

Biological synthesis of bimetallic Au/Ag nanoparticles using Persimmon (*Diopyros kaki*) leaf extract

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Abstract—Persimmon (*Diopyros kaki*) leaf extract was used for the synthesis of bimetallic Au/Ag nanoparticles. Competitive reduction of Au³⁺ and Ag⁺ ions present simultaneously in solution during exposure to Persimmon leaf extract leads to the formation of bimetallic Au/Ag nanoparticles. UV-visible spectroscopy was monitored as a function of reaction time to follow the formation of Au/Ag nanoparticles. The synthesized bimetallic Au/Ag nanoparticles were characterized with energy dispersive X-ray spectroscopy (EDS), scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS). SEM images showed that large Au/Ag particles of 50-500 nm were formed with some cubic structure, while pure Ag particles obtained by reduction of only Ag⁺ ion were smaller with diameter of 15-90 nm and predominantly spherical. The atomic Ag contents of the bimetallic Au/Ag nanoparticles from EDS and XPS analysis were 36 and 71 wt%, respectively, suggesting that bimetallic Au core/Ag shell structure was formed by competitive reduction of Au³⁺ and Ag⁺ ions with Persimmon leaf extract.

Key words: Biological Synthesis, Nanoparticles, Plant Extract, *Diopyros kaki*, Bimetallic Gold/Silver

INTRODUCTION

Nanoparticles exhibit completely new or improved properties based on specific characteristics such as size, distribution and morphology, if compared with larger particles of the bulk material of which they are made [1-5]. Nanoparticles present a higher surface-to-volume ratio with decreasing size of nanoparticles. Specific surface area is relevant for catalytic reactivity and other related properties such as antimicrobial activity in silver nanoparticles. Value of nanomaterials increases from the bulk materials due to change of unique physical, mechanical, optical and electromagnetic properties. For example, the sales costs of silver and gold increase from \$95/lb silver and \$6,650/lb gold for standard grades, to \$415/lb silver and \$26,000/lb gold for nanoscale grades [6].

Nanoparticles can be produced through different methods, with chemical approaches being the most popular. However, these methods can not avoid the use of toxic chemicals in the synthesis protocol. Gold, silver and platinum nanoparticles are widely applied to human contact areas such as shampoos, soaps, detergents, shoes, cosmetic products and toothpaste as well as medical and pharmaceutical applications [7]. Therefore, there is a growing need to develop environmentally friendly processes of nanoparticles synthesis that do not use toxic chemicals. Biological methods of nanoparticles synthesis using microorganisms [8-10], enzymes [11], and plants or plant extracts [12] have been suggested as possible ecofriendly alternatives to chemical and physical methods. Using plants for nanoparticles synthesis can be advantageous over other biological processes because it eliminates the elaborate process of maintaining cell cultures and can also be suitably scaled up for large-scale

synthesis of nanoparticles [12].

We used several common Korean plant extracts to synthesize gold, silver and platinum nanoparticles and could obtain synthesis rates comparable to those of chemical methods by screening process and increasing the reaction temperature [13]. The particle size could also be controlled from 15 to 500 nm by changing temperature and composition of the reaction mixture. In addition to pure metallic nanoparticles, bimetallic nanoparticles either in the form of alloys or core-shell nanostructures are being increasingly investigated because of their unusual electronic/optical and catalytic properties [14]. In this study, we synthesized bimetallic Au/Ag nanoparticles by the competitive reduction of Au³⁺ and Ag⁺ ions using Persimmon leaf broth, and suggested that bimetallic Au core/Ag shell structure was formed through the characterization data.

MATERIALS AND METHODS

Persimmon (*Diopyros kaki*) leaves were collected and dried for 2 days at room temperature. The plant leaf broth solution was prepared by taking 5 g of thoroughly washed and finely cut leaves in a 300 mL Erlenmeyer flask with 100 mL of sterile distilled water and then boiling the mixture for 5 min before finally decanting it. They were stored at 4 °C and used within a week.

