GOLD NANOPARTICLE FORMATION BY OAT AND WHEAT BIOMASSES

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ABSTRACT

In this study, the bio-reduction of Au(III) to Au(0) by wheat biomass and the subsequent production of gold nanoparticles of various shapes and sizes is presented. The dry biomass was ground and sieved to 100 mesh in order to assure a uniform particle size and having more area of biomass exposed to the gold. Wheat biomass was exposed to a 0.3mM potassium tetrachloroaurate solution at pH values of 2, 3, 4, 5, and 6 for 3.5 hours at room temperature. After that time, the biomass pellets were analyzed using a high resolution JOEL-4000 Fx microscope in order to characterize the gold nanoparticles. Results showed that wheat biomass produced nanostructures of the following morphologies: Fcc tetrahedral, Fcc hexagonal platelets, irregular shaped, rod shaped, decahedral multiple-twined, and icosahedral multiple-twined. However, the highest percent of the nanoparticles formed had a particle size ranging from 10-30 nm in diameter.

Key words: wheat biomass, gold, nanoparticles

INTRODUCTION

Use of gold nanoparticles dates back to the 16th century when they were used for both medical purposes and for the staining of glass and silverware. However, in recent times, nanoparticles have drawn the attention of scientists and engineers because of their extensive application in the development of new technologies such as the chemical industry, electronics, catalysis, and biotechnology at the nanoscale (Tanaka, 1999). Gold nanoparticles have been widely studied because their special properties allow their potential utilization in nanoelectronics and semiconductors (Brust et al., 1998; McConnell et al., 2000; Thomson and Collins, 1992; Dawson and Kamant, 2001). Gold nanoparticles have also been studied for their potential application in analytical methods such as colorimetric techniques, which are used for the determination of heavy metal ions in aqueous solutions (Youngjin et al., 2001). In biology, gold nanoparticles are used for the development of biosensors and DNA labeling (Kohler et al., 2001; Schatz and Lazarides, 2000). However, all of these applications demand nanoparticles with a well-defined size and shape, which requires special QA/QC production conditions.

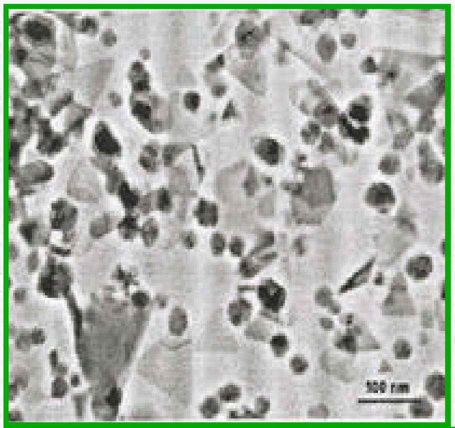
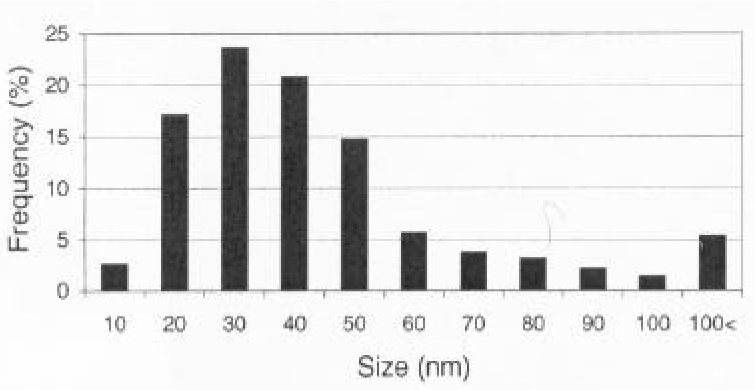


Figure 1. Gold nanoparticles produced by wheat biomass at pH 2.

