Optical and Electrical Properties of Gold-Silver Nanoalloys Synthesized through Photochemical Reduction using Femtosecond Laser

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ABSTRACT

In this work, we investigated the optical and electrical properties of Au-Ag nanoalloys in various volume ratios. The nanoparticles have been prepared from gold and silver ions reduced by direct irradiation femtosecond laser. The samples were added into a quartz cuvette and irradiated for 10 minutes. The optical property where Localized Surface Plasmon Resonance (LSPR) peaks occurred was observed for each sample. In addition, electrical conductivity of the colloids was derived from the measurement of the zeta potential by dynamic light scattering (DLS) method. The results showed that the LSPR peak of Au-Ag nanoalloy were shifted almost linearly around 409 nm for Ag and 530 nm for Au depends on their volume fraction. The conductivity measurement showed that Au0Ag100 (pure Ag) nanoparticles has the highest value while the Au100Ag0 (pure Au) nanoparticles has the lowest value. Interestingly, Au-Ag nanoalloys have the values between Au0Ag100 and Au100Ag0. Briefly, this work revealed that both optical and electrical properties of Au-Ag nanoalloys can be easily tuned by regulating the volume fraction between the two elements.

Keywords: optical properties, electrical properties, Au-Ag nanoalloys, photochemical reduction, femtosecond laser

INTRODUCTION

Recently, investigation and expansion of nanotechnology and their extensive application have become main routine to search new material that can improve applications in various technology, including catalysts, optical and electronic devices [1-2] and every field related to industry [3-4]. The global demand for diverse nanoparticles (NPs) has stimulated rapid advances in the development of both chemical, physical and also biological synthesis techniques [5]. There are two types of approaches used in the synthesis of metal nanoparticles: bottom-up and top-down methods. The top-down approach implies removal from a large bulky material to get nano sized particle using physical, mechanical or chemical methods [6]. The bottom-up refers to the build up from the bottom: atom-by-atom, molecule by molecule and clusters which forms a building block (nano particles) [7]. From this point of view, the bottom-up method is the appropriate method in regulating and controlling the particle size, considering the reduction process of chemical precursors in the solution using reducing agents such as chemicals, mechanical waves (ultrasound), and electromagnetic waves [8]. The photochemical reduction method using femtosecond laser in the synthesis of nanoparticles is attracting...
attention recently due to this technique is simple, fast, and “green” in which no dangerous chemicals are used, except metal salt and dispersing agent. In this method, a metal salt is reduced to its zero valence metal atoms, forming nanoparticles [9-10].

Nanoparticles (NPs) of noble metals such as Au and Ag NPs are the most studied and attracting materials because of their Localized Surface Plasmon Resonance (LSPR) absorption properties in the visible spectra region [11]. LSPR shift is affected by the size, shape and dielectric constant of the environment medium [12]. The combination of Au and Ag NPs into Au-Ag nanoalloys is interesting to investigate further due to the possibility of combining the properties of Au and Ag NPs, not only the optical but also electrical and catalytic properties could be tuned between Au and Ag NPs [13-14]. In addition, the formation of Au-Ag nanoalloys enhances these nanoparticles applications to be more diverse than that of Au or Ag NPs alone [15-16].

Therefore, this paper is aiming to investigate the optical properties of mixed Au-Ag nanoalloys that synthesized through photochemical reduction using a femtosecond laser. The optical properties are about the shifting Localized Surface Plasmon Resonance (LSPR) of Au-Ag nanoalloys in various volume ratios. Because the LSPR of Au-Ag nanoalloys can be tuned between the Au and Ag NPs, it is suspected that the electric properties of Au-Ag nanoalloys can also be tuned between that of the Au and Ag. This paper also studies the electrical conductivity of Au-Ag nanoalloys via zeta potential measurement using dynamic laser scattering method.

EXPERIMENT
Chemicals and instrumentation

The Au-Ag nanoalloys were synthesized in various volume ratio combination of gold and silver metal ions through photochemical reduction method using a high pulsed femtosecond laser. During irradiation, this process generates abundant solvated electron and hydrogen radicals [17]. Firstly, gold and silver ions solution were prepared separately, by dissolving potassium gold (III) chloride (K[AuCl₄], 99.995%, Sigma-Aldrich) and silver nitrate (AgNO₃, 99%, Rofa Lab). The gold and silver ions were prepared in a water medium in the presence of (PVP, 99.9% purity, Sigma Aldrich) as a capping agent.