For synthesis of Au/Ag bimetallic nanoparticles, 190 mL of a 1 : 1 mM solution of AgNO₃ and HAuCl₄ was taken along with 10 mL of Persimmon broth. The reduction reaction was carried out in water bath at 95 °C with reflux. The Au/Ag bimetallic nanoparticle solution thus obtained was purified by repeated centrifugation at 15,000 rpm for 20 min followed by redispersion of the pellet in deionized water. UV-vis spectra were recorded as a function of reaction time on a UV-1650CP Shimadzu spectrophotometer operated at a resolution of 1 nm. After freeze drying of the purified Au/Ag bimetallic nanoparticles, the structure and composition were analyzed by scanning electron microscopy (SEM, Hitachi S-2500C), energy

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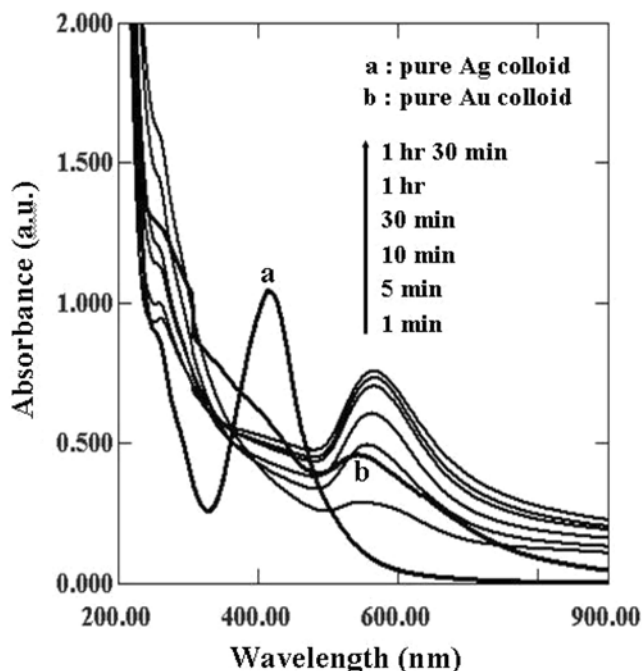


Fig. 1. UV-vis spectra recorded as a function of reaction time of 1 : 1 mM solution of AgNO_3 and HAuCl_4 with 5% *Diopyros kaki* leaf broth. Curves a and b represent UV-vis spectra of pure silver and gold nanocolloids, respectively.

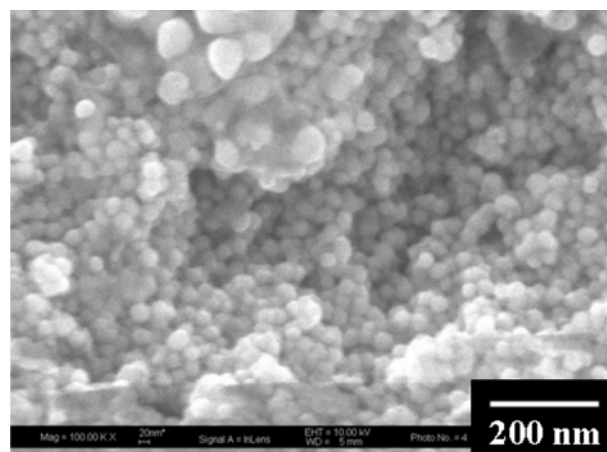
dispersive X-ray spectroscopy (EDS, Sigma), and X-ray photoelectron spectroscopy (XPS, ESCALAB 210).