Current techniques utilized in the production of gold nanoparticles with a well-defined size and shape are often divided into wet and dry methods. Wet methods usually involve the chemical oxidation of salts via hazardous substances such as sodium borohydride, hydroxylamine, tetrakishydroxymethylphosphonium chloride (THPC), and poly vinylpyrrolidone (PVP) (Vorobyova et al., 2001; Koel et al., 2001; Esumi et al., 2001; Halas et al., 1998; Han et al., 1999). Dry methods include ultraviolet irradiation, aerosol technology, and lithography (Chen et al., 1999; Magnusson et al., 1999; Tolles, 1996). Although these methods may successfully produce pure, well-defined gold nanoparticles, they remain quite expensive and are potentially dangerous to the environment. Intensive efforts are constantly being made in the development of cost effective and environmentally safe methods regarding the bio-reduction of gold and subsequent formation of gold nanoparticles. In such efforts, materials such as sugar-persubstituted, poly (amidoamine) dendriomers (Esumi et al., 2000), and *Medicago sativa* (alfalfa) biomass (Gardea-Torresdey et al., 1999) have been studied. The studies have shown that alfalfa biomass reacted with gold in aqueous solutions from gold nanoparticles with similar shapes to those obtained by physical

Figure 2. Size distribution of gold nanoparticles produced by wheat biomass at pH 2.



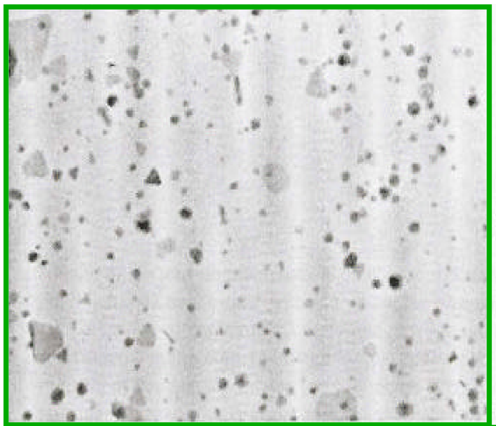


Figure 3. Gold nanoparticles produced by wheat biomass at pH3.

methods (Gardea-Torresdey et al., 1999). Thus, we hypothesized that other biological materials may also provide the chemical stability needed for the formation of gold nanoparticles.

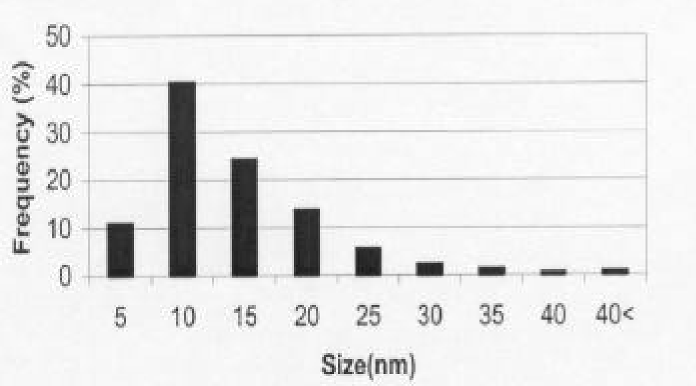
The present paper reports the use of *Triticum aestivum* (wheat, Delicias variety) biomass as a cost-effective and environmentally friendly alternative in the bio-production of gold nanoparticles.

PROCEDURE

Wheat by-product (consisting of shoots and leaves) was collected from the Juarez Valley, Chihuahua, Mexico, after the harvest of the grain. The biomass was carefully washed with deionized water and oven dried at 95°C for one week. The dry biomass was ground and sieved to 100 mesh in order to have particles of uniform size and more area of biomass exposed to the gold. Prior to the execution of the experiment, the sieved biomass was washed twice with HCl 0.01M and twice with deionized water in order to remove any material that might interfere with the binding of Au(III) and the formation of the nanoparticles.

The washed biomass was separated in several samples of 10 mg. Each sample was exposed to 2 ml of a 0.03mM Au(III) solution (prepared from potassium tetrachloroaurate salt). The pH values of the

Figure 4. Size distribution of gold nanoparticles produced by wheat biomass at pH3.



