Effect of ablation time on femtosecond laser synthesis of Au-Ag colloidal nanoalloys

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Abstract. Au-Ag nanoalloys have been synthesized by laser irradiation technique. First, Au and Ag nanoparticles were prepared from Au and Ag pure metal (99.9%) ablated using an 800 nm femtosecond laser in distilled water. Using the same laser, Au and Ag nanoparticle with 1: 1 ratio were subsequently mixed and irradiated with various irradiation time, i.e. 0, 5, 20, and 35 minutes. We varied the ablation time for each metal nanoparticles, i.e. 25 minutes and 1 hour to see its effect on the production of nanoalloys in the subsequent irradiation. Au-Ag nanoalloys were characterized and analyzed using transmission electron microscope and UV-Vis spectrophotometry. The result shows that Au-Ag nanoalloys were already formed in 20 minutes irradiation, either for the sample ablated for 25 minutes or 1 hour. The result of TEM shows that the size of Au-Ag nanoalloys prepared from 1 hour ablation was around 15.03 nm.

1. Introduction

Metallic nanoparticles (NPs) have been studied for more than a century and in the last ten years because of their special optical, electronic and catalytic properties, which may be very useful in chemistry, engineering, or biomedical application and those properties depend on plasmonic oscillation [1 – 3]. The combination of desirable features of mono-metallic and bimetallic NPs, either as alloy or as core-shell structures, is an attractive material. They have a diverse range of application related to photonics, catalysis, information storage, chemical/biological sensing, and surface-enhanced Raman scattering (SERS) [4 – 7].

Amongst the metallic alloy nanoparticles, Au-Ag bimetallic systems have unique surface plasmon resonance (SPR) band, which can absorb and scatter in the visible spectral region [8 – 9]. The Au-Ag system is interesting because the SPR band is tunable between ~520 nm for Au [10] and ~410 nm for Ag [11]. One important observation of Au-Ag bimetallic systems is that alloy and core-shell nanoparticles often show different optical properties, although the composition of Au and Ag within the nanostructures is same [12]. Core/shell and alloy bimetallic NPs are especially interesting because they provide opportunities to tune the NPs’ optical and catalytic properties [13 – 14].

Pulse laser ablation of solid target in liquids (PLAL) has been known for a method to obtain monometallic Au and Ag nanoparticles [15]. Theory and experiment demonstrate that if NPs posses a strong absorption band whose energy coincides with the photon energy of a laser, the NPs can selectively be heated above their melting point into related liquid [16]. Therefore, the subsequent laser irradiation of the mixture of Au and Ag nanoparticles synthesized by a laser ablation can be expected
to form their respective AuAg alloy nanoparticles in the medium. In this work, we will investigate
effect of irradiation time on Au-Ag nanoalloys synthesis.

2. Experiment
Au-Ag nanoalloys were synthesized from the mixture of the colloidal Au and Ag NPs irradiated by a
femtosecond laser. The colloidal Au and Ag NPs were previously prepared separately by the same
laser using PLAL method. We use a Ti/Sapphire laser (Mai Tai, Spectra Physics), with 100 fs full-
width-half maximum (FWHM) pulses at wavelength of 800 nm for ablation and irradiation source.
Experimental setup of laser ablation for monometallic nanoparticle synthesis is shown in figure 1.

Au and Ag NPs were prepared from pure gold and silver targets with 99.9% purity. The target was
placed in the glass vessel with 5 ml distilled water ablated using a femtosecond laser with a power of
2.1 Watt, which was focused with a focusing lens (focal length of 10.0 cm) on the target surface. All
of Au and Ag NPs were prepared for both 25 minutes and 1 hour ablation time. Then, they were mixed
with 1:1 ratio (2.5 ml Au: 2.5 ml Ag), placed in the glass vessel again and irradiated with the same
laser with irradiation time of 0, 5, 20, and 35 minutes. Absorption spectra of the mixture were
measured before and after irradiation.

The absorption spectra of Au NPs, Ag NPs, and Au-Ag nanoalloys were measured using UV-Vis
spectrophotometry. Size and morphology of Au-Ag nanoalloys in 35 minutes irradiation time were
investigated using transmission electron microscope (TEM). The size distribution of Au-Ag NPs was
measured with software ImageJ and plotted with Origin. From the characterization, we can study
optical properties and morphology of Au-Ag nanoalloys.

3. Results and discussion
Our research purpose is to analyze optical properties, morphology and the influence of irradiation time
of femtosecond laser to the surface plasmon resonance, formation, and size distribution of Au-Ag
nanoalloys.

3.1. Preparation Au NPs and Ag NPs
Au and Ag NPs have been prepared by femtosecond laser ablation with different ablation time of 25
minutes and 1 hour. The absorption spectra of colloidal Au and Ag NPs were shown in figure 2. UV-
Vis absorption spectra relate to surface plasmon resonance (SPR) of Au and Ag NPs. The absorption
spectra of Au NPs show a characteristic SPR at around 500 – 530 nm, while SPR of Ag NPs is at
around 318 – 405 nm. We can see from figure 2a that the different ablation time of Au target resulted
in a similar characteristic SPR for both 25 minutes and 1 hour, i.e. 517 nm. However, the absorption
spectra of Ag NPs show different results or characteristics, where peaks of 25 minutes and 1 hour ablation times are at 403 nm and 408 nm, respectively. We can also observe form figure 2 that longer ablation time of pulsed femtosecond laser results in higher absorbance because ablation time is about how long the laser is interacting with matter. When laser interacts with matter (Au or Ag plate) in distilled water, there are phenomena occurred such as heating, melting, and evaporation of the matter. Longer ablation time means a longer interaction time between the laser and the matter, resulted in more material ablated from the bulk matter (Au and Ag) forming nanoparticles in distilled water.

