Green Chemistry Used in The Synthesis and Characterization of Silver and Gold Nanoparticles

Ramón Vallejo*, Paulina Segovia*a, **, Nora Elizondo*a, Odilón Vázquez*b, Víctor Coello**, Víctor Castaño***

*a Facultad de Ciencias Físico-Matemáticas, *b Instituto de Ingeniería Civil, Universidad Autónoma de Nuevo León, San Nicolás de los Garza, N. L., CP 66451, México, Tel.: (52-81) 83294030, Fax.: (52-81) 83522954, nelizond@yahoo.com

**CICESE, Monterrey, Km 9.5 Nva. Carretera Aeropuerto, PIIT, Apodaca, N. L., México, C.P. 66600, vcoello@cicese.mx

***Centro de Física Aplicada y Tecnología Avanzada, Universidad Nacional Autónoma de México, Boulevard Juriquilla 3001, Querétaro 76230, México, castano@fata.unam.mx

ABSTRACT

Gold (Au) and silver (Ag) nanoparticles have a diversity of interesting properties between which they emphasize the electrical ones, optical, catalytic and the applications in biomedicine like antibacterial and antiviral, same that depend on their morphology and size. The nanoparticles were synthesized using polyol and green methods. We made a comparison of these methods in order to investigate the influence of reaction parameters on the resulting particle size and its distribution. In the first method we use polyol process with poly (vinylpyrrolidone) (PVP) acting as a stabilizer and ethylenglycol as a reductor. The green method is an ecological synthesis technique. In this article, we made use of chemical compounds of plants in order to obtain ascorbic acid as reductor agent and saponins with surfactant properties. Here, we show that green method allows synthesize metallic nanoparticles and reduces the temperature requirement which is in contrast to the obtained with the polyol method.

Keywords: characterization, synthesis, metallic nanoparticles, green chemistry, polyol method

INTRODUCTION

Metallic nanoparticles are of great interest because of the modification of properties observed due to size effects, modifying the catalytic, electronic, and optical properties of the monometallic nanoparticles.[1-3] For this purpose, many colloidal methods of synthesis have been approached to obtain metallic nanoparticles, such as homogeneous reduction in aqueous solutions,[4]or phase transfer reactions,[5] with sodium citrate, hydrazine, $NaBH_4$, and lithium trietilborohydride ($LiBEt_3H$) as reducing agents, each of them yielding products with different physicochemical and structural characteristics.[6] Among these, the polyol method has been reported to produce small nanoparticles as the final product, easily changing composition and surface modifiers. This technique does not require an additional reducing agent since the solvent by itself reduces the metallic species. However, besides the stoichiometry and order of addition of reagents in the synthesis process, one of the most important parameters in the preparation is the temperature. Modifications in temperature influence the reaction by changing the stabilization of the nanoparticles formed and the surface modifiers, e.g., PVP, and the nucleation rate of the reduced metallic atoms.[7]

Gold (Au) and silver (Ag) nanoparticles have a diversity of interesting properties between which they emphasize the electrical ones, optical, catalytic and the applications in biomedicine like antibacterial and antiviral, same that depend on their morphology and size.

Characterization of these systems has been a difficult process where researchers have employed indirect measurements to identify the localization of the elements within the nanoparticles. A novel approach to study this kind of particles is based on the use of a high angle annular dark field (HAADF) technique, in a transmission electron microscope (TEM), which allows the observation of the elements due to atomic number, densities, or the presence of strain fields due to differences in lattice parameters. structure, the presence of surfactants or any other surface modifier besides the size of the particle and also by near-field scanning optical microscopy (NSOM) we determine the size of the particles.[8, 10]

The nanoparticles were synthesized using polyol and green methods. We made a comparison of these methods in order to investigate the influence of reaction parameters on the resulting particle size and its distribution. In the first method we use polyol process with poly (vinylpyrrolidone) (PVP) acting as a stabilizer and ethylenglycol as a reductor [11, 12]. Such procedure yield different morphologies of metal nanoparticles (including gold and silver) [13-15]. The green method is an ecological synthesis technique. There, we made use of chemical compounds of plants like rosa berberifolia and geranium manculatum in order to obtain ascorbic acid as reductor agent. Ascorbic acid ($C_6H_8O_6$) is an abundant component of plants which reaches a concentration of over 20 milimols in chloroplasts and occurs in all cell compartments including the cell wall. Additionally the acid has functions in photosynthesis as an enzyme cofactor (including synthesis of ethylene, gibberellins and anthocyanins) and in the control of cell growth [16]. We use for the synthesizes other kinds of plants also with compounds that have surfactant properties like saponins. Here, we show that green method reduces the temperature requirement which is in contrast to the obtained with the polyol method. The use of these natural components allows synthesize gold and silver nanoparticles.

