Tuning Localized Surface Plasmon Resonance (LSPR) of Au-Ag Nanoalloys by Femtosecond Laser

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Abstract. Au-Ag nanoalloys have been synthesized using the photochemical reduction method by femtosecond laser from dissolved of potassium gold (III) chloride (KAuCl₄) and silver nitrate (AgNO₃) added into a quartz cuvette in various volume ratios with a total volume of 3 ml. The samples were then called AuₓAgᵧ, where x and y were the volume fraction for Au and Ag ions, respectively. The samples were irradiated for 15 minutes of irradiation time and characterized by UV-Vis spectrophotometry to observe the absorption spectra in 300-800 nm range and determine the wavelength at which the Localized Surface Plasmon Resonance (LSPR) peak was observed. The process occurred in a water-only medium, in water medium added with 0.01 wt% polyvinylpyrrolidone (PVP) and in water medium added with 0.1 wt% polyvinylpyrrolidone (PVP). The result showed that LSPR of Au-Ag nanoalloys could be tuned between ~525 nm for Au and ~403 nm for Ag in a water-only medium, ~521 nm for Au and ~412 for Ag in water medium added with 0.01 wt% PVP and ~522 nm for Au and ~419 nm for Ag in water medium added with 0.1 wt% PVP.

1. Introduction
Investigation of nanoparticles (NPs) become as promising tools to search new material that can improve applications in various technology including catalysts, optical and electronic devices [1-2], whose these properties depend on plasmonic oscillations [3]. Metal nanoparticles such as Au and Ag are interesting material and the most extensively studied because their Localized Surface Plasmon Resonance (LSPR) phenomenon shows a high absorption band in the visible region [4]. Localized Surface Plasmon Resonance depends on the size, shape and dielectric constant of the medium [5]; it is sensitive to the environment. This phenomenon is what makes metal nanoparticles promising in the field of optoelectronics and sensing [6].

Au-Ag nanoalloys have stimulated increasing interest due to the possibility of combining the properties of Au NPs and Ag NPs. With the combination, the optical, electrical, and catalytic can be tuned [7] and have a more diverse range of applications than only Au NPs and Ag NPs application [8]. Particularly, Au-Ag bimetallic systems have unique optical properties in terms of an LSPR band, where is tunable between ~520 nm for Au and ~410 nm for Ag [10].

There is a challenge associated with nanoparticles that control the stability of nanoparticle. Control dispersion stability in synthesis nanoparticles can be useful to develop chemical, biological, or physical nanosensors. A capping agent is usually used to coat and stabilize the particles. One of the most frequently used protective agents in metal nanoparticle synthesis is poly (N-vinyl-2-pyrrolidone) (PVP). This water-soluble polymer has been extensively used as a protecting agent against the
agglomeration of metal colloids [11]. Significantly, PVP can be a stabilizer, growth modifier, nanoparticle dispersant, and reducing agent depending on the specific synthetic conditions and material system [12]. Besides, as a capping agent, PVP on gold nanoparticles will enhance anti amyloidogenic propensity towards hen egg-white lysozyme, as explained by Tulika Das et al. [13].

In our previous experiment, we have been synthesized Au-Ag nanoalloys only in Au0Ag100, Au50Ag50, and Au100Ag0 using PVP as a capping agent [14]. So that in here, we will synthesize of Au-Ag nanoalloys in all complete volume ratio Au (%) in AuxAgy not only in a water medium but also in water added 0.01 wt% and 0.1 wt% of PVP. We are not only using PVP as a capping agent but also we will use PVP in different concentrations in nanoparticles. From the synthesis, we will observe the tuning and shifting of LSPR in three different conditions.

