Synthesis of Au50Ag50 Alloy Nanoparticles From Metal Ions and Colloidal Nanoparticles Through Photochemical Reduction Methods Using Femtosecond Laser

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Abstract: Nanoparticles synthesized through photochemical reduction using femtosecond involve reducing agent that reduces metal ions into nanoparticles. We synthesized Au50Ag50 from metal ions and colloidal nanoparticles in four different conditions: (i) gold metal ions and silver metal ion, (ii) colloidal gold nanoparticles (AuNPs) and silver nanoparticles (AgNPs), (iii) gold metal ions and colloidal silver nanoparticles (AgNPs), and (iv) colloidal gold nanoparticles (AuNPs) and silver metal ions. Gold and metal ions were obtained from dilution of gold and silver metal salts. While gold and silver nanoparticles were obtained from gold and metal ions added into a quartz cuvette and irradiated by femtosecond laser in 10 minutes irradiation time. In the synthesis, every condition respectively mixed in 3 ml solution into a 10x10x45 mm quartz cuvette and irradiated by femtosecond laser in 5-, 10- and 15- minutes irradiation time. The result showed that Au50Ag50 alloy nanoparticles were successfully synthesized in four different conditions, and the LSPR (Localized Surface Plasmon Resonance) in 15 minutes irradiation time was observed at 454.51, 458.74, 459.60, and 457.29 nm in the condition (i), (ii), (iii), and (iv), respectively.

Keywords: Au50Ag50 alloy nanoparticles; Photochemical reduction; Femtosecond laser

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I. INTRODUCTION

Metal alloy nanoparticles have received considerable attention and attracting growing interest because of their unique optical properties, electrical properties, and catalytic properties [1–3] and possible future applications including electronic and optical devices [4, 5], which depends on plasmonic oscillations. Plasmonic properties from the noble metal such as silver and gold can couple and enhance of local optical and electromagnetic fields which is widely used for sensor applications [6, 7].

The Au-Ag alloy nanoparticle is one of the particular interests because the absorption peak of surface plasmon resonance (SPR) can be tuned from $\sim$ 520 nm (AuNPs) to $\sim$ 400 nm (AgNPs) [8, 9]. In addition, Au-Ag alloy nanoparticles also have better properties as compared to only Au or Ag nanoparticles. The SPR depends on composition, shape, size, and the environment of the nanoparticles.

The preparation for Au-Ag alloy nanoparticles have been already reported by various techniques from chemical reduction technique [10, 11] to physical technique using various methods such as γ-ray [12, 13], microwave [14], and laser. In recent years, laser irradiation has also begun to be used to make metal nanoparticle solutions. Nanoparticles could be synthesized using laser-induced ablation method. The bulk of metal like Au and Ag is placed in a glass cuvette or glass beaker and irradiated using nanosecond or femtosecond laser until Au or Ag NPs successfully formed. Au-Ag alloy nanoparticles can be produced by mixing together of pure Au and Ag colloidal nanoparticles and then performing further irradiation by the pulsed laser [15, 16]. There was a challenge in the synthesis of Au-Ag uses laser ablation method due to the process of making each Au or Ag nanoparticles takes about 20 minutes [17] until 1 hour and has been described in our previous paper [18]. Another Au-Ag NPs synthesis involves the bottom-up photochemical reduction of Au and Ag ions. In this method, Au-Ag nanoalloys could be synthesized by only one step. Au and Ag ion obtained from diluting metal salts were mixed together into a glass cuvette and irradiated with laser femtosecond in only 5 minutes to form Au-Ag nanoalloys [19, 20]. The prolonged irradiation time in this method would decrease particles size that have been described in our previously experiment [21]. Au-Ag alloy nanoparticles synthesized using a photochemical reduction method is particularly interesting to be further developed with various mixtures of metal ions and colloidal metal nanoparticles.

