Synthesis of mono-dispersed nanofluids using solution plasma

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Small-sized and well-dispersed gold nanoparticles (NPs) for nanofluidics have been synthesized by electrical discharge in liquid environment using termed solution plasma processing (SPP). Electrons and the hydrogen radicals are reducing the gold ions to the neutral form in plasma gas phase and liquid phase, respectively. The gold NPs have the smallest diameter of 4.9 nm when the solution temperature was kept at 20 °C. Nucleation and growth theory describe the evolution of the NP diameter right after the reduction reaction in function of the system temperature, NP surface energy, dispersion energy barrier, and nucleation rate. Negative charges on the NPs surface during and after SPP generate repulsive forces among the NPs avoiding their agglomeration in solution. Increasing the average energy in the SPP determines a decrease of the zeta potential and an increase of the NPs diameter. An important enhancement of the thermal conductivity of 9.4% was measured for the synthesized nanofluids containing NPs with the smallest size. © 2014 AIP Publishing LLC.

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I. INTRODUCTION

Recently, the development of high-speed devices and their integrated circuits are subjected to defect-generated heat that reduces significantly the performance of the equipment and needs an improved cooling system. Generally, the thermal conductivity of the conventional heat transfer fluids such as water and ethylene glycol are not high enough, therefore nanofluids technology was developed for high efficiency heat transfer.¹ Nanofluids, defined as fluids with suspended nanometer-sized particles, are considered to be the next generation heat transfer materials as they have greatly enhanced thermal conductivity compared to pure liquids. The nanoparticles (NPs) diameter is one of the most important parameter in order to develop a highly efficient heat transfer system.

Nanofluids are produced in a two-step process in which the NPs are produced by a physical or chemical method and then mixed with the base liquid.^{1–3} This process commonly used for the nanofluids synthesis raises some problems like the NPs oxidation, unsatisfactory dispersion and stability, high fabrication complexity, and high costs. Therefore, to mitigate some of these problems a one-step method was developed, which are divided in physical top-down approach and bottom-up chemical reduction.^{4–6}

Recently, our research group has proposed a new SPP-method that produces NPs with controlled size-distribution, high dispersibility, allows various compositions, and surroundings in an aqueous solution.^{7–17} Compared to the chemical methods SPP displays much shorter processing

times (from a few minutes up to a several tens of minutes) takes place at room temperature and atmospheric pressure and uses only low energy plasma. The novelty of our SPP method is that the plasma operates in glow discharge limits that in turn offer a suitable medium to control the chemical reactions inside the solutions. This is possible because the plasma generates hydrogen, hydroxyl and oxygen radicals, and also electrons. The electrons are reducing the gold ion to a neutral atom without any reduction agent. The SPP method is able to control the composition by using a combination of reduction reactions with simultaneous eroding of the electrodes,¹⁰ and to control the size by tuning the surrounding chemistry of the gold NPs,^{7–9} or by simply adjusting the solution temperature during the process. In this research, small sized gold NPs directly synthesized in solution which display enhanced thermal conductivity and dispersion stability that are important for nanofluid applications.

The properties of the gold nanofluids were investigated by UV–VIS–NIR spectrophotometer, transmission electron microscope (TEM), and zeta-potential analyzer. Based on the results, the NPs nucleation and growth were correlated with the plasma characteristics which determine the surface charge and accordingly a possible mechanism for the NPs synthesis. In addition, the thermal conductivity was evaluated in function of the NPs diameter.

II. EXPERIMENTAL PROCEDURE

A schematic of the synthesis device used for the SPP is shown in Figure 1. The discharge was generated between two tungsten wire electrodes with 0.6 mm diameter using a bipolar pulsed power supply (MPS-R06K01C-WP1-6CH, Kurita, Japan) at 1 kV voltage, with a repetition frequency of 15 kHz, and a pulse width of 2 μ s during 600 s. Before each

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FIG. 1. A schematic diagram of the solution plasma process (SPP) for the NPs synthesis.

experiment, the surface of both electrodes was carefully polished and aligned at a gap distance of 0.6 mm.

The gold NPs were synthesized at various temperatures: -10°C , 0°C , 10°C . The cooling tube with a length of 300 mm and a diameter of 7 mm, containing 0.115 l water, was introduced in the solution during the NPs processing. The maximum flow of the cooling circulator (TBG 120AA, Advantec, Japan) was 161min^{-1} , and the consumed power for cooling was approximately 250 W at -10°C , 400 W at 0°C , 450 W at 10°C starting from room temperature.

