

HRTEM characterization of gold nanoparticles produced by wheat biomass

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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 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 three and a half hours at room temperature. After that time, the biomass pellets were analyzed using a high resolution transmission electron microscope, JEOL-4000 EX, in order to characterize the gold nanoparticles. The results showed that wheat biomass produced nanostructures of the following morphologies: Fcc tetrahedral (T), decahedral (Dh), hexagonal (He), icosahedral multitwinned (I), irregular shape (Irr), and rod shape nanoparticles. The highest percent of the nanoparticles formed had a particle size ranging from 10-30 nm.

Keywords: Wheat biomass, Gold, Nanoparticles, HRTEM.

En este estudio se presenta la bio-reducción de Au(III) a Au(0) por la biomasa de trigo y la formación de nanopartículas de oro. La biomasa de trigo fue lavada, molida y tamizada para incrementar el área de biomasa expuesta a la solución de Au. La biomasa de trigo fue reaccionada con una solución 0.3 mM de tetraclorourato de potasio a pH de 1, 2, 3, 4, 5 y 6 por un periodo de tres horas y media a temperatura ambiente. La biomasa fue analizada usando un microscopio JEOL-4000 EX de alta

resolución para caracterizar el tamaño y forma de las nanoestructuras obtenidas. Las nanopartículas observadas fueron: Fcc tetraedral (T), decaedral (Dh), Hexagonal (He), Icosaedral “multitwinned” (I), forma irregular (IRR), y nanopartículas con forma de columnas. El mayor porcentaje de nanopartículas obtenidas fueron aquellas de 10-30 nm de diámetro.

Descriptores: Biomasa de trigo; oro; nanopartículas; HRTEM.

Introduction

The 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 [1]. Gold nanoparticles have been widely studied because their special properties allow their potential utilization in nanoelectronics and semiconductors [2-5]. 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 [6]. In biology, gold nanoparticles are used for the development of biosensors and DNA labeling [7,8]. However, all of these applications demand nanoparticles with a well-defined size and shape, which requires special QA/QC production conditions.

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, tetrakis(hydroxymethyl)phosphonium chloride (THPC), and poly vinylpyrrolidone (PVP) [9-13]. Dry methods include ultraviolet irradiation, aerosol technology, and lithography [14-17]. 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 sugarpersubstituted poly (amidoamine) dendriomers[18] and *Medicago sativa* (alfalfa) biomass [19], have been studied. The studies have shown that alfalfa biomass reacted with gold in aqueous solutions form gold nanoparticles with similar shapes to those obtained by physical methods [19]. 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* *delicias* variety (wheat) biomass, as a cost effective and environmentally friendly alternative in the bio-production of gold nanoparticles.

Experimental details

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 0.01M HCl 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 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 during three and a half hours and then analyzed using a high resolution JEOL-4000 EX microscope, following the same procedure previously described for the analysis of gold nanoparticles formation by alfalfa biomass [19].

Results and Discussion

The wheat biomass solutions exposed to Au(III) changed in color as the time of exposition increased. After one hour of exposure, 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. Previous investigations demonstrated that different functional groups naturally present in death plant tissues are able to bind and reduce gold ions [19]. 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 shapes of these nanoparticles over the range of pH studied are shown in Fig. 1. Some of this shapes are Fcc tetrahedral (T), decahedral (Dh), hexagonal (He), icosahedral multitwinned (I), irregular shape (Irr), and rod shape nanoparticles, which are pointed out by arrows on the micrographs. It is important to note that the truncated icosahedral nanoparticle had been previously observed only through the reaction of alfalfa biomass with the Au(III) solution [19,20]. The rod shaped nanoparticles have been produced mainly by electrodeposition [21,22], and had incidentally not been reported in previous literature, as a product of reaction of a 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 below.

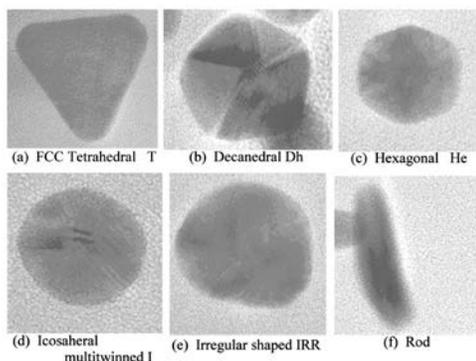


FIGURE 1. Classification of gold nanoparticles obtained in this study.