Here, we focus on Au50Ag50 alloy nanoparticles resulting in four different conditions from metal ion solution and colloidal nanoparticles. Au50Ag50 were synthesized from different raw materials, namely (i) gold and silver metal ions, (ii) colloidal gold nanoparticles (AuNPs) and silver nanoparticles (AgNPs), (iii) gold metal ions and colloidal AgNPs, and (iv) colloidal AuNPs and silver metal ions. Nanoparticles synthesized in the condition (i) and (ii) have been reported pre-

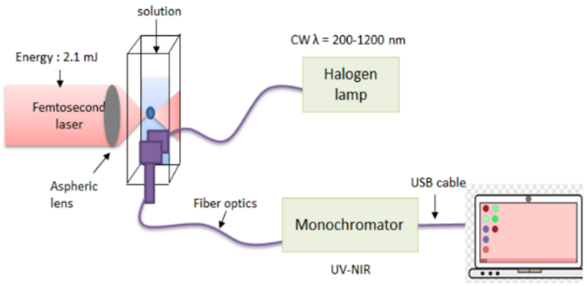

FIG. 1: The Schematic of the experiment.

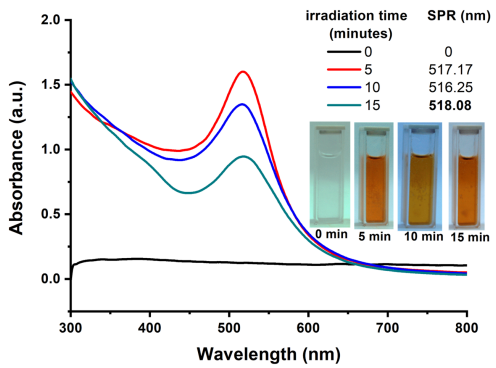

FIG. 2: UV-Vis spectra of Au50Ag50 synthesized from gold and silver ions [condition (i)], showing the presence of a surface plasmon resonance (SPR). Inset shows a change in the solution color by laser irradiation.

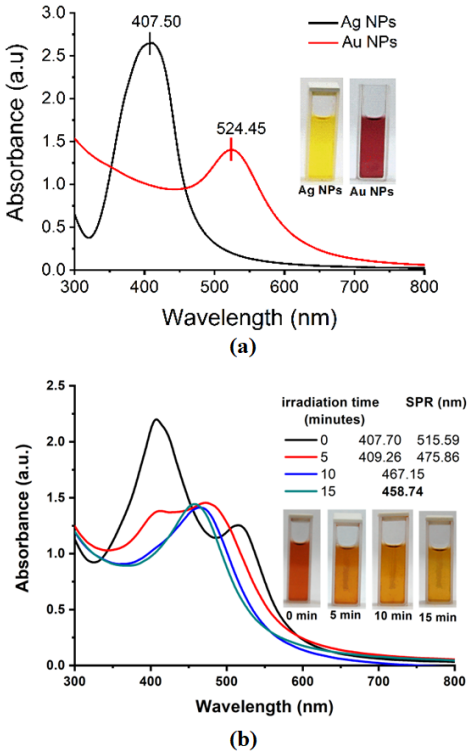

FIG. 3: UV-Vis spectra of (a) AgNPs and AuNPs and (b) Au50Ag50 synthesized from a mixture of colloidal AuNPs and AgNPs [condition (ii)], showing the presence of a surface plasmon resonance (SPR).

viously. In condition (i), we synthesis nanoparticles with a different molarity of Au and Ag ions with that described in [19–21]. In the previous report, AuNPs and AgNPs [condition (ii)] were synthesized by reduction of metals ions using photochemical process [15–17] rather than laser ablation we apply in this study. While the condition (iii) and (iv) represent completely new synthesis strategies. The contribution of hydrated electrons and hydrated radicals is considered a strong reducing agent and influences of irradiation of femtosecond laser. By applying four different conditions of synthesis routes, we want to know whether Au50Ag50 can be successfully produced in these conditions. These observations are particularly interesting to be explored furthermore.

II. METHOD

A. Materials

Potassium gold (III) chloride ($KAuCl_4$, 98% purity, Sigma Aldrich) and silver nitrate ($AgNO_3$, 99.9% purity, Sigma Aldrich) were diluted in a water and added with 0.01 wt% of polyvinylpyrrolidone (PVP, 99.9% purity, Sigma Aldrich) as a capping agent needed to stabilize nanoparticles and ammonia (NH_4OH).

B. Instrumentation

Ti-sapphire femtosecond laser (SpitfireAce, Spectra-Physics) which generates 100 fs full-width-half-maximum (FWHM) pulses at a fundamental wavelength of 800 nm with 2.1 mJ of energy per pulse at a repetition rate of 1 kHz is used as tool to produce colloidal metal nanoparticles. 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. During the synthesis process, nanoparticles are measured in real time directly by using a home-built UV-Vis spectrophotometry from a Halogen Lamp (Ocean Optics) and spectrophotometry (MayaPro 2000, Ocean Optics) that depicted absorption spectra in the 300-800 nm range as Surface Plasmon Resonance (SPR). The set-up of the experiment is illustrated in Fig. 1.