The gold NPs were obtained by reacting 0.1 mM of hydrogen tetrachloroaurate (III) tetrahydrate ($\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$, 99.0%, Wako Co. Ltd., Japan), with 0.4 mM potassium hydroxide (KOH, 85.0%, Wako) in 300 ml distilled water. The pH of the HAuCl_4 solution was kept at 7.0 by adding potassium hydroxide (KOH).

In-situ optical emission spectra were recorded using a spectroscope with a spectral resolution of 0.7 nm (USB4000, Ocean Optics, USA). The current-voltage waveforms were measured using an oscilloscope (DLM 2022, Yokogawa, Japan) to evaluate the electrical parameters. The water temperature was measured by an IR camera (InfraRed, NEC Avio, Japan) with an automatic recording interval of 5 s.

The absorption spectrum of the gold nanofluids was measured in the visible region from 200 to 800 nm using a UV-vis-NIR spectrophotometer (UV3600, Shimadzu, Japan). The yield of the reduction reaction was determined by adding 0.8 mM NaBr (99.0% Sigma Aldrich) to the solution. The dispersion stability of the gold NPs was characterized by zeta potential (ELS-7300 K, Otsuka electronics, Japan) and their morphology was determined by TEM (JEM 2500TS, JEOL, Japan) operating at 200 kV. The thermal conductivity of the nanofluids was evaluated using the thermal property analyzer (KD2 pro, Decagon, USA) based on the transient hot wire method in ASTM D2717. The temperature was kept at $17 \pm 1^{\circ}\text{C}$ using an immersion cooler (TBC 120DA, Advantec, Japan).

III. RESULTS AND DISCUSSION

A. Solution plasma characterization

The characteristics of the gold NPs depend on the plasma parameters such as the electron number density, the stability of the excited atoms, molecules, and radicals, and the temperature. During high voltage pulses an electron avalanche is initiated inside the bubbles generated by the local heating of the solution, that leads to breakdown and subsequent discharge is produced. In this non-equilibrium plasma, the electrons are responsible for the production of radicals and excited species from water molecules^{19,20} Figure 2(a)

FIG. 2. (a) Typical optical emission spectrum of the SPP. The inset shows the spectral region of the OH radical emission; (b) Profile of $\text{H}\beta$ line (scattered points) fitted with a Voigt line profile (red curve), from which FWHM was found to be 2.34 nm and the average n_e was calculated to be $6 \pm 2 \times 10^{22}\text{m}^{-3}$; (c) Time dependence of the OES intensity of the main peaks showing the plasma stability.

shows a typical optical emission spectrum which provides information about the excited atoms, molecules, and radicals in the solution plasma. The excited oxygen and hydrogen atoms present in the plasma gas phase were identified by their major emission peaks detected at 777.1 and 844.34 nm for O and 434.0, 486.1, and 656.3 nm for H_γ , H_β , and H_α respectively. The electrons produce not only water dissociation and excitation of atoms, molecules, and radicals but also contribute to the gold ion reduction by collisions in the gas and liquid phase, even though the electron lifetime in solution is very short (picoseconds range).^{21,18,23}

To better characterize the plasma produced in solution, the electron number density (n_e) was estimated from the Stark broadening of the H_β line which is typically used for this calculation, even if the values of n_e are of the order of 10^{20} m^{-3} .²¹ For SPP, one has to consider that the plasma operates at atmospheric pressure and room temperature. The hydrogen lines are broadened by the combined effects of the electric field of the surrounding electrons, the collisions with other atoms and molecules (van der Waals broadening), the temperature of the gas (Doppler Effect), and instrumental broadening. The natural line broadening has been neglected and the gas temperature was considered to be 1600 K.^{21,22} To calculate n_e , a spectral deconvolution procedure has been applied to the H_β line considering the van der Waals, Doppler and instrumental broadenings to be 0.01, 0.005, and 0.7 nm, respectively. Figure 2(b) shows the profile of H_β line (scattered points) fitted with a Voigt line profile (red curve), from which the full width at half maximum (FWHM) was found to be 2.34 nm and the electron density was calculated from the equation: $\text{FWHM} = 4.800 \times (n_e \times 10^{-23})^{0.68}$.^{9,16} The average n_e was calculated to be $3.4 \pm 1.1 \times 10^{22} \text{ m}^{-3}$.

