Stabilization of Au-Ag Nanoalloys with Polyvinylpyrrolidone (PVP) as Capping Agent

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Abstract. Van der Waals attraction between nanoparticles will create aggregation, therefore, adding a capping agent is needed to stabilize the nanoparticles. We have synthesized Au₅₀Ag₅₀ nanoalloys from a mixture of silver and gold metal ions using a femtosecond laser irradiated for 5, 10, and 15 minutes. The process occurred in a water-only medium and in a water medium added with 0.01 wt% polyvinylpyrrolidone (PVP). Only Au₅₀Ag₅₀ with 5 minutes irradiation times that was characterized by TEM. From TEM result, PVP was proven to generate stabilization of the nanoparticles. It was confirmed that the nanoparticles in Au-Ag nanoalloys with PVP are more disperse than the Au-Ag nanoalloys without PVP. From the result, the particle size of Au-Ag nanoalloys without PVP is 10.72 nm, and 7.94 nm with PVP. This indicates that not only reducing the van der Waals attractive forces and stabilizing the nanoparticles, PVP can also reduce the particle size.

1. Introduction

Metal nanoparticles such as Au and Ag are interesting materials and are the most extensively studied materials because their Surface Plasmon Resonance (SPR) shows high absorption band in the visible region [1]. The Surface Plasmon Resonance is dependent on the size, shape and dielectric constant of the medium [2], thus it is very sensitive to the environment. This phenomenon is what makes metal nanoparticles promising materials in the field of optoelectronic and sensing [3].

The formation of Au nanoparticles (NPs) and Ag nanoparticles (NPs) into Au-Ag nanoalloys has been receiving a great deal of interest, especially in developing the possibility of combining both Au and Ag NPs properties. By combining both NPs, the optical, electrical and catalytic properties can be tuned [4, 5] and a more diverse range of applications can be explored [6, 7]. Formation of Au-Ag nanoalloys can be done using a photochemical reduction method with laser irradiation. This method is a bottom-up approach of metal salt in solution irradiated by laser [8, 9]. Aside from the numerous applications of Au-Ag nanoalloys, still, there is a challenge on how to control the stability of the nanoparticles.

Dispersion stability control in the synthesis of nanoparticles can be useful to develop chemical, biological or physical nanosensors [10]. In general, nanoparticles are unstable and tend to agglomerate because they are attracted to each other under the influence of van der Waals attractive forces at short
inter-particle distances. Thus, there must be a stabilization mechanism in which the nanoparticles cannot attract each other, hence the increase in the stability [11].

Aggregation in nanoparticles is described by Derjaguin-Landau-Verwey-Overbeak (DLVO) theory. A theory that has been developed and experimentally studied for decades, involving an alternative approach that is statically thermodynamics [12]. According to the DLVO theory, there are two forces that dominate the interaction between particles, namely van der Waals attractive force and electrostatic double layer (EDL) force [13]. The EDL force is a repulsive electrostatic force which can stabilize the nanoparticles when they are surrounded by a double layer of electric charges [14, 15].

Aggregation can be avoided with the use of a capping agent. A capping agent is usually used to coat and to stabilize the particles. Many of these agents also play a crucial role in the control of the size and shape of the nanocrystals [16, 17]. One of the most frequently used protective agents in metal nanoparticles synthesis is poly (N-vinyl-2-pyrrolidone) (PVP). This water-soluble polymer has been extensively used as a protecting agent against agglomeration of metal colloids [18].

Here, our purpose is to investigate the effect of PVP as a capping agent on the stabilizing process of the nanoparticles. It is expected that PVP as a capping agent can reduce the van der Waals attraction in Au50Ag50 nanoalloys synthesized from metal salt ions with the irradiation of femtosecond laser.

2. Experimental Methods
A high pulsed femtosecond laser was used to synthesize Au-Ag nanoalloys which had been made with a photochemical reduction method. The gold and silver metal ions were mixed in a 3 ml solution inside a 10 × 10 × 45 mm quartz cuvette. The solutions were prepared in a water-only medium and in a water medium with the addition of 0.01 wt% PVP which acts as a capping agent. The solutions of gold and silver metal ions with the concentration of 4.22 × 10⁻⁴ M were prepared separately by dissolving 98% potassium gold (III) chloride (K(AuCl₃)) and 99 % Ag Nitrate (AgNO₃).

We prepared a mixed solution between gold and silver ions. Then, Au50Ag50 (1.5 ml Au and 1.5 ml Ag) were irradiated for 5, 10 and 15 min. Surface Plasmon Resonance (SPR) spectra of Au50Ag50, both in a water-only medium and in a water medium with 0.01 wt% PVP’s addition, were then observed with a UV-Vis spectrophotometer. The Au50Ag50 with 5 min irradiation time was characterized with TEM to study the effect of PVP on particle distribution, stabilization and particle size.

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

3. Results and discussion
Photochemical reduction method was applied to synthesize the Au-Ag nanoalloys of Au50Ag50 samples. Au and Ag NPs were irradiated for 5, 10 and 15 minutes, respectively. The different time duration was applied to determine the optimum irradiation time for fabricating Au-Ag nanoalloys.

Ag NPs (Au0Ag100) and Au NPs (Au100Ag0) in water-only media were synthesized from a 3-ml-gold-metal ions and a 3-ml-silver-metal ions, respectively. They were synthesized inside a 10 × 10 × 45 mm³ quartz cuvettes and were irradiated by a femtosecond laser for 5, 10 and 15 minutes. The result shows that both Au and Ag NPs were already formed in 5 min irradiation time and were perfectly formed in 15 min irradiation time. The different irradiation time also affected the values of SPR spectra in Au and Ag NPs. Synthesis results along with SPR spectra of Ag and Au NPs are presented in figure 1 and figure 2.

