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# Characteristic stability of bare Au-water nanofluids fabricated by pulsed laser ablation in liquids

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ABSTRACT

Gold nanoparticles (Au-NPs) suspended in water where the suspension is a kind of nanofluid, were produced by pulsed laser ablation in liquids. Under the laser irradiation conditions up to 18 h, the average size of the Au-NPs ranged from 7.1 to 12.1 nm while their size-distribution tended to become narrower with effects of laser-induced fragmentation. Interestingly, the nanofluid showed an outstanding colloidal stability even after 1 month although no dispersants were used. The characteristic stability of bare Au-NPs suspension in water was found to be due to a large negative zeta potential of Au-NPs in water. The thermal conductivity of the Au-NPs (0.018 vol%)/water suspension increased by $9.3\pm5.4\%$ compared to that of pure water.



## 1. Introduction

High-performance cooling is one of the most vital needs in many industrial technologies. However, the thermal conductivity of conventional coolants such as water and ethylene glycol is essentially fixed and difficult to achieve high-performance cooling [1].

Choi [2] reported that suspension of nanoparticles (NPs) in a fluid, which is so-called "nanofluids", enhances the thermal conductivity of the fluid. Recently, when Au-NPs were suspended in water by chemical reduction method (Au-colloids solution), it was found that the thermal conductivity of the solution with 0.00026 vol% of Au-NPs becomes larger by 5–21% than that of pure water in the temperature range of 30–60 °C [3]. Similarly, the addition of a small amount of NPs into base fluids can provide a remarkable enhancement in the thermal properties of the fluids [3–7].

There have been two kinds of preparation methods for nanofluids. One is "two-step method" in which NPs are produced separately and subsequently dispersed into base fluids, and the other is "one-step method" in which NPs are produced and directly introduced into base fluids in the same apparatus [8]. For the former method, although ultrasonic-wave is used to disperse NPs uniformly in liquids, NPs are readily agglomerated in fluids, particularly for heavy-metal NPs. To avoid the agglomeration among NPs in fluids, surfactants are used for stabilizing NPs, or pH control of suspension by adding HCl or NaOH makes NPs charged positively or negatively, respectively. On the other hand, for the latter method, it has been recently reported that metal–oxides and metal NPs are produced and dispersed into fluids by a direct evaporation technique [9–12]. Although this technique is a one-step method for nanofluids, this process requires a vacuum system and complex procedure. Alternative one-step methods for producing metal NPs such as Au and silver (Ag) have also been reported [13–16]. Stable mono-dispersed metal NPs with an average size of less than 20 nm were produced in water or water–oil by chemical reduction and reverse micelles. Although these techniques can produce nanofluids with well-dispersed metal NPs, they require precursors and surfactants [17–18].

Table 1 summarizes previous reports on several kinds of one-step methods. In any case, uniform and stable dispersion of NPs in fluids is important to obtain a high thermal conductivity [1].

Phuoc et al. [19] reported on a novel one-step method for producing nanofluids by pulsed laser ablation in liquids (PLAL) process. They employed a double-cross-beam configuration in de-ionized water using two beams ($\lambda = 1024$ nm) for production of Ag-NPs/water nanofluids. Stable well-dispersed Ag-NPs (18–30 nm in diameter) were produced in de-ionized water without any surfactants. The thermal conductivity of Ag-NPs

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**Table 1**
Summary of previous works on nanofluids prepared by one-step method.

| Type | Material | Average size (nm) | Base liquid | Technique | Ref. |
|---|---|---|---|---|---|
| Physical | ZnO | 45–50 | Water | Cylindrical flow cooling in an induction heating | [9] |
| | CuO | ~10 | Water–ethylene glycol | Submerged arc NPs synthesis (SANSS) | [10] |
| | $Al_2O_3$ | ~20 | Water | Plasma arc synthesis | [11] |
| | Ag | ~3 | Silicon–oil | Magnetic sputtering with oleic acid | [12] |
| Chemical | CuO | 30–80 | Ethylene glycol | Chemical-reducing $CuSO_4 \cdot 5H_2O$ with $NaH_2PO_2 \cdot H_2O$ under microwave irradiation | [13] |
| | Au | ~18 | Water | Chemical citrate reduction of $AuCl_4^-$ with pH tunable | [14] |
| | Ag | ~4 | Water–oil | Sodium di-(2-ethylexyl) sulfosuccinate (AOT) reverse micelles of $AgNO_3$ | [15] |
| | Ag | ~10 | Ethylene glycol | Chemical-reducing $AgNO_3$ with poly (acrylamide-*co*-acrylic acid) | [16] |