The stability of plasma was assessed using the time behavior of the line emission intensity (Figure 2(c)). Generally, plasma in liquids are highly instable^{12–14} but using carefully aligned and well-polished electrodes, and a small gap we obtained a stable plasma, that under a bipolar pulsed power supply can hardly switch to an arc discharge.

During the NPs synthesis plasma was monitored by measuring the current and voltage. Figure 3 shows typical

FIG. 3. Typical current-voltage waveforms showing the breakdown produced by the pulsed bipolar voltage in the SPP and the plasma evolution after the breakdown. The average electrical energy of a single pulse is 2 mJ.

current-voltage waveforms with a breakdown produced by the pulsed bipolar voltage in the solution plasma, and the plasma evolution after the breakdown that corresponds to an average electrical energy of a single pulse of 2 mJ. This low energy allows the generation of gold NPs with controlled morphologies at different temperatures.

B. Synthesis of NPs

Plasma characteristics determine the reduction process and the properties of the NPs. The temperature of the water solution influences the ignition and operation of the plasma, the plasma in turn increases the solution temperature by Joule effect. In the case of an arc discharge in the solution plasma, unstable optical emission spectra and irregular breakdown voltage were observed.^{12–14} In addition, arc plasma generates approximately 30 kJ min^{-1} due to unstable currents which can reach maximum value of 250 A. However, the solution plasma powered by a bipolar pulsed voltage generates approximately 3.7 kJ min^{-1} with a stable pulsed current which reaches a maximum of 4 A. In the solution plasma the Joule effect is low since even if we assume a total conversion of the electrical energy of 3.7 kJ into heats in water (with the specific heat capacity of $4.2 \text{ kJ kg}^{-1} \text{ K}^{-1}$) this energy would determine a temperature increase from 16 to 27.6°C in 10 min. Figure 4 shows the temperature change of the solution for different temperatures of the cooling circulator. The final temperature of the solution was measured to be 30, 25, and 20°C for temperatures of 10, 0, and -10°C , respectively.

The diameter of the NPs was assessed by UV-vis-NIR spectroscopy and TEM analysis and was found to depend on the solution temperature during the synthesis. Figure 5 represents the absorbance spectra of the solution before the SPP, and after the synthesis of the NPs for different temperatures. A complete reduction of the anion AuCl_4^- occurs during the gold NPs synthesis since the absorbance peaks of the $\text{AuCl}_2(\text{OH})_2^-$ anion at 252 nm and that of AuBr_4^- at 382 disappear after the SPP and the surface plasmon resonance

FIG. 4. Time dependence of the solution temperature for each cooling temperature. The final temperature of the solution was measured to be 30, 25, and 20°C corresponding to the set temperature of 10, 0, and -10°C , respectively.

FIG. 5. Absorbance spectra of the solution before the SPP and after the synthesis of the NPs for different cooling temperatures. A complete reduction of the anion AuCl_4^- happens during the gold NPs synthesis since the absorbance peaks of the anion $\text{AuCl}_2(\text{OH})_2^-$ at 252 nm and AuBr_4^- at 382 disappear after the SPP and the surface plasmon resonance (SPR) band appears as a result of the NPs formation.

(SPR) band appears as a result of the NPs formation.^{7–10} The presence of KOH in the solution determines the formation of $\text{AuCl}_2(\text{OH})_2^-$ anion.²⁴ The main reaction during the reduction of AuCl_4^- is:²⁵

In aqueous surfactant solutions the electrons are essential to the reduction reaction.²⁵ Reaction (1) shows that one precursor molecule needs 3 electrons for the reduction. The initial concentration of HAuCl_4 was 0.1 mM which means that in the solution there were 6.023×10^{19} molecules. In this case, the total number of electrons necessary for the reduction of the entire amount of HAuCl_4 in the solution is 1.8×10^{20} electrons. The plasma phase surrounded by the solution has approximately a volume of $1.25 \times 10^{-7} \text{ m}^3$ which means a total number of electrons of 4.3×10^{15} electrons. This suggests that the reduction of the gold ion Au^{3+} to neutral Au^0 is also produced in the liquid phase of plasma as:^{9,10}

where the hydrogen radicals ($\text{H}\cdot$) are provided by the gas phase plasma. The hydrochloric acid released in the reaction (2) lowers the acidity of the gold solution, decreasing the solution pH, and increasing the conductivity.⁹

