Effect of irradiation time in the synthesis of Au-Ag nanoalloys by femtosecond laser

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Abstract. The synthesis of metallic nanoparticles can be performed by femtosecond laser-induced photoreduction of the metallic ion solution. Due to hydrogen radical and the solvated electron generated through the interaction of ultrafast laser and water medium, the dissolved metallic ion in the medium can be converted to their respective metallic atom and then precipitated into nanoparticles. When there is more than one metallic ion available in the solution, alloy nanoparticles can be generated. One parameter that affects this laser-based synthesis was the duration of laser irradiation time that has an advantage for size modification of nanoparticles. In this work, we have synthesized Au-Ag nanoalloys from the mixture of Au and Ag ion in various volume fraction in water medium added with 0.01wt% polyvinylpyrrolidone (PVP) as a capping agent and irradiated for 5 and 10 minutes. The result showed that there was linear shifting in surface plasmon resonance (SPR) of the nanoalloys in respect with their volume fraction of the ions. The results also revealed that the nanoparticle size was indeed reduced as the laser irradiation was prolonged, i.e., Au50Ag50 has a particle size of 7.98 nm and 5.18 nm for 5 and 10 minutes irradiation time, respectively.

1. Introduction
Currently, significant attention has been given to the nanoalloy material synthesis due to the emergence of their novel catalytic, energy storage, and optical functionalities beyond those of pure metals [1]. These new functionalities are related to the electron binding and charge distribution of the alloy which alters their chemical behavior, mostly defined by electronic properties at the surface [2]. Especially for Au-Ag alloy nanoparticles (NPs). The combination of Au and Ag into one entity has opened up the possibility in varying the combined properties (i.e. electrical, optical and catalytic properties) which can be tuned in between those of pure elements [3-4] and thus, more diverse range of application can be applied [5-6]. Particularly, Au-Ag bimetallic systems have unique optical properties in terms of a surface plasmon resonance (SPR) band, where SPR band is tunable between ~520 nm for Au [7] and ~410 nm for Ag [8].

Many applications using nanoparticles generally require a good characteristic of the material, to maximize the quantum size effect on a particular application of interest. On the other hand, it has been challenging to adopt a suitable method for synthesizing metal NPs with controllable shape and size [9-10]. In the laser-based synthesis, size modification was mainly achieved through laser irradiation of a colloidal solution at a particular wavelength corresponding to the resonant excitation of surface
plasmon [11] or an interband transition [12]. When laser interacts with nanoparticles, the nanoparticles evaporate or fragment to form smaller colloids. From the theoretical calculations and experimental confirmation, the mechanisms of photothermal evaporation and Coulomb explosion are believed to be responsible for the size reduction during laser fragmentation in liquid [13].

In this research, we report a femtosecond laser-induced photoreduction to produce Au-Ag alloy nanoparticles from their mixture of metallic ions with a varying volume ratio. We also varied the laser irradiation times for 5 and 15 minutes. It is expected that longer duration irradiation will reduce particle size and have an influence on the shifting of their surface plasmon resonance (SPR).

2. Experimental
A high pulsed femtosecond laser was used to synthesize Au-Ag nanoalloys through a photochemical reduction, facilitated by the abundant solvated electron and hydrogen radicals generated during the irradiation [14]. Firstly, the solutions of gold and silver ions with the same concentration of $4.22 \times 10^{-4}$ M were prepared separately by dissolving of potassium gold (III) chloride (KAuCl$_3$, 98% purity, Sigma Aldrich) and silver nitrate (AgNO$_3$, 99.9% purity, Sigma Aldrich) in a water medium. We added a trace amount of ammonia into AgNO$_3$ solution to enhance the production of nanoparticles. Each solution was then mixed with 0.01 wt% polyvinylpyrrolidone (PVP, 99.9% purity, Sigma Aldrich) as a capping agent needed to stabilize nanoparticles. Just before irradiation, gold and silver metal ion solutions were added into a quartz cuvette ($10 \times 10 \times 45$ mm dimension) in various volume ratios with a total volume of 3 ml and flushed using a micropipette to homogenize the mixture. The samples were then called Au$_x$Ag$_y$, where $x$ and $y$ were the volume fraction for Au and Ag ions, respectively. For example, Au$_{30}$Ag$_{70}$ means that 30% (0.9 ml) and 70% (2.1 ml) volume fraction for Au and Ag ions were available in the solution.

