SYNTHESIS OF GOLD NANOPARTICLES FROM CHLOROAURIC ACID USING RED WINE

T. Pavliashvili[1], T. Kalabegishvili[2,3], M. Janjalia[2], E. Ginturi[2] and G. Tsertsvadze[4]

Keywords: gold nanoparticles, chloroauric acid, red wine, transmission electron microscopy, UV–Visible spectrophotometer.

Gold nanoparticles were synthesized from chloroauric acid using the red wine of two types. The synthesis was carried out at room temperature. The optical absorption spectrum of the obtained gold nanoparticles was studied by using a UV-visible spectrophotometer, and the structure and particle sizes – by a transmission microscope. It was found that the geometric shapes of nanoparticles depended on the concentration of the working solution and the reducing agent. Nanoparticle size distribution histograms were plotted and assessed. The applications of obtained results were defined.

*Corresponding Authors
E-Mail: pavliashvilitamaz@yahoo.com
[a] Institute of Micro- and Nanoelectronics, 13 I. Chavchavadze Ave., Tbilisi, 0179 Georgia
[b] I. Javakhishvili Tbilisi State University, 3 I. Chavchavadze Ave., Tbilisi, 0128 Georgia
[c] Ilia State University, Institute of Applied Physics, 3/5 K. Cholokashvili Ave., Tbilisi 0162, Georgia
[d] Georgian Technical University, 77 M. Kostava Str., Tbilisi 0175 Georgia

Introduction

Recently, gold nanoparticles have found wide application in medicine and biophysical research. They are also promising for designing the devices of a new generation. It is suggested by their unique properties. Unlike bulk gold, the gold nanoparticles possess ferromagnetic, catalytic and tunable optical properties. In particular, the optical properties of gold nanoparticles are determined by their plasmon resonance associated with the excitation of conduction electrons and localized in a wide spectral region, from visible to infrared, depending on the size, shape, and structure of nanoparticles.[1]

The gold nanoparticles are chemically stable and biocompatible. Various physical and chemical methods are used for the synthesis of gold nanoparticles. However, these methods are expensive and involve the use of toxic reducing agents. Hence preference is given to alternative environment-friendly methods of green chemistry. Recently it has been revealed that many biological objects such as plants, bacteria, fungi, etc. can transform the ions of inorganic metals into metal nanoparticles. For this purpose, they more often use plant extracts. Synthesis of nanoparticles with the help of green reducing agents has a number of advantages over other methods. Short synthesis time, low cost of the process, the safety of personnel and the environment, etc. makes this method attractive for production of nanoparticles. The use of plant extracts allows carrying out more convenient monitoring of nanoparticle size and shape and simplifying subsequent purification.[2]

Various plant extracts and dry red wine are used for the synthesis of metal nanoparticles. Healing properties of dry red wines are known since ancient times. The dry red wines have a complex chemical composition and contain ethyl and methyl alcohols, sugars (mainly glucose and fructose), and various organic acids (catechins and anthocyanins). From polyphenols, resveratrol is of special noteworthy. Resveratrol is contained in grape skins and seeds and passes into the wine from there during the process of its production. The content of resveratrol in the red wine varies from 0.2 to 5.8 mg L^{-1}. The content of resveratrol in the white wine is much less. This useful substance possesses antioxidant, anti-inflammatory and cardioprotective properties. It is also effective as a cancer-preventive.

Materials and Methods

In this work, the process of production of gold nanoparticles from chloroauric acid ($HAuCl_4$) by using the red wine Saperavi is discussed. The wine of two types was used: 1. The wine produced by ancient Georgian technology in qvevri (clay vessel) buried in the ground. 2. The wine produced in oak barrels. Red wine Saperavi is produced from the eponymous local grape cultivar in the province of Kakheti. Big clay vessels, so-called qvevri, are buried in such a way that its hole is at the level of the ground. Such a position of qvevri, which first the grape must is fermented and then the wine is aged in, provides the temperature of about 14 °C. This temperature is optimal for long-term storage of wine.

As is well known, the properties and flavor of wine depend on the grape variety, the place of its growth and the production technology. The main difference of the qvevri technology from the European one is that stems and seeds are not separated from grape flesh before fermentation. The European technology involves separation of seeds and stems from grape flesh and then pouring of grape juice into the vessels for fermentation. The wines produced by qvevri technology contain more tannin and polyphenols.

The synthesis was carried out at room temperature. The aqueous solution of $HAuCl_4$ of concentration 10^{-3} M was used. The wine was poured in small portions into the flask with the working solution. The Saperavi wine was used simultaneously as a reducing agent and a stabilizer of the solution. The changed color of the solution pointed to the formation of nanoparticles in it.