The SPR absorbance peak of the synthesized gold NPs is a broadband located between 520 and 700 nm. If the temperature decreases during the synthesis process, the maximum of the SPR band, λ_{max} , shifts from 529 nm to 522 nm, indicating that the diameter of the gold NPs is decreasing.^{25,26} The red shift of λ_{max} , produced by the increase of the particles diameter can be easily explained by the classical Mie scattering theory.²⁷

The dependence of the gold NPs diameter on the temperature during the synthesis was confirmed by TEM

analysis as is shown in Figure 6. As the temperature of the solution lowers, the average diameter of the NPs decreases. The gold NPs synthesized at a coolant temperature of -10°C have a diameter of $4.9 \pm 2.7 \text{ nm}$ and a narrow size distribution, as shown in Figure 6(a). A significant increase of the nanoparticle diameter to $22.1 \pm 6.9 \text{ nm}$ was observed when the synthesis was performed at 10°C , as shown in Figure 6(c).

One of the most important property of a nanofluid is the dispersion stability which was observed to be affected by the synthesis method, i.e., the SPP characteristics.^{12–14} A negative zeta potential of over 30 mV produces repulsive forces among the NPs pushing each other away and therefore the nanofluid shows an excellent dispersion stability (Figures 7(a) and 7(b)).¹⁷

Electrons are considered to be responsible for the formation of the gold NPs in the gas phase of the SPP (reaction (1)).^{7,8} and then the following works^{9–17} reported that the reduction reaction occurs at the interface between the gas and liquid phase in the solution plasma, termed “the reaction field.” In the reaction field, the radicals and electrons are highly reactive and responsible for the reduction reaction of the gold precursor (reaction (2)). Figure 8 shows a schematics of the NPs synthesis based on the nucleation and growth theory^{28–31} and on plasma charge effect which will be further discussed.^{32–34}

The smallest diameter of the NPs synthesized in streamer solution plasma was approximately 20 nm, as was reported in previous researches.^{12–14} In the SPP using a bipolar power supply the smallest diameter of the synthesized NPs was less than 2 nm.^{9,15} These results suggest that the plasma input energy that changes the solution temperature and the final temperature during the process are the main factors which determine the NPs size.

Nucleation and growth theory explains the evolution of the NPs diameter during the reduction reaction^{28–31} closely related with the system temperature, the surface energy of the particle, the dispersion energy barrier, and the nucleation rate. For a spherical NP formation with the radius r the free energy change, ΔG is balanced by two competitive factors, the volume free energy and interfacial energy:³⁰

$$\Delta G = -\frac{4}{3}\pi r^3 |\Delta G_V| + 4\pi r^2 \gamma, \quad (3)$$

$$\Delta G^* = \frac{16\pi\gamma^3}{3|\Delta G_V|^2}, \quad (4)$$

where ΔG_V is the difference in the bulk free energy per unit volume between the initial and final phases, γ is the surface free energy per unit area, and ΔG^* is the activation energy of nucleation or nucleation barrier. Equation (3) shows that the free energy to create a droplet is increasing up to a maximum value of ΔG^* at the critical radius of the NP which is $r^* = 2\gamma/\Delta G_V$. The maximum of the $\Delta G(r)$ curve, where $dG/dr = 0$, gives r^* . In the subsequent step, the particles tend to aggregate with each other to decrease the surface energy in the solution. In addition, the change of the free energy per unit volume depends on temperature, the molar volume of the relevant species (v_m) and the degree of supersaturation (S) as

FIG. 6. TEM images and size distribution of the synthesized gold NPs corresponding to a cooling temperature of (a) -10°C , (b) 0°C , and (c) 10°C . (d) Dependence of the gold NPs diameter on the cooling temperature.

$\Delta G_v = -(RT/v_m)\ln S$, where R is the ideal gas constant. The activation free energy for nucleation accordingly increases with temperature as is shown in Figure 9.

The dispersion stability is based on the Brownian motion of the NPs. As temperature increased in the system, the average kinetic energy of the particles increases and the number of collisions among the particles grow. This is one of the main driving forces that generate the NPs aggregation by collision with each other. Smoluchowski reported that the Brownian motion increases with temperature and the aggregation increases according to the impact probability in the unit of time³⁴

$$-\frac{dn}{dt} = 4\pi D n^2 e^{-V_{\max}/kT} = \frac{4kT}{3\eta} n^2 e^{-V_{\max}/kT}, \quad (5)$$

$$D = kT/6\pi\eta r, \quad (6)$$

where n is the number of particles, D is the diffusion coefficient, η is the viscosity, k is Boltzmann constant, and $V_{\max}$ is the energy barrier of the particles related with the dispersion stability factor. Smoluchowski's equation (5) gives the aggregation rate. The first expression in Eq. (5) shows that when the temperature increases, the diffusion also increases, and the aggregation rate becomes higher. The factor

containing the exponential term tells us that the aggregation rate decreases with the dispersion energy barrier $V_{\max}$, which is known as the electrical double layer or zeta potential.