For laser irradiation of the mixed ion solutions, we used a Ti:sapphire femtosecond laser (SpitfireAce, Spectra-Physics) with 100 fs full-width-half-maximum (FWHM) pulses at a fundamental wavelength of 800 nm, a laser power of 2.1 Watt/pulse and a repetition rate of 1 kHz. The laser beam was focused using an aspheric lens with a focusing length of 8 mm (NA = 0.5), directed perpendicularly to the side-wall of the glass cuvette. The samples were irradiated for 5 and 15 minutes of irradiation time. After irradiation, each sample was characterized by UV-Vis spectrophotometry (MayaPro 2000, Ocean Optics) to observe the absorption spectra in 300-800 nm range and determine the wavelength at which the Surface Plasmon Resonance (SPR) peak was observed. A transmission electron microscope (TEM, FEI Tecnai 20G $S$-Twin 200 kV) was used to investigate the morphology of the produced alloy nanoparticles.

3. Results and Discussion
When femtosecond laser interacts with the distilled water, the interaction will produce the hydrated electrons, hydroxyl radicals, a hydrogen atom, and hydrogen cation via multiphoton absorption mechanism [15]. These short-lived hydrated electrons and hydrogen radicals were believed as a strong reducing agent for any ions dissolved in the water. As a consequence, when metallic $M^+$ cations were present in the solution during the irradiation, they will be readily converted into $M^0$ atoms and precipitated into nanoparticles. So as for more than one metallic ion available in the solution, alloy or composite nanoparticles can be generated.

In this work, we irradiated the mixture of Au and Ag ions solution with a varying volume ratio by a femtosecond laser. Figure 1 and 2 showed not only the UV-Vis absorption spectra of Au-Ag ion mixtures in various volume ratios after 5 and 15 minutes irradiation time, respectively, but also their photographs of the produced colloidal alloy nanoparticles. From figure 1a, we can see that each Au-Ag nanoalloys have different SPR peaks placed in between 410 nm (SPR of Ag NPs) and 530 nm (SPR of Au NPs) that were shifted almost linearly as shown in figure 1b. This shifting in SPR peaks depends on the combined dielectric values of Au-Ag nanoalloys [16-17]. This result was verified by the color of Au-Ag nanocolloids colloidal solutions that have a different color changing from yellow (color of colloidal AgNPs) to red (color of colloidal AuNPs).
Figure 1. (a) UV-Vis absorption spectra, (b) SPR peaks vs. Au$^{3+}$ volume fraction and (c) their photographs of the colloidal Au-Ag nanoalloys was synthesized by femtosecond laser for 5 minutes.

Figure 2. (a) UV-Vis absorption spectra, (b) SPR peaks vs. Au$^{3+}$ volume fraction and (c) their photographs of the colloidal Au-Ag nanoalloys was synthesized by femtosecond laser for 15 minutes.
To reduce the particle size of the nanoalloys, we prolonged the irradiation time up to 15 minutes. Figure 2 showed the UV-Vis absorption spectra and their photograph of the colloidal Au-Ag nanoalloys for 15 minutes irradiation, while another experimental parameter remained the same. We found the same linear pattern in the SPR wavelength shifting of the nanoalloy from those for pure Ag to those for pure Au NPs (see figure 2b) with 2 – 10 nm shifting as compared with the same sample with 5 minutes irradiation. It is also interesting to note that for Au$^{3+}$ volume ratios less than 50, the SPRs peaks were red-shifted to the longer wavelength, and on the contrary, the blue-shifted was applied for the SPR. The decrease in the SPR peaks and the blue shifted to the shorter wavelength may indicate the reduced in the particle size [18-19]. To prove the hypothesis, we characterized the morphology of Au50Ag50 samples using TEM for both samples irradiated for 5 and 15 minutes.