The optical transmission spectra of the nanoparticles were studied with the help of UV–Vis Spectrophotometer Sintra 10e. The absorption peak was recorded at 550 nm. The structure and sizes of nanoparticles were determined by using transmission microscope JEM–100SX. The size of nanoparticles varied over the range of 3 – 30 nm. Both types of wine showed good reducing and stabilizing properties.

The presence of gold nanoparticles was also confirmed by the appearance of absorption in the visible region at the wavelength of 550 nm. The optical transmission spectra of the solutions based on these wines were identical (Fig. 1).

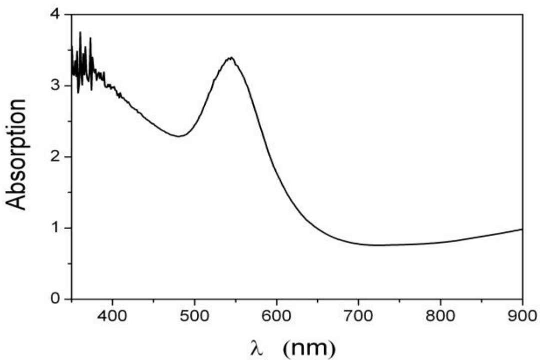

Figure 1. The optical transmission spectra of the red wine.

It was revealed that the geometric shape of nanoparticles depended on the concentration of the working solution, and on the ratio between the concentrations of the working solution and the reducing agent. In diluted solutions of both types of wine, nanorods, and spheroid and ellipsoid nanoparticles were formed (Figs. 2 and 3), while, with the excess of the reducing agent (wine), the nanoparticles of triangle, cubic, hexagons and other geometric shapes were formed (Figs. 4 and 5).

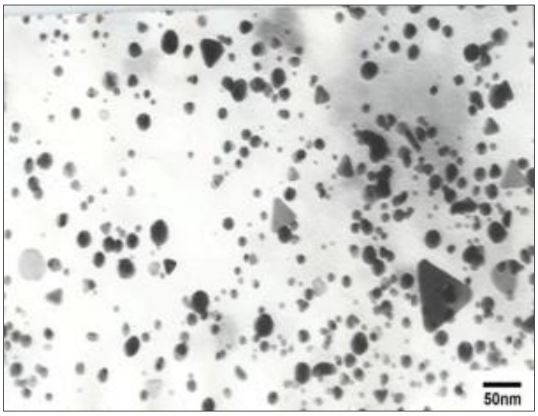

Figure 2. Microphoto of gold nanoparticles synthesized by using the red wine produced by the qvevri method.

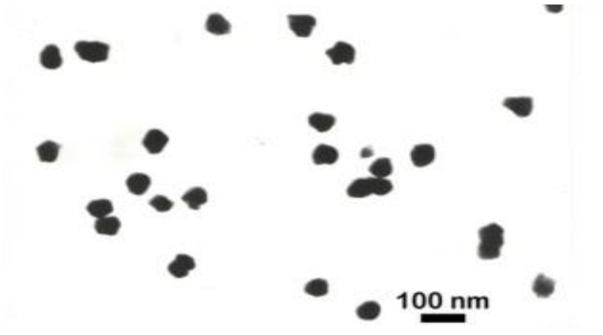

Figure 3. Microphoto of gold nanoparticles produced using the wine produced in oak barrels.

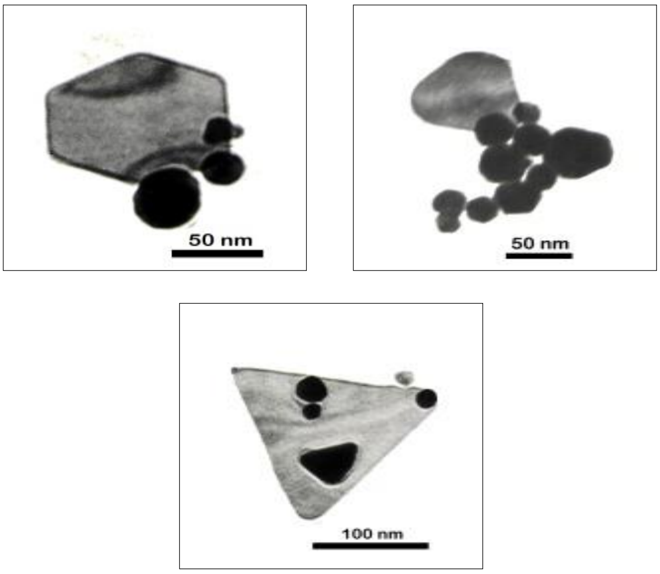

Figure 4. Microphoto of gold nanoparticles synthesized by using the supersaturated solution of the red wine produced by the qvevri method.