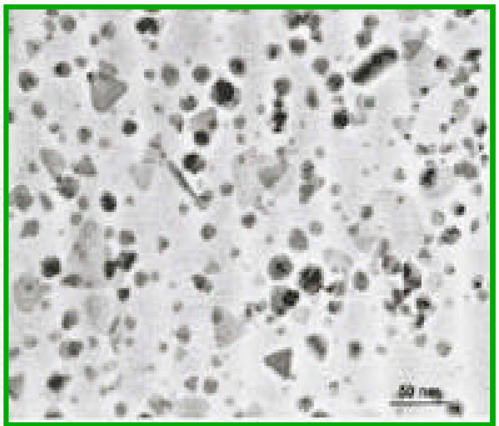


Figure 5. Gold nanoparticles produced by wheat biomass at pH 4.

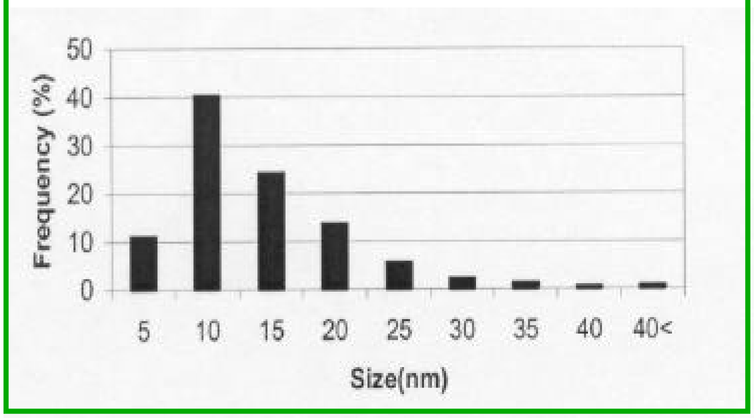
solutions containing the biomass were adjusted to 2, 3, 4, 5, and 6, using different low concentrations of HCl and NaOH as needed. After the adjustment of the pH, the samples were rocked for 3.5 hours and then analyzed using a high resolution JOEL-4000 Fx microscope, following the same procedure previously described for the analysis of gold nanoparticles formation by alfalfa biomass (Gardea-Torresdey et al., 1999).

RESULTS AND DISCUSSION

The wheat biomass solutions exposed to the Au(III) changed in color as the time of exposition was augmented. After one hour of exposition, the color of the solutions adjusted at pH values of 5, 3, and 4 changed from transparent to pink-violet. Solutions adjusted at pH 2 and pH 6 changed from clear to dark purple color after two hours of exposure. Such changes in color usually occur when a metal changes its oxidation state. In this case, presumably different functional groups present in the cell walls of the wheat biomass reduced Au(III) to Au(0).

The microscopy analysis of samples of the wheat biomass reacted with gold solutions at the pH values described above showed the presence of gold nanoparticles varying in shapes and size. The observed

Figure 6. Size distribution of gold nanoparticles produced by wheat biomass at pH 4.



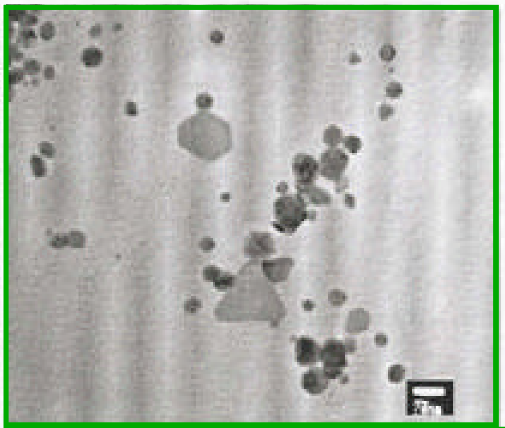
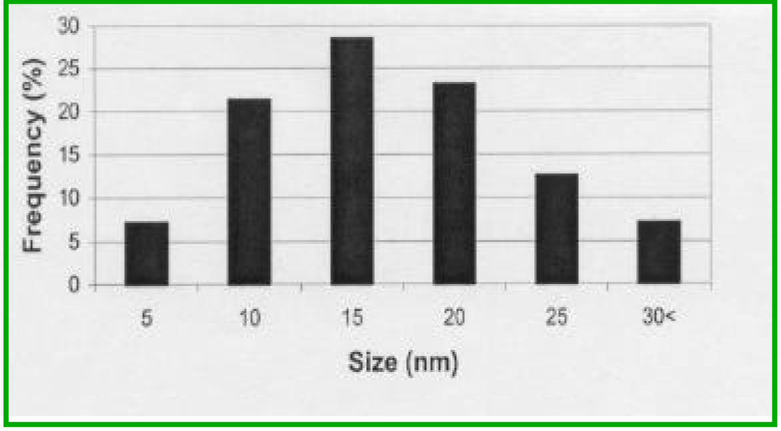