The samples were called AuₓAgᵧ, where x and y are the volume fraction for each gold and silver ions in the solution shown in table 1. Each sample was added into a quartz cuvette with a total volume of 3 mL and was irradiated using laser for 10 minutes.

| Ratio   | (Au:Ag)       | Ratio   | (Au:Ag)       |
|---------|---------------|---------|---------------|
| Au₁₀₀Ag₁₀₀ | 0 mL : 3 mL   | Au₆₀Ag₄₀ | 1.8 mL : 1.2 mL |
| Au₇₀Ag₃₀  | 0.3 mL : 2.7 mL | Au₇₀Ag₃₀ | 2.1 mL : 0.9 mL |
| Au₂₀Ag₈₀  | 0.6 mL : 2.4 mL | Au₈₀Ag₂₀ | 2.4 mL : 0.6 mL |
| Au₉₀Ag₁₀  | 0.9 mL : 2.1 mL | Au₉₀Ag₁₀ | 2.7 mL : 0.3 mL |
| Au₄₀Ag₆₀  | 1.2 mL : 1.8 mL | Au₁₀₀Ag₀ | 3 mL : 0 mL    |
| Au₅₀Ag₅₀  | 1.5 mL : 1.5 mL |         |               |

A Ti-sapphire femtosecond laser (Spitfire Ace, Spectra-Physics) with 100 fs full-width-half-maximum (FWHM) pulses at a fundamental wavelength of 800 nm, and a laser power of
2.1 Watt/pulse and a repetition rate of 1 kHz were used in this procedure. The experimental set-up is shown in Figure 1.

After irradiation, Localized Surface Plasmon Resonance (LSPR) peaks of each sample was observed using UV-Vis spectrophotometry (MayaPro 2000, Ocean Optics). Moreover, the obtained colloids were then characterized by particle size analyser (PSA Nano Plus 3, Micromeritics USA) to measure the zeta potential and conductivity. Then, X-ray diffraction (XRD, Rigaku Smartlab 3kW) and transmission electron microscopy (TEM FEI Tecnai G 20 S-Twin, 200kV) analyses were carried out to obtain the crystalline structure and the morphology, respectively.

![Figure 1. The schematic set-up of the experiment [18].](image)

**Procedure reaction**

Gold and silver ions solution (with a concentration of $4.22 \times 10^{-4}$ M) (100 mL) were prepared separately by dissolving potassium gold (III) chloride ($\text{K[AuCl}_4]$, 99.995%, Sigma-Aldrich) (1 gram) and silver nitrate ($\text{AgNO}_3$, 99%, Rofa Lab) (1 gram) with distilled water. Ammonia ($\text{NH}_4\text{OH}$, 25wt%, Rofa Lab) was added 0.01 μl into the 100 mL of $\text{AgNO}_3$ solution to enhance the production of nanoparticles. Polyvinylpyrrolidone (PVP, 99.9% purity, Sigma Aldrich) (0.01 gram) also added into 100 mL of gold and silver ions.

**RESULT AND DISCUSSION**

Au-Ag nanoalloys in various volume ratio were synthesized from irradiated mixture of Au and Ag ions solution by a femtosecond laser. Intense femtosecond laser interacts with a liquid solvent and will be produced highly species that are useful to induce chemical reactions in the solution through the multiphoton excitation and ionization of solvent molecules as shown in Figure 2. High reactive species, such as solvated electron ($e_{\text{aq}}^-\text{)},$ hydroxyl radical ($\text{OH}^\bullet$), hydrogen radical ($\text{H}^\bullet$) and hydronium cations ($\text{H}_3\text{O}^+$), have a sufficient energy to reduce metal ions present in the solution [19]. Amongst them, the short-lived $e_{\text{aq}}^-$ and $\text{H}^\bullet$ were strong reducing agents for any ions dissolved in the water [20]. When metallic $\text{M}^+$ cations were present in the solution during the irradiation, the strong reducing agent will convert the $\text{M}^+$ into $\text{M}^0$ atoms and then precipitated into nanoparticles. The schematic description is shown in Figure 3. If two metal precursors which have different reduction potential were irradiated using high
intense femtosecond laser, the reduction agent will reduce metallic cations and the formation of homogenous alloy can be possibly generated [21]. For Au and Ag systems, where the elemental Au and Ag are miscible to each other in their phase diagram, a homogeneous nanoalloy is more likely to be formed.

Figure 4 showed the UV-Vis absorption spectra, the Localized Surface Plasmon Resonance peaks as a function of volume ratio and their photographs of the produced colloidal alloy nanoparticles in 10 minutes irradiation time. From Figure 4a and 4b, Au-Ag nanoalloys have LSPR peaks between 409 nm, originated from the Localized Surface Plasmon Resonance of silver nanoparticles (Au0Ag100), and 530 nm, originated from the Localized Surface Plasmon Resonance of gold nanoparticles (Au100Ag0). This shift of LSPR were almost linear, as shown in Figure 4b.

**Figure 2.** Schematic description of the primary events following the multiphoton absorption of femtosecond laser energy by water molecules [22].