2. Experimental

Au-Ag nanoalloys were synthesized from gold and silver ion metal with the same concentration of 4.22 × 10−4 M mixed into a quartz cuvette (10 × 10 × 45 mm dimension) in various volume ratios with a total volume of 3 ml and irradiated in 15 minutes by femtosecond laser. The gold and silver ion were prepared from potassium gold (III) chloride (KAuCl, 98% purity, Sigma Aldrich) and silver nitrate (AgNO3, 99.9% purity, Sigma Aldrich) in a water medium. We added a trace amount of ammonia into the AgNO3 solution to enhance the production of nanoparticles. Each solution was then mixed with 0.01 wt% and 0.1 wt% of polyvinylpyrrolidone (PVP, 99.9% purity, Sigma Aldrich) as a capping agent needed to stabilize nanoparticles. The sample was called AuxAgy, where x and y were the volume fraction for Au and Ag ions, respectively. For example, Au40Ag60 means that 40% (1.2 ml) and 60% (1.8 ml) volume fraction for Au and Ag ions were available in the solution.

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. X-ray Diffraction and Transmission electron microscopy (TEM, FEI Tecnai 20G S-Twin 200 kV) was also used to investigate the lattice and morphology of alloy nanoparticles.

We use a Ti/Sapphire laser (Mai Tai, Spectra-Physics), 100 fs full-width-half maximum (FWHM) pulses at a wavelength of 800 nm and around 2.1 Watt to synthesis Au-Ag nanoalloys. The laser beam was focused using an aspheric lens with a focusing length of 8 mm (NA = 0.5) and directed perpendicularly to the side-wall of the glass cuvette.

3. Results and discussion

Mixed gold and silver ion in various volume ratio was irradiated by femtosecond laser. There was an interaction between laser and solution. When laser interacts with distilled water, intense pulses laser induce multiphoton ionization of water molecules forming a plasma. The formation of plasma includes several reactions that are reactive radical species such as hydrated electrons ($e^{-}_{wa}$) and hydroxyl radicals (OH) [15-16]. They acted as a reducing agent of metal ion to metal nanoparticles (NPs) [17].

The radicals acted as a reducing agent of gold metal ion K[AuCl] to Au NPs [18] and silver metal ion Ag[NO3] to Ag NPs [19]. In the synthesis of Au-Ag nanoalloys, the solution irradiated with pulsed femtosecond laser has both gold and silver metal ion in a certain volume ratio. When laser interacts with the solution, both hydrated electrons and hydroxyl radicals will reduce gold and silver metal ion to Au-Ag nanoalloys.

Au-Ag nanoalloys were synthesized in three different conditions that were a water-only medium, in water medium added with 0.01 wt% polyvinylpyrrolidone (PVP), and in water medium added with 0.1 wt% polyvinylpyrrolidone (PVP). Each sample characterized by UV-vis spectrophotometry to know the shifting of localized surface plasmon resonance (LSPR). Added of PVP were predicted to affect the shifting of LSPR of Au-Ag nanoalloys. Moreover, only Au0Ag100 (gold nanoparticles), Au50Ag50, and Au100Ag0 (silver nanoparticles) in an only water medium were characterized using X-ray Diffraction to know lattice constant and crystal structure.
Au0Ag100, Au50Ag50 and Au100Ag0 has five similar lattice constant (111), (200), (220), (311) and (222). They have also had similar fcc (face center cubic) crystal structure. Because Au and Ag NPs have a similar lattice constant and crystal structure, so this indicates that there is no new lattice constant in Au-Ag nanoalloys.

![Figure 1](image1.jpg)

**Figure 1.** The XRD pattern, lattice constant and crystal structure of Au-Ag nanoalloys

![Figure 2](image2.jpg)

**Figure 2.** (a) UV-Vis absorption spectra, (b) SPR peaks vs. Au$^{3+}$ volume fraction, and (c) their photograph of the colloidal Au-Ag nanoalloys was synthesized by femtosecond laser pulse for 15 minutes in an only water medium.
Figure 3. (a) UV-Vis absorption spectra, (b) LSPR peaks vs. Au$^{3+}$ volume fraction, and (c) their photograph of the colloidal Au-Ag nanoalloys was synthesized by femtosecond laser pulse for 15 minutes in water medium added with 0.01 wt% polyvinylpyrrolidone (PVP).