EXPERIMENTAL SECTION

The polyol method was followed to obtain nanoparticles passivated with poly(vinylpyrrolidone) (PVP). Hydrogen tetrachloroaurate ($HAuCl_4$) (III) hydrate (99.99%), silver nitrate($AgNO_3$) (99.99%), and poly (N-vinyl-2-pyrrolidone) (PVP-K30, MW = 40000) were purchased from Sigma Aldrich, and 1,2-ethylenediol (99.95%) was purchased from Fischer Chemicals; all the materials were used without any further treatment. A 0.4 g sample of Poly (N-vinyl-2-pyrrolidone) (PVP) was dissolved in 50 mL of 1,2-ethylenediol (EG) under vigorous stirring, heating in reflux, until the desired temperature was reached (working temperatures ranged from 140 to 190 °C in increments of 10 °C). For the monometallic nanoparticles, a 0.1 mM aqueous solution of the metal precursor was added to the EG-PVP solution, with continuous agitation for 3 h in reflux.

The green method is an ecological synthesis technique. There, we made use of chemical compounds of plants like rosa berberifolia and geranium manculatum in order to obtain ascorbic acid as reductor agent from the extracts of these plants. Ascorbic acid ($C_6H_8O_6$) is an abundant component of plants, which reaches a concentration of over 20 milimols in chloroplasts and occurs in all cell compartments including the cell wall. We use for the synthesizes also cactus extracts with compounds that have surfactant properties like saponins.

The extracts were prepared as of 1 to 40 grams of the mentioned plants. Then from 10 to 50 milliliters of the extracts of these plants respectively were dissolved in water or in ethanol under vigorous stirring, heating in reflux, until the desired temperature was reached, when were drastical changes of the color of the solutions from yellow to dark brown in the case of silver nanoparticles and in the case of gold nanoparticles synthesizes the color of the solutions changed from pink to brown. For the gold and silver nanoparticles, a 0.1 mM aqueous solution of the metal precursor was added to the solutions with extracts, with continuous agitation for 30 minutes to 1 h in reflux in a working temperatures range from 60 to 100 Celsius.

The synthesis of colloidal metallic nanoparticles was carried out taking into account the optimization of the conditions of nucleation and growth. For this reason the variation of parameters like the concentration of the metallic precursors, reductor agent, amount of stabilizer, temperature and time of synthesis were realized.

For the electron microscopy analysis of the metallic nanoparticles, samples were prepared over carbon coated copper TEM grids. HAADF images were taken with a JEOL 2010F microscope in the STEM mode, with the use of a HAADF detector with collection angles from 50 mrad to 110 mrad. also by near-field scanning optical microscopy (NSOM) we determine the size of the particles. UV-vis spectra were obtained using a 10 mm path length quartz cuvette in a Cary 5000 equipment.

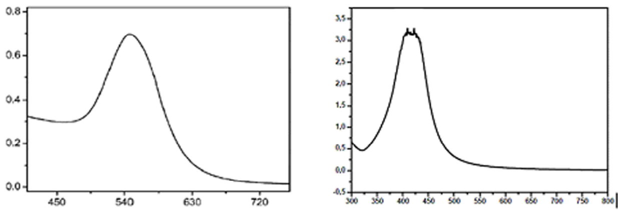
RESULTS AND DISCUSSION

The use of these natural components allows synthesize metallic nanoparticles. In the green method, gold and silver nanoparticles were prepared by the same reduction of $HAuCl_4$ and $AgNO_3$ respectively using extracts of plants, ascorbic acid as reducing agent obtained from geranium manculatum leaves, rosa berberifolia petals and like surfactants and simultaneous reducing agents in some cases were used cactus extracts.

The reaction time for the polyol method was around 3 hours and the nanoparticles were synthesized between 140 and 190 ^oC. In the green method the reaction time is reduced from 3 hours to 30 minutes until 1 hour at 60^oC.