**Table 2**
Present experimental conditions of PLAL.

| Materials | Starting material | Au-tablet (99.99% pure) 10 mm diameter × 3 mm thickness |
|---|---|---|
| | Base liquids | Pure water (pH 6.8) |
| | Experimental parameter (unit) | Value |
| Preparation condition (PLAL) | Wavelength (nm) | 532 |
| | Pulsed duration (ns) | 6–7 |
| | Repetition rate (Hz) | 10 |
| | Energy (mJ/pulse) | 120 |
| | Beam size (mm) and divergence (mrad) | 6 and 0.8 |
| | Focal length (mm) | 300 |
| | Spot size (cm) and energy density ($J/cm^2$) in the focal-plane | $2.4 \times 10^{-2}$ and ~265 |
| | Distance between water surface and target (mm) | ~5 |
| | Processing time (h) | 1–18 |

**Table 3**
Present experimental conditions of ultrasonic treatment.

| Materials | Starting material | Commercial Au-powder (99.9% pure and 45–130 nm of primary size-range) |
|---|---|---|
| | Base liquids | Pure water (pH 6.8) |
| | Experimental parameter (unit) | Value |
| Ultrasonic-wave irradiation condition | Output power (kW) | 160 |
| | Frequency (kHz) | 40 |
| | Processing time (h) | 6 |

(0.01 vol%)/water nanofluids was increased by 3–5%. This shows that stable nanofluids containing mono-dispersed NPs can be prepared by PLAL without any surfactants. However, the reason for the stability of the suspension is still unclear.

In the present study, we examined PLAL using a single-pulsed laser beam ($\lambda = 532$ nm) for preparation of bare Au-NPs/water nanofluids, because Au has a high thermal conductivity (317 W/m K) and chemical stability against oxidation. To discuss the stability of Au-NPs in water, pH of the suspension and the zeta potential of Au-NPs were also examined with characterization of particle size and its distribution.

## 2. Experiments

Tables 2 and 3 summarize present experimental conditions (PLAL and ultrasonic-wave irradiation) and Fig. 1 shows schematic illustration of the present preparation system. A gold-tablet (10 mm in diameter and 3 mm thick) with a purity of 99.99% was placed at the bottom of a glass-beaker filled with pure water (15 ml). As shown in Table 2, a Q-switched Nd:YAG laser (wavelength: 532 nm, repetition rate: 10 Hz, pulse duration: 6–7 ns, output energy: 120 mJ/pulse) was used to produce Au-NPs/water nanofluids by varying the irradiation time from 1 to 18 h. The pulsed laser beam with 6 mm diameter and 0.8 mrad divergence was focused using a biconvex lens with a focal length of 300 mm, and thereafter incident on the Au-tablet placed in pure water. The focused laser spot size was estimated to be about $2.4 \times 10^{-2}$ cm from the product of $\theta$ (beam divergence) $\times f$ (focal length). Accordingly, the laser fluence was estimated to be about 265 $J/cm^2$ in the focal-plane under the present irradiation condition. However, the spot size was larger than the calculations, because it was strongly affected by the surface morphology of the target, pulsed laser beam optics, and the kinds of liquids, etc. In addition, the present laser wavelength (532 nm) is almost overlapped with the transverse plasmon band (TPB: 520–580 nm) of Au-NPs [20], which makes the PLAL processing time much longer.

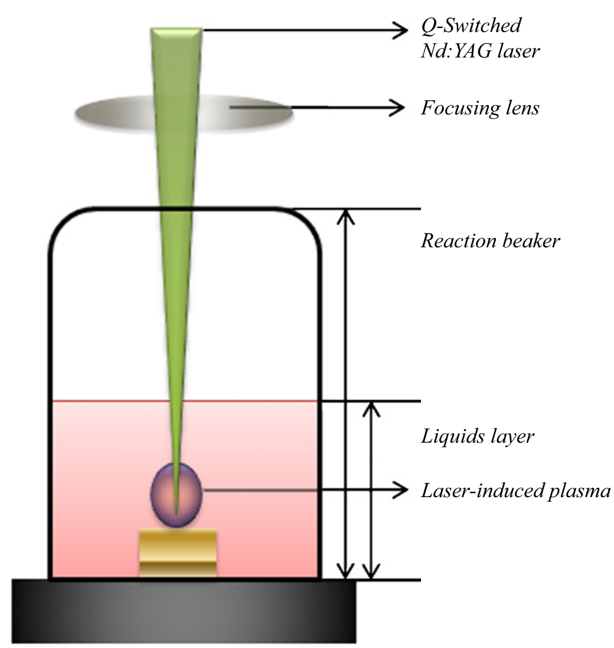


**Fig. 1.** Schematic illustration of the experimental apparatus for PLAL.