The syntheses of Au and Ag NPs have influenced the formation of Au-Ag nanoalloys. If the Au and Ag NPs have different formation duration time, then the Au-Ag nanoalloys will not be formed. Figures 1 and 2 show that at 5 min irradiation time, Au and Ag NPs have the same properties which began to form and still continue to form at 15 min duration time. From figures 1 and 2, we can also see
that irradiation time affected the value of SPR. The long duration time will create a Coulomb explosion, which is related to the size reduction [19]. In addition, nanoparticles with different size will result in different values of SPR spectra as well. From figures 1 and 2, we can predict that Au-Ag nanoalloys would begin to form at 5, 10 and 15 min irradiation time.

Au50Ag50 nanoalloys were synthesized in a water-only medium and in a water medium with 0.01 wt% PVP’s addition. The addition of PVP in the synthesis of Au-Ag nanoalloys works as a capping agent. PVP will cap every nanoparticle that will eventually prevent the van der Waals attractive forces between nanoparticles to occur. By using photochemical reduction method, Au50Ag50 nanoalloys were synthesized with irradiation time of 5, 10 and 15 minutes. Figure 3 represents the synthesis results and SPR spectra of Au-Ag nanoalloys in a water-only medium, while figure 4 represents the results of Au-Ag nanoalloys in water medium with 0.01 wt% PVP’s addition.
From figures 3 and 4, Au-Ag nanoalloys had begun to form at 5 min irradiation time and still continue to form at 15 min irradiation time. The formation of Au-Ag nanoalloys is denoted by the orange-colored line with SPR spectra located at the center of Ag NPs and Ag NPs SPR peaks. In the figures, we could see that SPR peaks in all irradiation time show perfect Gaussian shape. Furthermore, starting from 5 to 15 min irradiation time, both Au-Ag nanoalloys in a water-only medium and in a water medium with 0.01 wt% PVP’s addition, tend to have similar behavior. They both display different SPR peaks caused by the Coulomb explosion.

Observation on SPR peaks alone cannot explain the effect of PVP on the increase of electrostatic forces which has higher value when compared to those of van der Waals attractive forces. TEM
characterization is needed for a better information on the particle distribution and could also provide a deeper analysis on the effect of PVP towards the reduced electrostatic forces. Here, the TEM analysis is focused on the Au50Ag50 at 5 min irradiation time as shown in figure 5. TEM images of Au50Ag50 in a water-only medium as seen in figure 5 (a), shows the particles aggregation with 10.72 nm of particle size. Figure 5 (b) shows TEM image of Au50Ag50 in water medium with 0.01 wt% PVP’s addition in which the particles distribution is more disperse than that of Au50Ag50 in a water-only medium. Besides the effect of PVP on the nanoparticles dispersion, PVP can also reduce the particle size. Au50Ag50 in water medium with PVP’s addition has particle size of 7.94 nm, smaller than those found in a water-only medium.

Au50Ag50 nanoalloys in a water-only medium have shown to create van der Waals attractive forces that would cause the nanoparticles to aggregate and attract each other. Each nanoparticle has electrical charges (positive charge and negative charge) around it. If there are two or more adjacent nanoparticles, then those nanoparticles will attract each other. Consequently, we need to reduce the van der Waals attractive forces by creating electrostatic repulsive forces higher than the van der Waals attractive forces. Hence, the nanoparticles will be in a stable condition. The addition of PVP surfactant is to act as a capping agent for every nanoparticle. With the cap, each of the nanoparticles will be stabilized and no aggregation will be visible.

However, if nanoparticles are not capped with surfactant, the van der Waals attractive forces will prevail. In this case, the particles would coagulate irreversibly in the deep primary potential well, forming large aggregation [20]. When the polymer surfactant (PVP) is added into the nanoparticles environment, the repulsive force will emerge. This is because, as the electrical charge on the particles surface adsorbed the polymer surfactant, the potential barrier would appear and thus hinder the

![Figure 5](image-url)

**Figure 5.** TEM images of Au50Ag50 nanoalloys irradiated for 5 min in: (a) water-only medium and (b) water medium with the addition of 0.01 wt% PVP.
aggregation. As the height of the potential barrier increased, the attractive force between particles would be decreased. When the repulsive force is strong enough, the particles will not be aggregating for a long period of time and the dispersion of the particles will be stabilized [21].

To thoroughly study the aggregation process in nanoparticles due to the van der Waals attractive force that involves kinetics equilibrium process, theoretical approach using simulations programs could be one the methods to be explored in the future. Widely known simulation-based programs such as Monte-Carlo, molecular dynamics, dissipative particles dynamics and the Brownian dynamics are just to name a few [22]. From our study in this report, we have demonstrated that aggregation and stabilization of nanoparticles are interesting and important phenomena; which would be a beneficial knowledge in the study of the synthesis of nanoparticles.

4. Conclusions

By using photochemical reduction method, we have synthesized Au-Ag nanoalloys in a water-only medium, and in a water medium with 0.01 wt% PVP’s addition. The added PVP in water medium functioned as a capping agent. This capping agent has few advantages, namely, reduced the van der Waals forces between nanoparticles, created electrostatic repulsive force and stabilized the nanoparticles. TEM result shows that particles distribution of Au-Ag nanoalloys in a water-only medium tends to aggregate. TEM images of Au-Ag nanoalloys in a water medium with PVP’s addition show that they are more disperse and smaller (7.94 nm) when compared to the nanoalloys in a water-only medium (10.72 nm). These results suggest that PVP helped to create stabilization of the nanoparticles in order to be successfully fabricated.

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