Figure 7. Gold nanoparticles produced by what biomass at pH 5.

shapes of these nanoparticles over the range of pH studied were the following: Fcc tetrahedral, Fcc hexagonal platelets, irregular-shape nanoparticles, decahedral multiple-twined, truncated icosahedral, and rod-shape nanoparticles. It is important to note that the truncated icosahedral nanoparticle had been observed only through the reaction of alfalfa biomass with the Au(III) solution (Gardea-Torresdey et al., 1999; Ascencio et al., 2000). The rod-shaped nanoparticles have been produced mainly by electrodeposition (Van der Zade et al., 2000; Van der Zar et al., 1997) and had incidentally not been reported in previous literature as a product of reaction of gold solution with an agricultural by-product. However, the number of rod nanoparticles observed using wheat biomass was minimal when compared with the number of other shapes observed in the figures described.

Figure 1 shows that wheat biomass-Au(III) solution adjusted at pH 2 mostly produced nanoparticles of irregular shape. Figure 2 shows the size distribution of gold nanoparticles formed at pH 2. Frequency of each size was determined by measuring the diameter of the nanoparticles. After classification, they were reported as a percentage of the total amount of nanoparticles present in the micrograph. The

Figure 8. Size distribution of gold nanoparticles produced by wheat biomass at pH5.



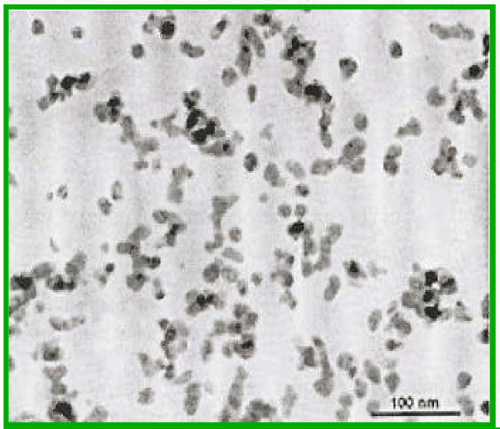


Figure 9. Gold nanoparticles produced by wheat biomass atpH 6.

size-distribution graph shows that most of the nanoparticles had sizes between 30 and 40 nm in diameter. However, at this pH, some of the nanoparticles observed were of 100 nm or more in size. These nanoparticles are very similar to the gold nanoparticles formed by alfalfa biomass as reported by Gardea-Torresdey et al. (1999).

The nanoparticles produced by wheat biomass-Au(III) solution adjusted at pH 3 are shown in Figure 3. This figure shows that these nanoparticles are smaller than those produced by the wheat biomass-Au(III) solution adjusted at pH 2, which is confirmed by the size-distribution graph shown in Figure 4. This figure shows that the majority of the nanoparticles formed at pH 3 had a diameter ranging between 10 and 20 nm; this indicates that while there was a reduction in size at this pH, there was an increase in the uniformity of the nanoparticles produced. In addition, at pH 3 the number of rod-shape nanoparticles increased.

Figure 5 shows the gold nanoparticles produced by the wheat biomass-Au(III) solution adjusted at pH 4, and the frequency of the nanoparticles' sizes is presented in Figure 6. Figure 5 shows that the shapes of the nanoparticles found at pH 4 were similar to those formed at pH 2 and 3. On the other hand, this

Figure 10. Size distribution of gold nanoparticles produced by wheat biomass at pH 6.