C. Procedure

Gold and silver ion solution in the same concentration of 4 $\times 10^{-4}$ M were prepared previously from dilute of potassium gold (III) chloride ($KAuCl_4$) and silver nitrate ($AgNO_3$) with 100 ml of distilled water and mixed with a capping agent of 0.01 wt% polyvinylpyrrolidone (PVP). Ammonia was added into $AgNO_3$ solution to inhibit the reduction of Ag^+ into Ag^0

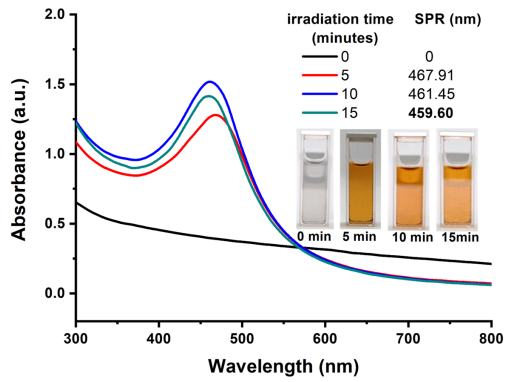

FIG. 4: UV-Vis spectra of Au50Ag50 synthesized from a mixture of gold metal ions and colloidal AgNPs [condition (iii)], showing the presence of a surface plasmon resonance (SPR). Inset shows a change in the solution color by laser irradiation.

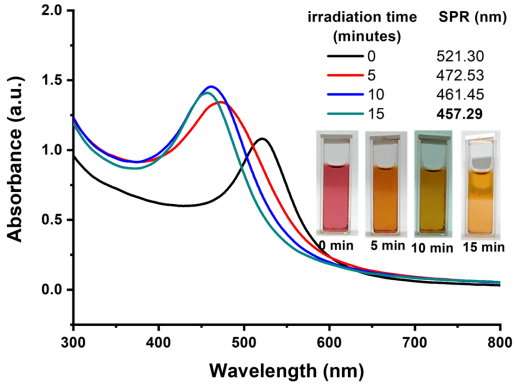

FIG. 5: UV-Vis spectra of Au50Ag50 synthesized from a mixture of colloidal AuNPs and silver metal ions [condition (iv)] and its respective SPR peak. Inset shows a change in the solution color by laser irradiation.

(AgNPs) back again to Ag^+ as a result of H_2O_2. Hydroxyl radical chemistry can be controlled through the addition of ammonia liquid. When ammonia solutions was irradiated with femtosecond laser, it will produce a reaction between NH_3 and OH, forming peroxynitrite and ONOO, significantly reducing the amount of the generated H_2O_2 [22]. In the next step, the solution of gold and silver ions was added respectively to the cuvette with a volume of 3 ml and then irradiated for 10 minutes to produce gold and silver nanoparticles.

Au50Ag50 were synthesized in four different conditions. Au50Ag50 means that 50% (1.5 ml) volume fraction of Au and 50% (1.5 ml) volume fraction of Ag. In the first condition, Au50Ag50 was synthesized from gold and silver metal-ions solution. The second condition, Au50Ag50 was synthesized from Au and Ag nanoparticles. As for the third condition, Au50Ag50 was synthesized from gold metal ions and colloidal silver nanoparticles (AgNPs) and in the fourth condition, Au50Ag50 was synthesized from colloidal gold nanoparticles (AuNPs) and silver metal ions. In every condition of preparation, the materials was added respectively into a quartz cuvette and irradiated using femtosecond laser until it forms Au-Ag nanoalloys. During the synthesis process, surface plasmon shifts are observed in a real time with UV-Vis spectrophotometer every 5 to 15 minutes irradiation times.

III. RESULTS AND DISCUSSION

A. The first condition mixture of gold ion ($KAuCl_4$) and silver ion ($AgNO_3$)

In the first condition, Au50Ag50 was synthesized from Au and Ag ions with the ratio of (1.5:1.5). They were added into a quartz cuvette, and the resulted solution was irradiated using femtosecond in 5 to 15 minutes irradiation times. The shifting of Surface Plasmon Resonance (SPR) in the first condition is shown in Fig. 2.