Figure 2(a) shows that wheat biomass-Au(III) solution adjusted at pH 2 mostly produced nanoparticles of irregular shape. Figure 2(b) shows the size distribution of gold nanoparticles formed at pH 2. The frequency of each size was determined by

measuring the diameter of the nanoparticles [23]. After classification, they were reported as a percentage of the total amount of nanoparticles present in the micrograph. The 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. [19].

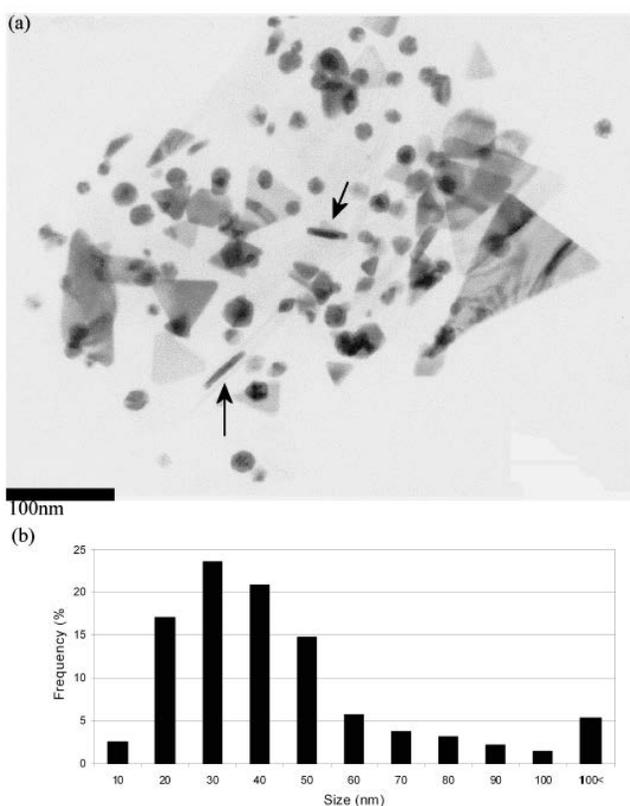


FIGURE 2. (a) Gold nanoparticles produced by wheat biomass at pH 2. (b) Size distribution of gold nanoparticles produced by wheat biomass at pH 2.

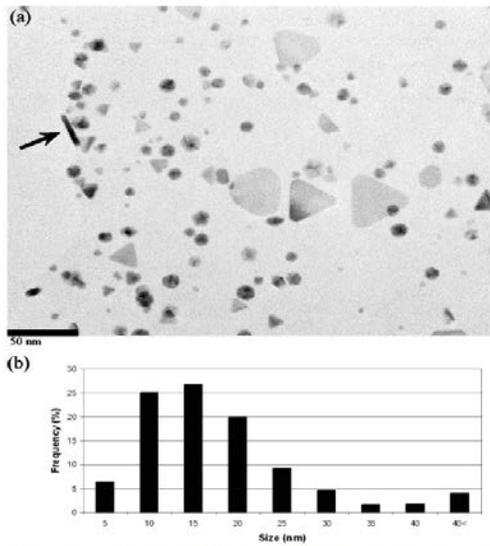


FIGURE 3. (a) Gold nanoparticles produced by wheat biomass at pH 3. (b) Size distribution of gold nanoparticles produced by wheat biomass at pH 3.

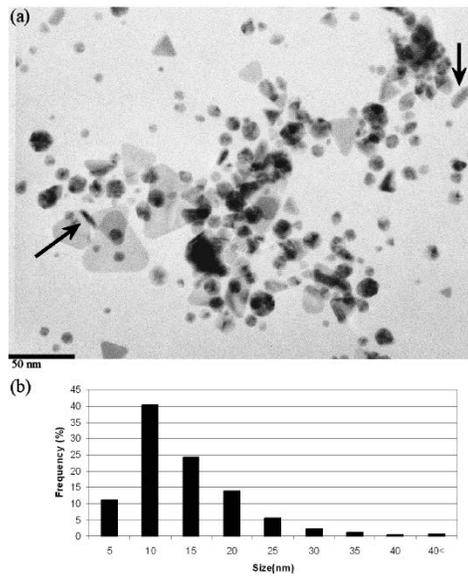


FIGURE 4. (a) Gold nanoparticles produced by wheat biomass at pH 4. (b) Size distribution of gold nanoparticles produced by wheat biomass at pH 4.