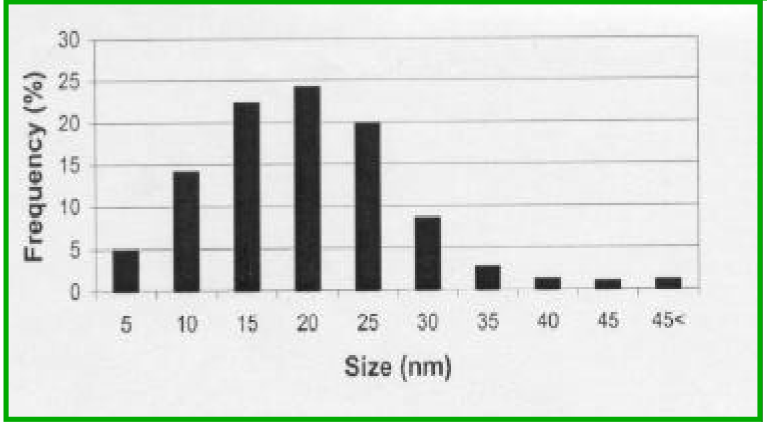


figure shows that most of these nanoparticles had an average size of 10 nm in diameter. Most of the particles were decahedral multiple-twined, icosahedral multiple-twined, and irregular shaped. The small difference in size of the nanoparticles formed at this pH shows that this method might provide an alternative for the controlled production of the size of gold nanoparticles by wheat biomass, which is essential for their use in nanotechnology.

When the pH was raised to 5, shapes of the observed nanoparticles were very similar to those observed at the previous pH values (Figure 7). However, from this figure, one can see that the rod-shaped nanoparticles were not formed at pH 7. As observed in Figure 8, most of the nanoparticles found at pH5 were approximately 15 nm in diameter.

The nanoparticles produced by the wheat biomass-Au(III) solution adjusted at pH 6 are shown in Figure 9. This figure shows that at pH 6, the Fcc tetrahedral, the rod-shaped, and the Fcc hexagonal platelets were not formed. Additionally, Figure 10 shows that the majority of the nanoparticles formed at pH 6 had a particle size ranging between 15 and 25 nm in diameter. According to Chow and Sukoski (1994), when using gold sol formation methods, the first gold nanoparticles formed are the largest ones, which fall apart in due time, giving shape to smaller nanoparticles. This is perhaps the reason why most of the nanoparticles encountered in these experiments had diameters between 10 and 30 nm, depending on the pH of the reaction.

CONCLUSIONS

The pellets of wheat biomass-Au(III) solution, adjusted at different pH values and observed with high-resolution transmission electron microscopy (TEM), demonstrated that wheat biomass is able to produce gold nanoparticles ranging from 5 to 100 nm in diameter. However, most of the particles had a particle size in the range of 10 to 30 nm. Many forms of gold nanoparticles were observed in this study; however, the rod-shaped nanoparticles formed by the wheat biomass had never before been observed from the reaction of Au with an agricultural by-product. Several studies, such as time and temperature dependence, ionic strength effect, and ultraviolet irradiation, will be performed in the future in order to improve our understanding of the mechanism of formation and the control of the shape of the gold nanoparticles produced by wheat biomass.

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REFERENCES

Ascencio J.A., Perez M., and Jose-Yacaman M., 2000. A Truncated Icosahidral Structure Observed in Gold nanoparticles, Surf. Sci., 447, pp. 73-80.

Brust M., Bethell D., Kiely C.J., and Schiffrin D.J., 1998. Self-Assembly of Gold Nanoparticle Thin Film with Nonmetallic Optical and Electronic Properties, Langmuir, 14, pp. 5425-5429.

Chen Z.Y., Zhou Y., Wang C.Y., and Zhu Y.R., 1999. A Novel Ultraviolet Irradiation Technique for Shape-Controlled Synthesis of Gold Nanoparticle at Room Temperature, Chem. Mater, 11, pp. 2310-2312.

Chow M.K., and Zukoski C.F., 1994. Gold Sol Formation Mechanisms: Role of Colloidal Stability, J. Coll. Interf. Sci., 165, pp. 97-109.

Dawson A., and Kamat P.V., 2001. Semiconductor-Metal Nanocomposited. Photoinduced Fusion and Photocatalysis of Gold-Capped TiO_2 (TiO_2/Gold) Nanoparticles, J. Phys. Chem., 105, pp. 960-966.

Esumi K., Hosoya T., Suzuki A., and Torigoe K., 2000. Spontaneous Formation of Gold Nanoparticles in Aqueous Solutions of Suger-Persubstituded Poly(amidoamine) Dendriomers, Langmuir, 16, pp. 2978-2980.