In this condition, Au50Ag50 was synthesized from the mixture of Au and Ag ions solution irradiated with femtosecond laser. When femtosecond laser interacts with water, the radicals such as hydrated electrons, hydroxyl radicals, a hydrogen atom, and hydrogen are generated and believed as a strong reducing agent [23]. The radicals will reduce gold metal ion of $K^+[AuCl_4]^-$ become Au NPs [24] and silver metal ion of $Ag^+[NO_3]^-$ become Ag NPs [25]. However, the hydroxyl radicals back-oxidize Ag metal to Ag^+ ions, which prevents the formation of Ag NPs. Therefore, the addition of liquid ammonia can reduce the amount of H_2O_2, and the silver metal ion was successfully reduced to be Ag NPs [22]. As the cuvette contains both gold and silver ions, the radicals will reduce gold and silver metal ions to Au-Ag nanoalloys.

Fig. 2 shows the result of Au50Ag50 synthesized in the first condition. Au50Ag50 has been successfully synthesized in 5 minutes irradiation times and has orange color. The prolonged irradiation of laser influences SPR shift toward to red shift. In 15 minutes irradiation times, Au50Ag50 has SPR of 454.51 nm.

The red shifted absorbance indicates the dynamic shift of the absorption maxima, and the process slowly reaches the equilibrium afterward. $[AuCl]^-$ reduction into Au NPs seemed to be occur first at the beginning and then followed $Ag^+[NO_3]^-$ to AgNPs began to take over at the center point. As the result, the peak position quickly shifts to blue region at 450.81 in just 5 minutes irradiation times. The formation of Au atom started dominated again to reach an equilibrium maximum to 452.66 nm in 10 minutes and 454.51 nm in 15 minutes irradiation times [19].

B. The second condition mixture of colloidal gold nanoparticles (AuNPs) and silver nanoparticles (AgNPs)

In the second condition, Au50Ag50 was synthesized from the mixture of colloidal gold nanoparticles (AuNPs) and silver nanoparticles (AgNPs). Firstly, we synthesized AuNPs and AgNPs from gold and silver ions in 10 minutes irradiation

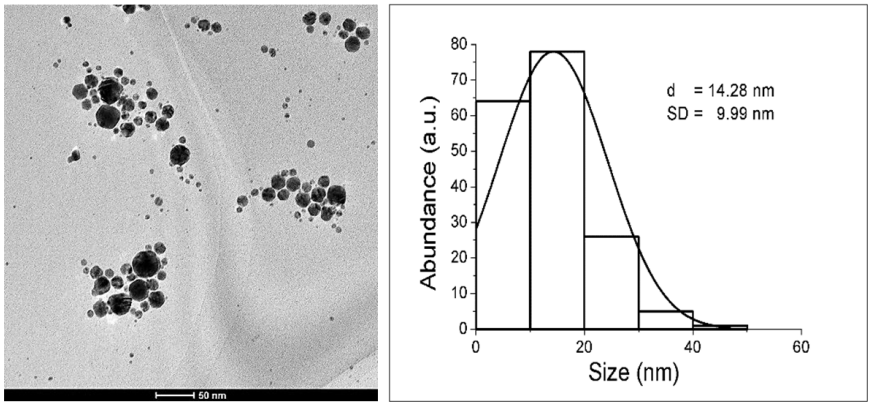

FIG. 6: (a) TEM images and (b) particle size distribution of Au50Ag50 nanoalloys prepared in condition (i).

times, respectively. The results of AuNPs and AgNPs and their SPR are shown in Fig. 3(a). Furthermore AuNPs and AgNPs mixture with the ratio of 1.5:1.5 were put into 3 ml of a quartz cuvette and irradiated using femtosecond laser with the real monitoring from 5 to 15 minutes irradiation time in every 5 minutes. The result of synthesis and SPR of Au50Ag50 obtained in the second condition is shown in Fig. 3(b).

