



# Preparation of submicron-sized spherical particles of gold using laser-induced melting in liquids and low-toxic stabilizing reagent



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## ABSTRACT

Laser-induced melting in liquids (LIML) was applied to prepare spherical submicron-sized particles of gold (AuSMPs) from gold nanoparticles (AuNPs) stabilized using NaCl. Because undesirable byproducts, which might be generated when organic reagents such as citrate are used as the stabilizing reagent, are not generated from NaCl by laser irradiation, AuSMPs fabricated from AuNPs stabilized by NaCl will be low toxic. The AuSMPs were obtained by laser irradiation of the source AuNPs in NaCl solutions stabilized by NaCl at the proper concentration. Similar to the preparation of AuSMPs from AuNPs stabilized by citrate, the agglomeration of the source AuNPs, which is necessary to obtain AuSMPs, was controlled both by the NaCl concentration and by laser irradiation. However, the formation process and the laser-fluence dependence of the particle size of AuSMPs differed for various NaCl solutions and citrate solutions.

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## 1. Introduction

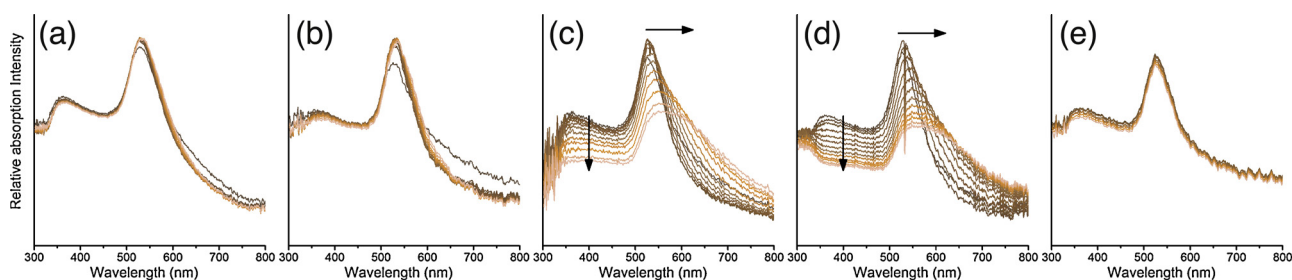
Laser irradiation (LI) for colloidal nanoparticles (NPs) attracts much attention as a promising technique of the NP size control. This technique has been used to reduce NP size of because focused LI at high fluence has generally been conducted to induce vaporization and fragmentation of NPs [1–5]. Moreover, recent works have shown that LI is also applicable to increase the particle size of colloidal NPs [6–13]. When non-focused LI at moderate fluence is applied for colloidal NPs, the melting and fusion of the NPs are induced, resulting in the formation of submicron-sized particles (SMPs). Hereinafter, we refer to the LI method conducted in such conditions to fabricate SMPs as laser-induced melting in liquids (LIML). Remarkably, SMPs prepared by LIML are spherical, with no facets and a narrow size distribution [7]. Such features of the SMPs enable us to use them as various important materials such as cell markers and light scattering media. For example, our previous report describes a random laser system developed using ZnO SMPs, fabricated using LIML very recently [14].

From our previous study, we also reported that gold SMPs (AuSMPs) with average size of ca. 200 nm have been obtained using LIML from source gold NPs (AuNPs) prepared using laser ablation in aqueous solutions of citrate [15]. Citrate was used as a stabilizing reagent to reduce AuNP sedimentation and to increase the formation efficiency of AuSMPs. Furthermore, important information related to the formation mechanism of AuSMPs was obtained using that study. First, the agglomeration of AuNPs prior to LI is necessary to produce AuSMPs, although excess agglomeration results in the sedimentation of AuNPs and decreases the formation efficiency of AuSMPs. The AuSMPs were formed at lower citrate concentrations (< 0.01 mM), although AuSMPs were not formed at high citrate concentrations (>0.05 mM). Second, results showed that the agglomeration of the source AuNPs is controlled not only by citrate statically, but also by LI dynamically. When LI is conducted for AuNPs stabilized by citrate, LI removes citrate ligands on AuNPs and induces the agglomeration of AuNPs. Such dynamic agglomeration process should be attributed to the reduction of the excess agglomeration and the sedimentation of the source AuNPs. Those findings suggest that using AuNPs stabilized by ligands is an efficient protocol to prepare AuSMPs.

Results revealed that using citrate as a stabilizing reagent entails some important shortcomings. Some unassigned substances were detected in the colloidal solutions after LIML [15]. Such products are expected to result from the decomposition of citrate by LI. They

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**Fig. 1.** (a)–(d) Changes in the absorption spectra of AuNPs in NaCl solutions at various concentrations during LIML. The laser fluence was  $60 \text{ mJ}/\text{cm}^2$ . The spectra were measured using the interval of 5 min and for 60 min. The concentrations of NaCl were (a) 1 mM, (b) 0.1 mM, (c) 0.05 mM, and (d) 0.01 mM. (e) Change in the absorption spectra of AuNPs in a 0.01 mM NaCl solution without LI.

might produce some undesirable side effects when AuSMPs are used on biocompatible applications. For that reason, as a stabilizing reagent to prepare “low-toxic” AuSMPs, we have used NaCl in the present study instead of citrate. Reportedly, NaCl is useful as a stabilizing reagent of AuNPs when AuNPs are prepared by laser ablation in NaCl aqueous solutions [16–19], although NaCl generally induces the sedimentation (salting-out) of colloidal particles. That result suggests that  $\text{Cl}^-$  ions are adsorbed onto oxidized parts ( $\text{Au}-\text{O}^-$  and  $\text{Au}-\text{OH}^-$ ) of AuNPs [16]. In addition, the high charge density of AuNPs adsorbing  $\text{Cl}^-$  ions suggests that  $\text{Cl}^-$  ions can be adsorbed onto the neutral Au atoms [18,19]. The adsorption of  $\text{Cl}^-$  ions causes supplemental electrostatic charge repulsion between the AuNPs. The most important point of the use of NaCl is that  $\text{Na}^+$  and  $\text{Cl}^-$  ions are not decomposed by LI. Therefore, AuSMPs prepared using NaCl must be more biocompatible than those prepared using citrate. This study investigates the basic conditions to obtain AuSMPs in NaCl solution and the differences in the formation processes of AuSMPs in NaCl solution from those in citrate solution.