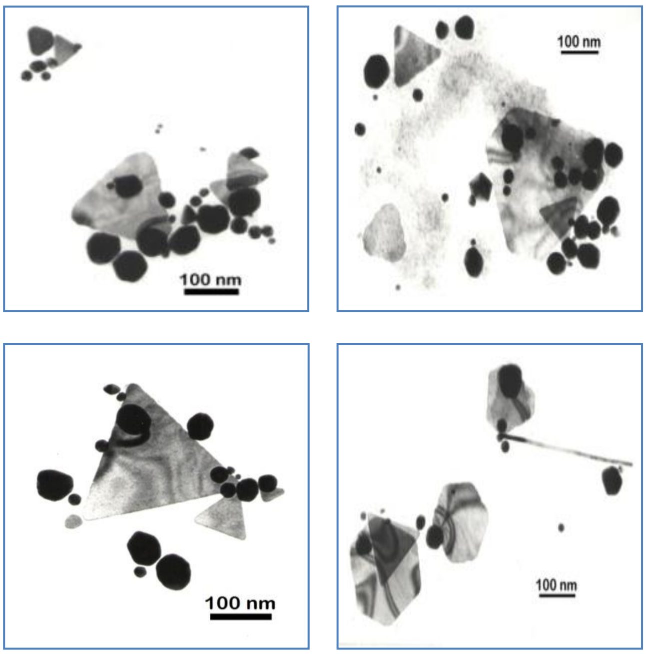

Figure 5 is continued in the next page.

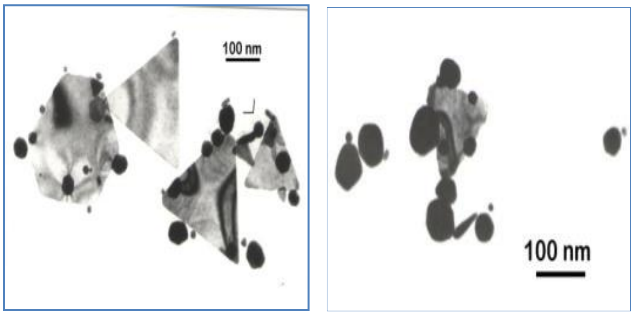

Figure 5. Microphoto of gold nanoparticles synthesized by using the diluted solution of the red wine produced in oak barrels.

To assess the size distribution of nanoparticles, relevant histograms were plotted (Figs. 6 and 7).

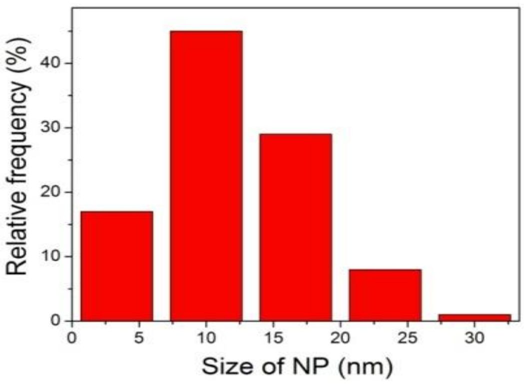

Figure 6. Distribution of gold nanoparticles synthesized by using the diluted solution of the red wine produced by the qvevri method.

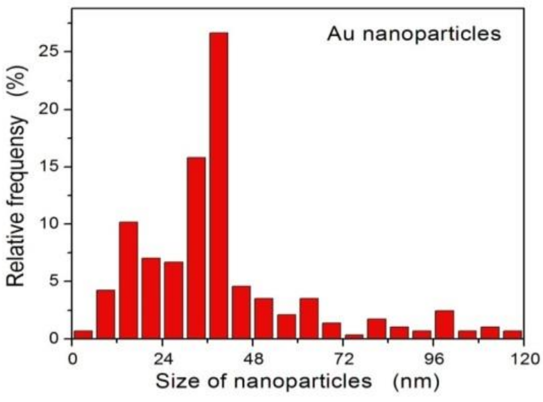

Figure 7. Distribution of gold nanoparticles synthesized by using the diluted solution of the red wine produced in oak barrels.