![Figure 3](image)

**Figure 3.** TEM images of Au50Ag50 nanoalloys in (a) 5 minutes irradiation time and (b) 15 minutes irradiation time

Figure 3 shows TEM images and particle size distribution of Au50Ag50 for 5 and 15 minutes irradiation. From this figure, we can see that Au50Ag50 nanoalloys have an average particle size of 7.94 ± 5.08 nm and 5.18 ± 2.76 nm for 5 and 15 minutes irradiation time, respectively. It means that Au50Ag50 nanoalloys synthesized by 15 minutes irradiation have a smaller particle size than those for 5 minutes irradiation time. This observation was in a good agreement with the result we mentioned before. Particularly from figure 1 and 2, we can see that the SPR wavelength of Au50Ag50 nanoalloys in 5 minutes irradiation is at 451.27 nm, while it was shifted to 453.59 nm for 15 minutes irradiation. If we assume that the linear relationship is applicable for Au-Ag nanoalloys, we can derive the SPR
Abroad, it is around 450 nm, which is 10 nm lower from the predicted value or more toward to the SPR peak position of Ag NPs. This finding may indicate that the kinetic growth rate of Ag NPs is larger than those of Au NPs, which is in a good agreement with the previous research done by Herbani et al. [20] who conducted the same experiment but at the lower repetition rate.

Furthermore, we also observed from figure 1a and 2a that the SPR peak intensity decreased from 1.8 to 1.5 a.u. as the irradiation time increased from 5 to 15 minutes. Both findings may prove that irradiation time effects in reducing the particle size of the nanoparticle. This result might be due to the fact when Au-Ag nanoalloys are synthesized in 15 minutes irradiation time; they may go through the fragmentation process by the laser after the time where all the metal cations have been consumed completely in the photoreduction process. Further investigation needs to be conducted to prove this hypothesis.

As for the fragmentation process, we may explain this process as follows. When laser interacts with a colloidal nanoparticle, there is a gradient intensity along the beam path volume in liquid. Nanoparticle present in this volume will be fragmented [21] and the longer irradiation, the more particles will be fragmented. In this case, there are two mechanisms responsible for this fragmentation, i.e., photothermal evaporation and Coulomb explosion phenomenon [22]. When nanoparticles absorb laser beam, the heat will be transferred from a nanoparticle to a liquid, and the liquid will reach the spinodal temperature forming a nanobubble around the particle. Photothermal evaporation starts during nanobubbles formation. After photothermal evaporation, the following mechanism is the Coulomb explosion phenomenon where the electrons are ejected to generate ionized nanoparticle that is immediately fragmented because of internal charge repulsion. Coulomb explosion expressed as $X = \frac{E_c}{2E_s}$, where $E_c$ is coulomb energy and $E_s$ is the surface energy given for metals and $X = (q^2/n) / (16\pi r_{WS}^3 \sigma/e^2)$ with $q$ is the charge state, $n$ is the number of particle atom, $r_{WS}$ is the Wigner-Seitz radius, $\sigma$ is the surface tension (both $r_{WS}$ and $\sigma$ are temperature-dependent quantities), and $e$ is the elementary charge [23]. Nanoparticles dissociate into smaller entities when $X \geq 1$ (Rayleigh limit). For $0.3 < X < 1$, both evaporation and Coulomb explosion occur and for $X < 0.3$ only evaporation occur [24].

In our research, we do not calculate how much the Coulomb explosion energy in Au-Ag nanoalloys is. We can only predict that in longer irradiation time femtosecond laser there may be a Coulomb explosion phenomenon responsible for reducing particle size as evidenced by the TEM observation.

4. Conclusions
Effect of irradiation time in Au-Ag nanoalloys synthesis was investigated to be responsible for reducing nanoparticle size due to the fragmentation process. To learn this phenomenon, we synthesized Au-Ag nanoalloys in 5 and 15 minutes irradiation time. The optical properties showed that the UV-Vis absorption spectra of Au-Ag nanoalloys with 5 minutes irradiation was different from the sample irradiated for 15 minutes. The shift of SPR peaks might be caused by the changes in nanoparticle size. From the result of TEM characterization, the average particle size of Au50Ag50 nanoalloys in 5 minutes irradiation time has 7.94 nm, relatively bigger than the sample samples irradiated for 15 minutes (5.18 nm). This finding revealed that irradiation time has the potential to reduce particle size. This research can be further developed in longer irradiation time than 15 minutes for the synthesis of Au-Ag nanoalloys.

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