Figure 4. (a) UV-Vis absorption spectra, (b) LSPR peaks vs. Au$^{3+}$ volume fraction, and (c) their photograph of the colloidal Au-Ag nanoalloys was synthesized by femtosecond laser pulse for 15 minutes in water medium added with 0.1 wt% polyvinylpyrrolidone (PVP).
Figures 2, 3, and 4 show Localized Surface Plasmon Resonance (LSPR) of Au-Ag nanoalloys and their photograph in an only water medium, in water medium added with 0.01 wt% polyvinylpyrrolidone (PVP) and in water medium added with 0.1 wt% polyvinylpyrrolidone (PVP), respectively. This result shows that LSPR of Au-Ag nanoalloys in an only water medium can be tuned between ~525 nm for Au and ~403 nm for Ag. While in water medium added with 0.01 wt% polyvinylpyrrolidone (PVP) can be tuned between ~521 nm for Au and ~412 for Ag and in water medium added with 0.1 wt% polyvinylpyrrolidone (PVP) can be tuned between ~522 nm for Au and ~419 nm for Ag. The LSPR for Au\[^{3+}\] volume ratios less than 50 in were red-shifted to the longer wavelength, and on the contrary, the blue-shifted was applied for the LSPR.

PVP in the synthesis of Au-Ag nanoalloys functions as a capping agent to make nanoparticles are stable. Nanoparticles are unstable and tend to agglomerate because at short interparticle distances, and they are attracted to each other by van der Waals attraction forces [20]. Aggregation can be avoided with a capping agent. A capping agent is usually used to coat and stabilize the particles [21]. If we compare figure 1, 2, and 3, the LSPR of Au-Ag nanoalloys in water medium added with 0.01 wt% polyvinylpyrrolidone (PVP) and in water medium added with 0.1 wt% polyvinylpyrrolidone (PVP) are different than in an only water medium. Our previous result of synthesizing of Au50Ag50 in water medium added 0.01 wt% PVP showed that the nanoparticles have a smaller size than Au50Ag50 in an only water medium. The TEM showed that added PVP in Au50Ag50 made nanoparticles more disperse and stable than in only water medium [14]. The result of M F Mohamad et all showed that the effect of PVP concentration on the formation of size and shape of gold nanoparticles. He said that the higher of PVP, the smaller the size of nanoparticles [22]. Another result described by Jinhui Li et al; was also the same that the increasing concentration of PVP would make the size of nanoparticles smaller [23]. If we regard in figure 3, the LSPR is different from figure 2. The same condition may have also happened in the synthesis of Au-Ag nanoalloys, where the effect of concentration PVP will influence the size of Au-Ag nanoalloys. Because one of Localized Surface Plasmon Resonance (LSPR) shift affected by the size of nanoparticles, so the LSPR in an only water medium, in water medium added 0.01 wt% PVP and in water, medium added 0.1% wt PVP are different. However, we found the same linear pattern in the LSPR wavelength shifting of the nanoalloy from those for pure Ag to those for pure Au NPs with the increase of volume ratio Au (%) in solution.

4. Conclusions

Au-Ag nanoalloys have been synthesized using a photochemical reduction method with a femtosecond laser in 15 minutes irradiation time. We synthesize nanoalloys in AuxAgy not only in a water medium but also in water added 0.01 wt% and 0.1 wt% of PVP. The result of Localized Surface Plasmon Resonance (LSPR) in three condition show that can be tuned from LSPR of Au and LSPR of Ag wherein water medium between ~525 nm and ~403 nm, in water medium added with 0.01 wt% tuned between ~521 nm and ~412 nm and in water medium added with 0.01 wt% tuned between ~522 nm and ~419 nm. Added PVP can make the size of nanoparticle is smaller and the lower concentration of PVP maybe also make smaller too. So, LSPR in three conditions are different and shifted.

Acknowledgments.

This work was supported by a research grant from the Ministry of Research, Technology, and Higher Education Republic of Indonesia: Intensif Riset Sistem Inovasi Nasional (INSINAS) 2019

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