**Figure 3.** A schematic mechanism of nanoparticle synthesis induced by highly intense femtosecond laser in water [23].
Figure 4. (a) UV-Vis absorption spectra, (b) LSPR peaks vs. \( \text{Au}^{3+} \) volume fraction and (c) their photograph of the colloidal Au-Ag nanoalloys; synthesized by femtosecond laser pulse for 10 minutes.

The Au-Ag nanoalloys were also characterised using DLS method to study their zeta potential and conductivity as electrical properties. The result is shown in Table 2, in which pure Ag NPs has the highest conductivity, while pure Au NPs has the lowest conductivity. Moreover, the Au50Ag50, Au20Ag80 and Au80Ag20 nanoalloys have conductivity values in between the Ag NPs and Au NPs.

Table 2. Zeta potential and conductivity of Au-Ag nanoalloys.

| Sample     | Zeta Potential (mV) | Conductivity (mS/cm) |
|------------|---------------------|----------------------|
| Au0Ag100   | -37.1               | 0.294                |
| Au20Ag80   | -23.5               | 0.291                |
| Au50Ag50   | -25.5               | 0.283                |
| Au80Ag20   | -26.5               | 0.265                |
| Au100Ag0   | -12.5               | 0.253                |

Moreover, only Au0Ag100 (gold nanoparticles), Au50Ag50 and Au100Ag0 (silver nanoparticles) were characterized using XRD to obtain the crystallographic information. Indeed, we validated that both pure nanoparticles and its alloy has similar lattice planes i.e. (111), (200), (220), (311) and (222) and have also similar \textit{fcc} (face center cubic) crystal structure as shown in their XRD diffractogram in Figure 5. There is no new lattice constant in Au-Ag nanoalloys, indicated that the produced colloid was homogenous nanoalloy, not core-shell or inhomogeneous alloy structure.
Figure 5. The XRD pattern, lattice constant and crystal structure of Au-Ag nanoalloys

Figure 6. TEM images of Au50Ag50 nanoalloys in 10 minutes irradiation time.

Figure 6 shows the Au50Ag50 nanoalloys that was fabricated by femtosecond laser in 10 minutes irradiation times. The Au50Ag50 nanoalloys have non-uniform particle size distribution from under 5 nm until around 30 nm-in which the nanoparticles have an average particle size of 8.15 ± 5.53 nm. TEM image also shows that morphologically homogeneous alloys are formed, as validated previously by their UV-Vis spectra which only has one LSPR peak rather than two peaks of those for core-shell nanoparticles. For the system of interest, the reduction process from metal salts into metal atoms by a femtosecond laser actually was finished in 5 minutes irradiation time [24]. When the laser irradiation time is prolonged to 10 minutes, there is laser melting phenomenon. The heat effect of the laser will melt the nanoparticles and makes the nanoparticles smaller. During the process, there is a possibility
that several nanoparticles will combine into one nanoparticle and cause non-uniform particle size.

The LSPR of Au-Ag nanoalloys can be tuned between LSPR of Au NPs and LSPR of Ag NPs as shown in the Figure 4. In addition, Table 1 shows that the conductivity of Au-Ag nanoalloys can also be tuned between the conductivity of Au and conductivity of Ag. The results show that the optical and electrical properties of Au-Ag nanoalloys can be tuned between the properties of Au NPs and Ag NPs.

Au-Ag nanoalloys were synthesized from the mixed solutions of gold and silver ions in various volume ratios called AuxAgy, where x and y were the volume fraction of Au and Ag ions, respectively. AuxAgy in various volume ratios has a different dielectric constant between Au (38.5 μΩ-cm) and Ag (19.4 μΩ-cm) as showed by Gaudry et al [25-26]. The dielectric constant variation as a function of volume ratios shifted the LSPR of Au-Ag nanoalloys. Since the dielectric constant was also related to the electrical conductivity, tuning the LSPR of Au-Ag nanoalloys may open the possibility to tune their electrical conductivity (as shown in Table 2) for more broader applications.

CONCLUSION

Au-Ag nanoalloys have been synthesized from the solution of gold and silver metal ions through photochemical reduction using femtosecond laser in 10 minutes irradiation times. The produced colloids were characterized using UV-Vis spectroscopy, XRD and DLS method. The result shows that not only optical properties but also the electrical properties of Au-Ag nanoalloys can be tuned between the properties of Au NPs and Ag NPs. LSPR of Au-Ag nanoalloys (manifested as their optical properties) can be tuned from 409.06 until 530 nm and the conductivity of Au-Ag nanoalloys can be tuned from 0.253 until 0.294 mS/cm. These results indicate the possibility of Au-Ag nanoalloys applications to have a more diverse range than that of pure Au and Ag NPs.

CONFLICT OF INTEREST

Authors declare that there is no conflict of interest in the published the manuscript.

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