![Figure 2. UV-Vis absorption spectra of colloidal (a) Au NPs and (b) Ag NPs.](image)

3.2. **Au-Ag nanoalloys: optical properties and morphology**

After synthesizing Au and Ag NPs, the next step is to mix Au NPs and Ag NPs with 1:1 ratio (2.5 ml: 2.5 ml). Mixture of Au and Ag NPs was then irradiated again with different irradiation time of 0 minutes, 5 minutes, 20 minutes, and 35 minutes. Results from different irradiation time are shown in figure 3. Figure 3a shows the UV-Vis absorption spectra of Au-Ag NPs originated from the mixture of the respective monomettalic nanoparticles which were prepared with an ablation time of 25 minutes. UV-Vis absorption relates to surface plasmon resonance (SPR) of Au-Ag NPs. Before irradiation time (0 minutes), two distinct SPR were observed at 397 nm and 518 nm, indicating isolated Ag and Au NPs in the mixture. At 5 minutes irradiation time, the SPR absorption peak of Ag NPs shifts to longer wavelength at 409 nm, whereas the SPR absorption of Au NPs shifts to shorter wavelength at 515 nm. After 20 minutes, the SPR shows only one peak of SPR absorption appears at 445 nm. At the last 35 minutes, the SPR is unchanged and still at 445 nm, but it shows decreasing absorbance intensity.

The same behavior is also observed for the mixture nanoparticles which are prepared for 1 hour ablation time as shown in figure 3b. The figure shows the SPR of Au-Ag NPs in varying different irradiation time in 1 hour ablation time. When Ag and Au NPs were only mixed and without irradiation (0 minutes), there are two SPR absorption peaks with maximum at 398 nm and 515 nm, corresponding to SPR absorption peak of Ag and Au NPs, respectively. After Au and Ag NPs were mixed and irradiated, the SPR changed. At 5 minutes irradiation time, two SPR peaks still remain but Ag NPs peak shifts to longer wavelength at 417 nm and Au NPs peak shifts to shorter wavelength at 498 nm. With 20 minutes irradiation time, only one peak of SPR absorption appears at 444 nm. However, at 35 minutes irradiation time, the SPR absorption shifts to longer wavelength at 455 nm. This condition differs with the result in figure 3a, where SPR at 35 minutes irradiation time has same characteristics with SPR of 20 minutes irradiation time.
Figure 3. Optical absorption spectra of a mixture Au and Ag NPs in distilled water with different irradiation time in (a) 25 minutes and (b) 1 hour ablation time.

Briefly, for both prepared samples using PLAL (25 minutes and 1 hour ablation time), Au-Ag nanoalloys have been formed in 20 minutes irradiation time (figure 3) that only one surface plasmon resonance was observed. Alloying process of Au and Ag nanoparticle is easy since it is a thermodynamically favorable process as indicated by their phase diagram [17]. Moreover, Au and Ag have almost identical lattice constants, so that alloying process may take place easily to form homogeneous Au-Ag alloy particles. A red shift of SPR peak to a longer wavelength for the mixture irradiated for a longer time (35 minutes) could result in the formation of coalescence structure, as in agreement with the result by Haiss et al. for Au nanoparticles [18]. We predicted that this might be due to a longer fragmentation time by the laser (1 hour ablation time). This result should be confirmed by transmission electron microscopy.

TEM image of Au-Ag nanoalloys after irradiation time of 35 minutes for both monometallic nanoparticles prepared with 25 minutes and 1 hour ablation time are shown in figure 4. Figure 4 indicates the morphology image and the histogram of alloy Au-Ag NPs distribution size. Distribution of alloy Au-Ag NPs prepared by PLAL for 1 hour was more dispersed and bigger than those for 25 minutes. Because the morphology of Au-Ag NPs is homogeneously spherical without any visible phase separation, we could say that the colloidal Au-Ag NPs prepared in this work contained alloy rather than core shell. Despite their chained structure, distribution size of Au-Ag NPs prepared from a 25 minutes ablation time shows the highest number of particles in 8 – 12 nm range, whereas those prepared from 1 hour ablation time shows the highest number of particles in 5 – 10 nm range. This result shows that particle size of sample prepared for 1 hour ablation time is bigger than those for 25 minutes, but the structure were more dispersed or unchained.

In short, we have successfully fabricated bimetallic alloy Au-Ag nanoparticles rather than core-shell nanoparticles as suggested by a single SPR peaks in UV-Vis absorption spectra and supported by TEM image where no phase observation was observed. We suggest similar study can be carried out with different mixing ratio of Au/Ag NPs to have a greater possibility to tune the composition of alloy nanoparticle.
Figure 4. TEM image of Au-Ag Nanoalloys in distilled water in different ablation time (a) 25 minutes and (b) 1 hour.

4. Conclusions

Au-Ag nanoalloys have been synthesized from mixture of Au and Ag NPs prepared with different ablation time of 25 minutes and 1 hour, respectively. Each mixing Au and Ag NPs in 25 minutes and 1 hour ablation time was then irradiated with different irradiation time of 0, 5, 20, and 35 minutes. After 20 minutes irradiation, absorption spectra of mixing nanoparticles shows different surface plasmon resonance (SPR) from their monometallic counterpart suggesting Au-Ag nanoalloys have been formed. TEM image shows the size of Au-Ag nanoalloys of around 15.03 nm for a longer ablation time. This result indicates that different ablation time gives different optical and structural properties. Further parameter investigation is needed to synthesize Au-Ag nanoalloys such as wavelength of laser, mixing ratio of Au and Ag NP, and power laser. Therefore, we can learn more about optical properties of Au-Ag nanoalloys.

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