Conclusion

Gold nanoparticles of different geometric shapes and sizes were synthesized. We obtained interesting preliminary results that could find wide application in the field of biological research and medicine. The range of these applications is quite extensive. Here are given just some of them:

Visualization of cancer cells. Traditionally visualization of nanoobjects is carried out by using highly sensitive fluorescent tags. However, this technique is not devoid of shortcomings, which is expressed in photochemical instability and the need for expensive detectors. Plasmon-resonant gold particles are very bright. The scattering cross section of nanoparticles is by 5 – 7 orders of magnitude higher than the fluorescent molecule cross section. One of the widespread methods of detection of micro- and nano-objects is dark-field microscopy. In dark-field microscopy, only the light scattered by an object under the side lighting enters the lens. In the result, the scattering object glows brightly on the dark background. Besides, the nanoparticles are mainly accumulated on the surfaces of tumors. Due to these properties of nanoparticles, the gold nanoparticles have great opportunities for visualization and diagnostics of oncological diseases by optical microscopy in the dark field mode (resonant scattering optical microscopy). The nanoparticles can be detected by a common digital CCD camera.[3] The fact that the metal nanoparticles have plasmon resonance makes them promising for designing biosensors for diagnostics and treatment of oncological diseases.

Gold nanoparticles as containers for target delivery of medicines. Until recently spherical gold particles were mainly used in biomedicine.[4.] With the development of the technology of synthesis of nanoparticles, there emerged the nanoparticles of other shapes. For nanoparticles of different shapes and structure, the desired frequency of plasmon resonance can be achieved by varying the relative sizes. The formation of gold nanoparticles of various shapes during their synthesis with the red wine Saperavi indicates the prospects of their application to target delivery of medicines.

Photothermal therapy. Currently, gold nanoparticles are widely used in photochemical therapy (PCT) of oncological diseases.[5] The surface plasmon resonance of gold nanoballs in water solution is in the vicinity of 520 nm. The wavelength of surface plasmon resonance depends on the shape and size of nanoparticles, the distance between nanoparticles, and the local dielectric environment. The use of lasers in PCT of oncological diseases ensured controlled and targeted impact on cancer tissues. When the gold nanoparticles are used, to heat them up at the plasmon resonance wavelength, the nanoparticles have to be irradiated with laser radiation at 520 nm wavelength. As the radiation with such a wavelength does not pass through a biological tissue, it is an acute problem to synthesize gold nanoparticles with the surface plasmon resonance wavelength in the transparency window of the biological tissue, which is 800 – 900 nm. For this, we could modify the shapes of nanoparticles. In this connection, the synthesis of gold nanoparticles of various geometric shapes with red wine in a single technological cycle is interesting and promising. To clarify the mechanism of the synthesis process, additional studies are needed.

Acknowledgements

This paper has been presented at the 4th International Conference "Nanotechnologies," October 24 – 27, 2016, Tbilisi, Georgia (Nano – 2016).

References

[1]Dicman, L. A., Khebcov, N. G., *Acta Naturae*, **2011**, *3(2)*, 34-55. Cataldo, F., Ursini, O., Angelini, G., *Eur. Chem. Bull*., **2016**, *5(1)*, 1-7, DOI: http://dx.doi.org/10.17628/ecb.2016.5.1-7; Habashi, F., *Eur. Chem. Bull*., **2016,** *5(10)*, 416-419, DOI: http://dx.doi.org/10.17628/ecb.2016.5.416-419; Kalabegishvili, T. L., Murusidze, I. G., Kirkesali, E. I., Rcheulishvili, A. N., Ginturi, E. N., Gelagutashvili, E. S., Kuchava, N. E., Bagdavadze, N. V., Janjalia, M. V., Pataraya, D. T., Gurielidze, M. A., Frontasyeva, M. V., Zinicovscaia, I. I., Pavlov, S. S., Tsertsvadze, G. I., Gabunia, V. N., *Eur. Chem. Bull.*, **2015**, *4(1-3)*, 45-49, http://dx.doi.org/10.17628/ecb.2015.4.43-49;

[2]Yamamoto Y. and Hori. H., *Rev. Mater. Sci*., **2006**, *12*, 23-25.

[3]Makarov, V. V., Love, A. J., Sinitsina, O. V., Makarova, S. S., Yavlinski, I. V., Tal'ianski, M. E., Kalinina N. O., *Acta Naturae*, **2014**, *6(1)*, 35-44

[4]Yegorov, A. M., Gukasov, V. M., Ivanin, A. I., Rubtsova, M. I., Yaminskiy. I. V., The Use of Gold Nanoparticles in Biomedical Applications Utilizing Optical Methods. Innovatics and Expert Examination. *SRI FRCEC (Scientific Research Institute – Federal Research Center for Project Evaluation and Consulting Service*, **2014**, *2(13)*, 243.

[5]Meshalkin, Y. P., Bgatova. N. P., *J. Siberian Fed. Univ., Biol*., **2008**, *3(1)*, 248-253.

Received: 27.04.2017.
Accepted: 10.06.2017.