In accordance with the studies of UV visible spectroscopy, whose plasmons are in figure 1 for Au and Ag synthesized nanoparticles the results shown an absorption energy in 547 nm and 415 nm respectively.

The TEM characterization reveal the formation of nanoparticles of these metals, independent of the employed method, with a size distribution between 20 and 120 nm for gold (see figure 2) and between 10 and 27 nm for the silver. The NSOM showed that the size of gold nanoparticles syntheised was of 15 nm with very narrow distribution.



Wavelength (nm) (1A) | Wavelength (nm) (1B)

Figure 1. UV-Visible absorption spectrum of the Au (1A) and Ag (1B) nanoparticles synthesized by polyol and green chemistry respectively.Formatting dimensions for manuscripts.

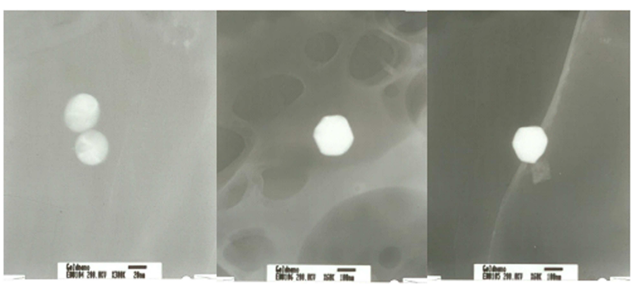


Figure 2. TEM images of Au nanoparticles synthesized by polyol method.

CONCLUSION

In this original work, we show that green method reduces the temperature requirement, which is in contrast to the obtained with the polyol method. The use of these natural components allows synthesize metallic nanoparticles with very narrow distribution.

ACKNOWLEDGMENT

Authors would like to acknowledge to Facultad de Ciencias Físico Matemáticas de la Universidad Autónoma de Nuevo León, México.

REFERENCES

[1]. Thomas, J. M.; Raja, R.; Johnson, B. F. G.; Hermans, S.; Jones, M. D.; Khimyak, T. *Ind. Eng. Chem. Res.* **2003**, *42*, 1563.

[2]. Bronstein, L. M.; Chernyshov, D. M.; Volkov, I. O.; Ezernitskaya, M. G.; Valetsky, P. M.; Matveeva, V. G.; Sulman, E. M. *J. Catal.* **2000**, *196*, 302.

[3]. Chushak; Y. G.; Bartell, L. S. *J. Phys. Chem B* **2003**, *107*, 3747.

[4]. Liz-Marzan, L. M.; Philipse, A. P. *J. Phys. Chem.* **1995**, *99*, 15120.

[5]. Han, S. W.; Kim, Y.; Kim, K. *J. Colloid Interface Sci.* **1998**, *208*, 272.

[6]. Schmid, G. *Clusters and Colloids, From theory to Applications*; VCH Publishers: Weinheim, Germany, 1994.

[7]. Turkevich, J.; Stevenson, P.; Hillier, J. *Discuss. Faraday Soc.* **1951**, *11*, 55.

[8]. Alvarez, M. M.; Khoury, J. T.; Schaaff, G.; Shafigullin, M. N.; Vezmar, I.; Whetten, R. L. *J. Phys. Chem. B* **1997**, *101*, 3706.

[9]. Henglein, A. *J. Phys. Chem. B* **2000**, *104*, 2201.

[10]. H. K. Park, Y. T. Lim, J. K. Kim, H. G. Park and B. H. Chung,Ultramicroscopy, **2008**, *108,10,* 1115.

[11].G. Cao, Nanostructures and Nanomaterials, synthesis, properties and applications, Imperial College Press (2004).

[12]. Y. Xia, P. Yang, Y. Sun, Y. Wu, B. Mayers, B. Gates, Y. Yin, F. Kim, H.Yan, Adv. Mater., 15, 353 (2003).

[13]. C. Burda, X. Chen, R. Narayanan and M. A. El-Sayed, Chem. Rev., 2005, 105, 1025.

[14]Y. Xia and N. J. Halas, Mater. Res. Soc. Bull., 2005, 30, 338.

[15]. N. L. Rosi and C. A. Mirkin, Chem. Rev., 2005, 105, 1547.

[16]. Nicholas Smirnoff, Glen L. Wheeler , Critical Reviews in Biochemistry and Molecular Biology, 2000, Vol 35, No. 4, Pages 291-314.