RESULTS AND DISCUSSION

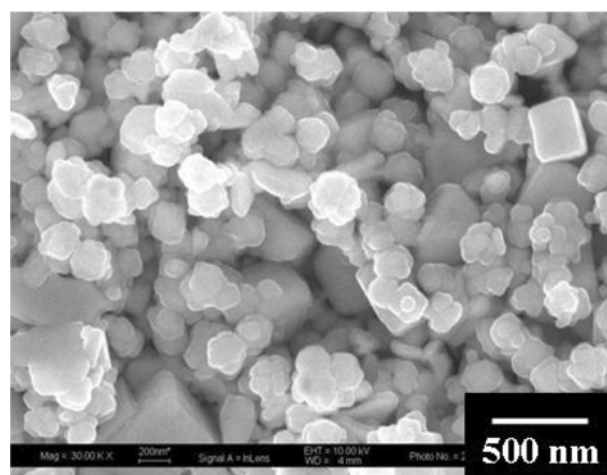
1. Synthesis of Bimetallic Au/Ag Nanoparticles

Reduction of the gold and silver ions to bimetallic nanoparticles during exposure to the Persimmon leaf extracts could be followed by UV-vis spectroscopy. It is known that gold and silver nanoparticles exhibit ruby-red and yellowish-brown color in aqueous solution due to excitation of surface plasmon vibrations in the metal nanoparticles [12]. Fig. 1 shows the UV-vis spectra recorded from the reaction medium as a function of reaction time using Persimmon leaf broth together with the spectra of pure metallic gold and silver nanoparticles. It is observed that the maximum absorbances of pure gold and silver occur at 544 and 420 nm, respectively. While the increase in intensity of the gold surface plasmon band for the Au/Ag bimetallic solution is quite distinct with some shift to 550-563 nm, a well-defined band corresponding to silver nanoparticles is not observed. Shankar et al. [12] obtained similar spectra for the Au/Ag bimetallic solution using Neem leaf broth and mentioned that the silver particles did not form a uniform layer around the gold nanoparticles, leading to considerable damping of a distinct silver plasmon vibration band at ca. 400 nm.

Fig. 2A and B show SEM images for the pure metallic silver and bimetallic Au/Ag particles, respectively, obtained with 5% Persimmon leaf broth at 95 °C. It is shown that relatively spherical and uniform silver nanoparticles were formed with diameters of 15-90 nm, while larger Au/Ag bimetallic particles with 50-500 nm were formed with some cubic structure. Regarding the reason of larger



(A)



(B)

Fig. 2. SEM images of (A) pure metallic silver nanoparticles formed with 1 mM AgNO_3 and 5% *Diopyros kaki* leaf broth at 95 °C and (B) bimetallic Au/Ag nanoparticles formed with 1 : 1 mM solution of AgNO_3 and HAuCl_4 with 5% *Diopyros kaki* leaf broth at 95 °C.

particles formation in Au/Ag bimetallics, we can hypothesize as follows. Gold nanoparticles are initially formed because the reduction rate of gold ion is faster than that of silver ion. Silver nanoparticles then assembled onto the surface of the gold nanoparticles possibly due to interactions such as hydrogen bonds and electrostatic interactions between the bioorganic capping molecules bound to the gold and silver nanoparticles.

2. EDS and XPS Analysis

EDS and XPS spectra recorded from the Au/Ag bimetallic particles are shown in Fig. 3A and B, respectively. EDS profile shows strong gold and silver signals along with a weak oxygen and carbon peak, which may originate from the biomolecules that are bound to the surface of the silver nanoparticles. Similar EDS profile was obtained with gold nanotriangles synthesized by using *Aloe vera* extract by Chandran et al. [15]. Together with transmission electron microscopy (TEM) images, they noted that nanoparticles synthesized from plant extracts are surrounded by a thin layer of some capping organic material from plant leaf broth. XPS spectrum shows