The gold NPs are synthesized in the SPP which contributes not only with electrons and hydrogen radicals to the reduction of the gold ion to the neutral atom but also has a role in the aggregation process through the discharge current and the charge accumulation on the NPs surface during the synthesis. In this way, the energy barrier can be increased through the plasma charging effect determining a better dispersion stability of the NPs in solution.^{12–14} It is known that when the particles are contained in a solution, the zeta potential of the surface can be enhanced using different methods as preferential adsorption of ions or accumulation or depletion of electrons at the surface.³² In plasma, the charge on the particle surface can range from zero to hundreds of thousands of electron charges, depending on the particle size and the plasma conditions.^{33–35} In the SPP, after the reduction and nucleation, the gold NPs become negatively charged. The charge Q is related to the surface potential Φ_s of particles as $Q = C\Phi_s$, where C is the capacitance of the particle in plasma and depends on the total discharge current I through plasma: $I = dQ/dt$. Experimentally, we observed that as the average energy per pulse and the discharge

FIG. 7. Zeta potential of gold NPs synthesized in various conditions: (a) dependence of zeta potential and the NPs diameter on the cooling temperature; (b) dependence of zeta potential and the NPs diameter on the average energy per pulse. The results of zeta potential show that as the NPs diameter decreases then the dispersion stability increases.

current increase then the negative zeta potential increases as absolute value and the diameter of the synthesized NPs is smaller, when the temperature during the process was kept constant (Figure 7(b)).

C. Thermal conductivity of nanofluids

The gold NPs synthesized by the SPP were tested as nanofluids. The thermal conductivity of the nanofluids is closely related with the NPs diameter, concentration, and material of the particles. The efficiency of the heat transfer

FIG. 8. A schematics diagram of the mechanism for small NPs synthesis in the SPP.

FIG. 9. Dependence of the activation free energy (ΔG) on temperature. As the temperature decreases, the maximum of the free energy (ΔG^*) for which nucleation decreases.

and the dispersion stability are improved by an increased Brownian motion due to a small NPs diameter.¹ In this experiment, the largest enhancement of the thermal conductivity of the synthesized nanofluids of 9.4% (0.660 W/mK) was detected for the smallest size NPs with a diameter of 4.9 ± 2.7 nm (Figure 10).

IV. CONCLUSIONS

Solution plasma was generated in water solution to synthesize mono-dispersed gold NPs with small diameter using a bipolar power supply and controlling the solution temperature. The stability of the SPP was confirmed by optical, electrical, and thermal measurements during the process.

Gold NPs were successfully synthesized at different temperatures using the SPP. The average particle diameter of the gold nanoparticles synthesized by SPP decreases with the decreasing of the solution temperature. The smallest gold nanoparticles, with an average size of 4.9 ± 2.7 nm, as well as mono-dispersed gold NPs were obtained keeping the solution temperature at 20 °C. Most of the synthesized gold NPs

FIG. 10. Enhancement of the thermal conductivity of the NPs compared with deionized water. The largest enhancement of the thermal conductivity of the synthesized nanofluids of 9.4% (0.660 W/mK) was detected for the smallest size NPs with a diameter of 4.9 ± 2.7 nm.

have a spherical shape. The gold NPs with the smallest diameter synthesized at the lowest temperature can be used as nanofluids showing the largest enhancement of the thermal conductivity of 9.4% as compare with deionized water.

A mechanism for the synthesis of the nanofluids in SPP was developed. The reduction of the gold ion to the neutral form is produced in the plasma gas-phase by electrons, as well as in the liquid phase by the hydrogen radicals. Considering the dependence of the activation free energy on temperature, lower solution temperature is essential for the synthesis of the small sized NPs. Brownian motion and surface charge effect explain the NPs stability in the SPP. During the synthesis, the surface of the NPs is negatively charged and this charge keeps the NPs away from each other for further agglomeration.

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