The SPR band of AuNPs and AgNPs which have been synthesized in 10 minutes irradiation times are found at 524.45 and 407.50 nm. In the second condition, Au50Ag50 from mixture of colloidal AuNPs and AgNPs was formed by an irradiation with femtosecond laser for 5, 10, and 15 minutes. We measured in real time the shift of SPR every 5 minutes. Fig. 3 shows the formation process of Au50Ag50, the changing color of nanoparticles, and the transition of nanoparticles to become Au50Ag50 nanoalloys. In 15 minutes irradiation times, Au50Ag50 formed only one SPR at 458.74 nm. The long irradiation times will make both AuNPs and AgNPs melting and alloying to form Au50Ag50 and shift two peaks of SPR to only single SPR [22]. When AuNPs and AgNPs were mixed and irradiated, colloidal AuNPs will be excited and heated to their boiling point. With the longer irradiation, the colloidal AgNPs will also be heated above their boiling point, thus there is a possibility of AgNPs reaching the melting point before AuNPs. When AgNPs contact with AuNPs, a homogeneous Au-Ag will be formed. The alloying process is successful when the two SPRs change into only one SPR. If the irradiation process continues, the fragmentation process occurs, and nanoparticles might be smaller [26, 27].

C. The third condition mixture of gold metal ions and colloidal silver nanoparticles (AgNPs)

Au50Ag50 was successfully synthesized from the mixture of gold and silver ions and also the mixture of AuNPs and AgNPs. In the third condition, Au50Ag50 was prepared from the mixture of gold metal ions and colloidal silver nanoparticles (AgNPs). AgNPs was successfully synthesized (in the second condition) from silver metal-ions solution which was irradiated in 10 minutes, and the result is indicated in Fig. 3(a). Here, colloidal AgNPs was mixed with Au- ions with a molar ratio of 1.5: 1.5, then put into a cuvette and irradiated in real monitoring every 5 minutes irradiation time until 15 minutes. The result described in Fig. 4.

Fig. 4 shows the UV-Vis spectra of the NPs prepared in the third condition, indicating the emergence of SPR after laser irradiation. Before irradiation, no peak of SPR was observed. After irradiation in 5 minutes, Au50Ag50 was successfully formed with orange color. With the prolong irradiation times, SPR gradually shifts toward to a blue range.

D. The fourth condition mixture of colloidal gold nanoparticles (AuNPs) and silver metal ions

In the last condition, we synthesize Au50Ag50 from the mixture of colloidal gold nanoparticles (AuNPs) and silver metal ions. As in the third condition, AuNPs was previously synthesized from gold metal-ions solution and irradiated in 10 minutes irradiation times, as illustrated in Fig. 3(a). Here, AuNPs solution was mixed with Ag^+ metal ions solution with the molar ratio of 1.5:1.5, then put into 3 ml of a quartz cuvette. The mixture of AuNPs and Ag^+ metal-ions solution was irradiated until 15 minutes. The real monitoring was done in every 5 minutes.

Fig. 5 shows SPR of Au50Ag50 nanoalloys synthesized from a mixed solution of colloidal AuNPs and Ag^+ ions, before and after irradiation. Before irradiation, the mixture of colloids has an SPR peak at 521.30 nm with red color. By 5 minutes irradiation, the color change to orange, and Au50Ag50 nanoalloys are formed. When irradiation times was prolonged, the characteristic of SPRs peak is a blue shift, where SPRs peak decreases to the shorter wavelength. In this synthesis condition, one can conclude that Ag^+ ions are reduced on heating of AuNPs and simultaneously melt and form Au50Ag50 nanoalloys [27].

Analysis of the NPs was then performed using TEM to

know particle size of the produced alloy nanoparticles. The result is presented in Fig. 6, which shows that Au50Ag50 is homogenous alloys and has average particle size of 14.28 nm.

IV. SUMMARY

Au50Ag50 has been successfully synthesized in four different combinations of raw materials, namely (i) a mixture of gold and silver ions, (ii) a mixture of colloidal gold nanoparticles (AuNPs) and silver nanoparticles (AgNPs), (iii) a mixture of gold ions and colloidal AgNPs, and (iv) a mixture of colloidal AuNPs and silver ions. TEM analysis revealed that Au50Ag50 nanoalloys had been formed. Surface plasmon resonance (SPR) of the obtained nanoalloys has a peak at about 454-459 nm, as indicated by the orange color of nanoparticles. These SPRs differ from those of AuNPs (520 nm) and AgNPs (410 nm). Moreover, TEM examination revealed homogeneous alloys with the average particle size of 14.28 nm. The synthesis in four different conditions can be used as a model for the synthesis of Au-Ag nanoalloys with varying molar concentrations.

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