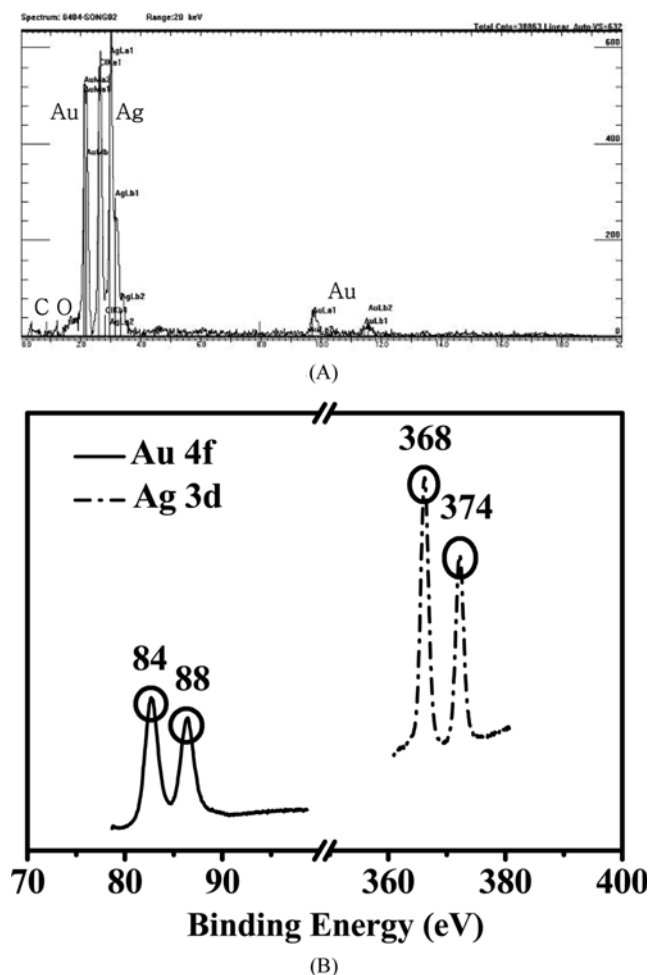


Fig. 3. Characterization of bimetallic Au/Ag nanoparticles formed with 1 : 1 mM solution of AgNO_3 and HAuCl_4 with 5% *Diopyros kaki* leaf broth at 95 °C. (A) Spot profile EDS spectrum. (B) XPS spectrum.

characteristic gold and silver peaks, suggesting that Au/Ag bimetallic nanoparticles are successfully synthesized by using Persimmon leaf broth in this study.

Shankar et al. [12] reported that bimetallic Au core/Ag shell nanoparticles were formed by competitive reduction of Au^{3+} and Ag^+ ions in the 1 : 1 molar mixture by Neem leaf broth. Although it is plausible that Au core/Ag shell nanostructures would be formed since the reduction rate of gold ion is faster than that of silver ion, no quantitative proofs on the core/shell nanostructures have been provided. We measured atomic contents of gold and silver in the bimetallic Au/Ag nanoparticles by EDS and XPS analysis (Fig. 4). The atomic Ag content from EDS analysis was 36 wt%, which was correlated with the theoretical atomic Ag content in the bimetallic Au/Ag nanoparticles synthesized from 1 : 1 molar mixture of Au^{3+} and Ag^+ ions. Meanwhile, the atomic Ag content from XPS analysis was 71 wt%, higher than that from EDS analysis. This shows that silver nanoparticles are richer near the surface of bimetallic Au/Ag nanoparticles because XPS is a surface chemical analysis technique that can be used to analyze from the top 1 to 10 nm of a material.

Biological methods of nanoparticles synthesis provide a new possibility of conveniently synthesizing pure metallic or bimetallic core-

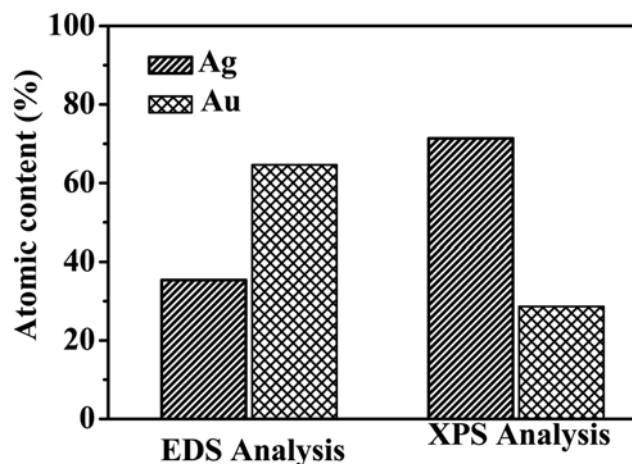


Fig. 4. Atomic content of bimetallic Au/Ag nanoparticles determined from EDS and XPS analysis. Nanoparticles were formed with 1 : 1 mM solution of AgNO_3 and HAuCl_4 with 5% *Diopyros kaki* leaf broth at 95 °C.