Esumi K., Kameo A., Suzuki A., Torigoe K., Yoshimura T., Koide Y., and Shosenji H., 2001. Preparation of Gold Nanoparticles Using 2-vinylpyridine Telomers Possessing Multi-Hydrocarbon Chain as Stabilizer, Coll. Surf., 176, pp. 233-237.

Gardea-Torresdey J.L., Tiemann K.J., Gamez G., Dokken K., Tehuacamanero S., and Jose-Yacaman M. 1999. Gold Nanoparticles Obtained by Bio-Precipitation from Gold(III) Solutions, J. Nanop. Res., 1(3), pp. 397-404.

Halas N.J., Westcott S.L., Oldenburg S.J., and Lee T.R., 1998. Formation and Adsorption of Clusters of Gold Nanoparticles onto Functionalized Silica Nanoparticle Surfaces, Langmuir, 14, pp. 5396-5401.

Han M.Y., Quek C.H., Huang W., Chew C.H., and Gan L.M., 1999. A Simple and Effective Chemical Route for the Preparation of Uniform Nonaqueous Gold Colloids, Chem. Mater, 11, pp. 1144-1147.

Koel B.E., Meltzer S., Resch R., Thompson M.E., Madhukar A., Requicha A.A.G., and Will P., 2001. Fabrication of Nanostructures by Hydroxylamine Seeding of Gold Nanoparticle Templates, Langmuir, 17, pp.1713-1718.

Kohler J.M., Csaki A., Reichert J., Moller R., Straube W., and Fritzsche W., 2001. Selective Labeling of Oligonucleotide Monolayers by Metallic Nanobeads for Fast Optical Readout of DNA Chips, Sens. Act. B., 76, pp. 166-172.

Magnusson M.H., Deppert K., Malm J., Bovin J., and Samuelson L., 1999. Size-Selected Gold Nanoparticles by Aerosol Technology, Nanos. Mat., 12, pp. 45-48.

Magnusson M.H., Deppert K., Malm J., Bovin J., and Samuelson L., 1999. Gold Nanoparticles: Production, Reshaping, and Thermal Charging, J.Nanop. Res., 1, pp. 243-251.

McConnell W.P., Novak J.P., Brousseau III L.C., Fuierer R.R., Tenent R.C., and Feldheim D.L., 2000. Electronic and Optical Properties of Chemically Modified Metal Nanoparticles and Molecularly Bridged Nanoparticles, J. Phys. Chem, 104, pp. 8925-8930.

Schatz G.C., Lazarides A.A., Kelly K.L., and Jensen T.R., 2000. Optical Properties of Metal Nanoparticles Aggregates Important in Biosensors, J. Mol. Struc. (Theochem), 529, pp. 59-63.

Tanaka. K, 1999. Nanotechnology Towards the 21st Century, Thin Solid Film, 341, pp. 120-125.

Thomson D.W., and Collins I.R., 1992. Electrical Properties of the Gold-Aqueous Solution Interface, J. Coll. Interf. Sci., 152(1), pp. 197-204

Tolles W.M., 1996. Nanoscience and Nanotechnology in Europe, Nanotechnology, 7, pp. 59-105.

Van der Zande B.M.I., Bohomer M.R., Fokkink L.G.J., and Schoneberg C., 1997. Aqueous Gold Sols of Rod-Shaped Particles, J. Phys. Chem., 101, pp. 852-854.

Van der Zande B.M.I., Bohomer M.R., Fokkink L.G.J., and Schoneberg C., 2000. Colloidal Dispersion of Gold Tods: Synthesis and Optical Properties, Langmuir, 16, pp. 451-458.

Vorobyova S.A., Sobal N.S., and Lesnikovich A.I., 2001. Colloidal Gold, Prepared by Interphase Reduction, Coll. and Surf., 176, pp. 273-277.

Youngjin K., Johnson R.C., and Hupp J.T., 2001. Gold Nanoparticle-Based Sensing of “Spectroscopically Silent” Heavy Metal Ions, Nano Lett., 1, pp. 165-167.