It is noteworthy that a similar approach to the preparation of SMPs using NPs containing electrolytes has been reported recently [20,21]. However, the purpose of the use of electrolytes in those works differs markedly from that of the present work. They added high concentration ( $\geq 10 \text{ mM}$ ) of electrolytes to the source NPs to induce agglomeration. In this study, a low concentration ( $\leq 0.1 \text{ mM}$ ) of electrolyte ( $\text{Cl}^-$ ) was added to stabilize the source NPs.

## 2. Experiment

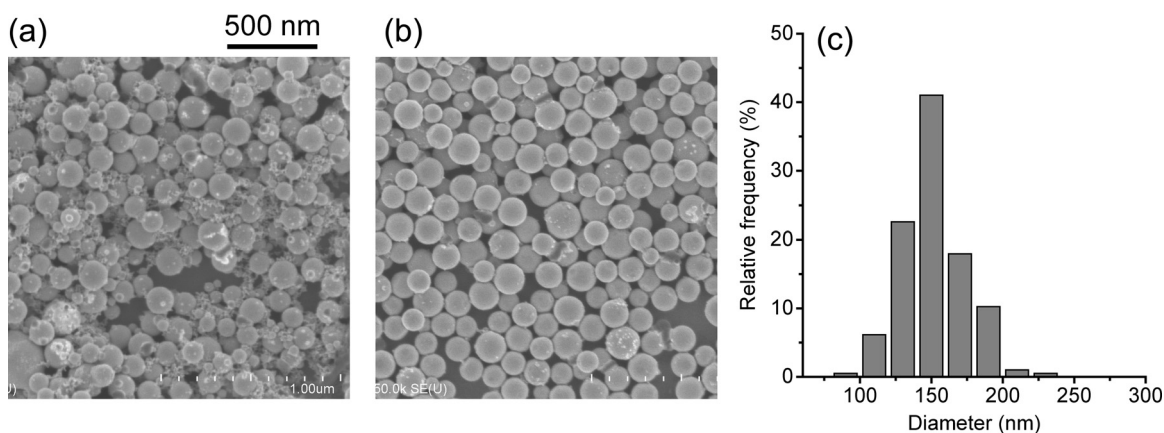
The laser ablation procedure used to prepare the source AuNPs and that of LIML to prepare AuSMPs from those source NPs were fundamentally the same as those used in the previous study, except

for the stabilizing reagent species [15]. Laser ablation was conducted for a piece of gold plate immersed in 5 mL of aqueous solution of NaCl in a glass cell ( $1 \times 3 \times 4 \text{ cm}^3$ ) using the focused laser beam of a nanosecond-pulse Nd:YAG laser (GCR-200; Spectra-Physics KK). The wavelength, pulse duration, and repetition rate were, respectively 1064 nm, 10 ns, and 10 Hz. The typical laser fluence at the focal point was  $36 \text{ J}/\text{cm}^2$ . LIML was conducted for 3 mL of the source AuNPs solution in a glass cell ( $1 \times 1 \times 4 \text{ cm}^3$ ) using a non-focused laser beam of another nanosecond-pulse Nd:YAG laser (GCR-100; Spectra-Physics KK). The wavelength, pulse duration, repetition rate were, respectively 532 nm, 10 ns, and 10 Hz. The non-focused laser beam diameter was 5 mm. The colloidal solutions were stirred during LI using a magnetic stirrer. The concentration of NaCl in AuNPs was adjusted at 0.01 mM and higher. Below 0.01 mM, the AuNPs without LI showed remarkable instability.

The products were analyzed using a UV-Vis spectrometer (UV-2450; Shimadzu Corp.) and a scanning electron microscope (SEM, SU8000; Hitachi Ltd.). To prepare SEM samples, a small amount of the colloidal solution was dropped on a Si plate. It was dried at room temperature. To observe the temporal changes of the absorption spectra of colloidal solutions during LIML, the probe light of a Xenon lamp, which was transmitted through the AuNPs colloidal solution, was detected using a multi-channel spectrometer (PMA-10; Hamamatsu Photonics K.K.). This apparatus was also used to observe the stability of the AuNPs colloids without LI.

## 3. Results and discussion

Figs. 1a–d portrays changes in the UV-Vis spectra of Au colloids in NaCl solutions at different NaCl concentrations during LIML. In 1 and 0.1 mM NaCl solutions, the spectral change of the plasmon



**Fig. 2.** SEM images of AuSMPs prepared from AuNPs in a 0.01 mM NaCl solution. LIML was conducted at  $60 \text{ mJ}/\text{cm}^2$  and for 60 min. (a) Before and (b) after purification treatment to remove NPs' residue using citrate and centrifugation. (c) Size distribution of AuSMPs estimated from (b). The average diameter and standard deviation are, respectively, 146 and 22 nm.

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