shell nanoparticles using natural products. However, the mechanism of biological nanoparticles synthesis is not fully understood. For gold nanoparticles synthesized extracellularly by the fungus *Fusarium oxysporum*, it was reported that the reduction occurs due to NADH-dependent reductase released into the solution [16]. With Neem leaf broth, it was reported that terpenoids are believed to be the surface-active molecules stabilizing the nanoparticles, and reaction of the metal ions is possibly facilitated by reducing sugars and/or terpenoids present in the Neem leaf broth [12]. More elaborate studies are required to elucidate the mechanism of biological nanoparticles synthesis.

CONCLUSION

An environmentally friendly method using Persimmon leaf extract was proposed to synthesize bimetallic Au/Ag nanoparticles. Large bimetallic Au/Ag particles of 50-500 nm were formed with some cubic structure, possibly due to interactions between the bioorganic capping molecules bound to the gold and silver nanoparticles, while pure Ag particles were smaller with 15-90 nm and predominantly spherical. From elemental analysis using EDS and XPS, it was shown that bimetallic Au core/Ag shell structure was formed by competitive reduction of Au^{3+} and Ag^+ ions with Persimmon leaf extract.

REFERENCES

1. Roadmap report on nanoparticles, W&W Espana s.l., Barcelona, Spain (2005).
2. J. H. Cha, K. S. Kim, S. Choi, S. H. Yeon, H. Lee, C. S. Lee and J. J. Shim, *Korean J. Chem. Eng.*, **24**, 1089 (2007).
3. S. Choi, K. S. Kim, S. H. Yeon, J. H. Cha, H. Lee, C. J. Kim and I. D. Yoo, *Korean J. Chem. Eng.*, **24**, 856 (2007).
4. Y. T. Yu and P. Mulvaney, *Korean J. Chem. Eng.*, **20**, 1176 (2003).
5. J. H. Fendler, *Korean J. Chem. Eng.*, **18**, 1 (2001).
6. J. N. Yoo, Proceedings of KICHe Meetings (2006).
7. D. R. Bhumkar, H. M. Joshi, M. Sastry and V. B. Pokharkar, *Pharm. Res.*, **24**, 1415 (2007).

8. T. Klaus, R. Joerger, E. Olsson and C.-G. Granqvist, *Proc. Natl. Acad. Sci. USA*, **96**, 13611 (1999).
9. Y. Konishi, K. Ohno, N. Saitoh, T. Nomura, S. Nagamine, H. Hishida, Y. Takahashi and T. Uruga, *J. Biotechnol.*, **128**, 648 (2007).
10. B. Nair and T. Pradeep, *Cryst. Growth Des.*, **2**, 293 (2002).
11. I. Willner, R. Baron and B. Willner, *Adv. Mater.*, **18**, 1109 (2006).
12. S. S. Shankar, A. Rai, A., Ahmad and M. Sastry, *J. Colloid Interf. Sci.*, **275**, 496 (2004).
13. J. Y. Song and B. S. Kim, *Proceedings of KICChE Meetings* (2007).
14. A. Rai, M. Chaudhary, A. Ahmad, S. Bhargava and M. Sastry, *Mater. Res. Bull.*, **42**, 1212 (2007).
15. S. P. Chandran, M. Chaudhary, R. Pasricha, A. Ahmad and M. Sastry, *Biotechnol. Prog.*, **22**, 577 (2006).
16. P. Mukherjee, S. Senapati, D. Mandal, A. Ahmad, M. I. Khan, R. Kumar and M. Sastri, *Chem. Bio. Chem.*, **5**, 461 (2002).