C and 12 MPa, respectively. It can be expected that the average size of the Au nanoparticle is 7.6 nm under that condition.

Based on the results above, the generated nanoparticles are spherical in shape due to the nucleation occurred in the liquid and expand their size in the direction where the pressure stress is minimal [25]. In the case of liquid medium, all directions in the space are equal. Therefore, the nanoparticles can have spherical shape in the liquid medium.

Elemental analysis

In order to understand the chemical composition of the generated Au nanoparticles, they were characterized using a STEM system equipped with EDS. This method distinguishes the characteristic X-rays emitted from the analyte by their energy levels. Since each element has a unique atomic structure, the atomic structure could be identified individually from one another. Hence, EDS analysis is a reliable way to investigate the sample using the interactions between electromagnetic radiation and matter.

Figure-4 shows STEM images and EDS patterns of the generated Au nanoparticles sample when PLA was applied at CO$_2$ temperature of 40 °C and pressure of 10 MPa. The EDS spectrum clearly shows that the Au, C, and O were detected.

Figure-4. Energy-dispersive X-ray spectroscopy mappings of particles generated at 40 °C and 10 MPa of supercritical CO$_2$.

No proper explanation for the exact mechanism of laser induced nanoparticles formation has been deduced due to the complexity of the process since the system is non-equilibrium [4]. However, the general physics behind nanomaterial creation via laser ablation can be simply viewed as the photon-electron, electron-electron and phonon-electron interactions [26]. In our experiment the Au nanoparticles were created from the pristine metal. The key point of the successful creation of the nanomaterial is the ability of the laser energy to eject some of the material from the bulk phases to the liquid medium phases in order to form the nanoparticles. Due to laser interaction with the bulk material more complex process may occur. The process includes heating, melting, ionization/vaporization and plasma plume creation as displayed in Figure-5.

Figure-5. Physical mechanisms of generation of particles by PLA method.

The ejected material that experiences extreme pressure and temperature at very short interval time (ns), which now in disordered plasma state, is a highly reactive material. The liquid (CO$_2$) acts as the quenching agent is able to suppress the high-energy particles into more stable species. The scheme of this process is displayed in Figure-6.

Figure-6. The schematic illustration of reaction between metal and liquid (CO$_2$) during PLA.

In the Au nanoparticle formation, Au remains in the neutral state since the oxidation of Au into its possible oxidized state, Au (III) require the Gibbs free energy of ca.
1300 kJ/mol [27]. The positive value of the Gibbs free energy means that the oxidation of Au into Au (III) is thermodynamically unfavorable. On the other hand, metal oxide nanoparticles can also be formed from the pristine metal, such as TiO$_2$ from Ti metal [28], apart that the oxidation of Ti into TiO$_2$ requires positive Gibbs free energy of ca. 500 kJ/mol [27]. This suggests that the work done to get the Gibbs free energy is provided by the energy of the incoming laser. The laser wavelength of 532 nm corresponds to the photon energy of 225 kJ/mol. It is reasonable to say that a two-photon adsorption likely occur on the oxidation of Ti. However, since the oxidation of Au into Au (III) requires larger amount of energy, the laser energy is probably not sufficient to oxidize Au.

The elemental analysis shows that the Au is covered by carbon network with the trace amount of oxygen on the surface. From the explanation above, it is unlikely that Au undergoes any redox reaction. Therefore, the most possible explanation is that the carbon atoms are covalently bond with each other to form large network of carbon nanostructures to cover the Au nanocluster similar to previous observation [15]. The dissociation energy of CO$_2$ → CO + O and CO → C + O are 525 and 1000 kJ/mol [29, 31], respectively. The two-photon adsorption can occur under near critical and critical phase of CO$_2$ [30]. It is likely that CO$_2$ molecules dissociation reaction into CO + O is the initiation reaction. Furthermore, these reactive species induce chain reaction with other CO$_2$ or themselves to form carbon matrix covering the Au nanoparticles. The O atoms can oxidize the carbon since O can still be covalently bound to the sp2 amorphous carbon type nanostructure. The carbon matrix inhibits the growth of Au nanoparticles. Amendola et al. observed similar type of carbon-covered Au nanoparticles when pristine Au metal was irradiated in toluene [14]. It can be presumed that similar type of Au nanoparticles can be generated using PLA technique under organic solvent [32]. However, it is well known that most of organic solvents are toxic and expensive. Therefore, the synthesis of Au-carbon (Au-C) via laser ablation of Au in liquid and supercritical CO$_2$ can be an alternative method to synthesize this type of nanomaterial. The Au-C composite has potential application as sensor [33].

CONCLUSIONS

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.

REFERENCES