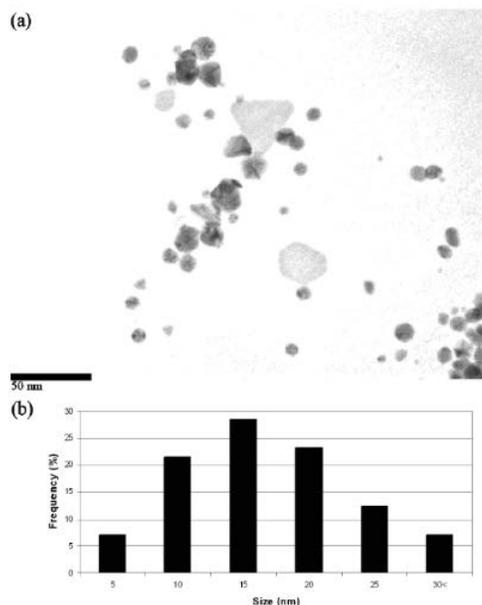


FIGURE 5. (a) Gold nanoparticles produced by wheat biomass at pH 5. (b) Size distribution of gold nanoparticles produced by wheat biomass at pH 5.

The nanoparticles produced by wheat biomass-Au(III) solution adjusted at pH 3 are shown in Fig. 3(a). 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 Fig. 3(b). 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 4(a) displays 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 Fig. 4(b). Figure 4(a) 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 shows that most of these nanoparticles had an average size of 10 nm in diameter. Most of the

particles were decahedral multiple twinned, icosahedral multiple twinned, 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, the shapes of the observed nanoparticles were very similar to those observed at the previous pH values [Fig. 5(a)]. However, from this figure one can see that the rod shape nanoparticles were not formed at pH 5. As observed in Figure 5(b), most of the nanoparticles found at pH 5 were approximately of 15 nm in diameter.

The nanoparticles produced by the wheat biomass-Au(III) solution adjusted at pH 6 are shown in Fig. 6(a). This figure shows that at pH 6 the Fcc tetrahedral, the rod shaped, and the hexagonal platelets were not formed. Additionally, Fig. 6(b) 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 Zukoski [24], when using gold solution 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.

The pellets of wheat biomass-Au(III) solution adjusted at different pH values and observed with high-resolution transmission electron microscopy, 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 shape 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

1. K. Tanaka, *Thin Solid Film*. 341 (1999) 120.
2. M. Brust, D. Bethell, C.J. Kiely, and D.J. Schiffrin, *Langmuir* 14 (1998) 5425.
3. W.P. McConnell et al., *J. Phys. Chem* 104 (2000) 8925.

4. D.W. Thomson and I.R. Collins, *J. Coll. Interf. Sci.* 152 (1992) 197.
5. A. Dawson and P.V. Kamat *J. Phys. Chem.* 105 (2001) 960.
6. K. Youngjin, R.C. Johnson, and J.T. Hupp, *Nano Lett.* 1 (2001) 165.
7. J.M. Kohler et al., *Sens. Actuators B.* 76 (2001) 166.
8. A.A. Lazarides, G.C. Schatz, K.L. Kelly, and T.R. Jensen, *J. Mol. Struc.* 529 (2000) 59.
9. S.A. Vorobyova, N.S. Sobal, and A.I. Lesnikovich, *Colloids Surf. A* 176 (2001) 273.
10. S.R.R Meltzer et al., *Langmuir* 17 (2001) 1713.
11. K. Esumi et al., *Colloids Surf. A* 176 (2001) 233.
12. S.L Westcott, N.J. Halas, S.J. Oldenburg, and T.R. Lee, *Langmuir* 14 (1998) 5396.
13. M.Y. Han, C.H. Quek, W. Huang, C.H. Chew, and L.M Gan, *Chem. Mater* 11 (1999) 1144.
14. Z.Y. Chen, Y. Zhou, C.Y.Wang, and Y.R. Zhu, *Chem. Mater* 11 (1999) 2310.
15. M.H. Magnusson, K. Deppert, J. Malm, J. Bovin, and L. Samuelson, *Nanostruct Mater.* 12 (1999) 45.
16. M.H. Magnusson, K. Deppert, J. Malm, J. Bovin, and L. Samuelson, *J. Nanopart. Res.* 1 (1999) 243.
17. W.M. Tolles, *Nanotechnology* 7 (1996) 59.
18. K. Esumi, T. Hosoya, A. Suzuki, and K. Torigoe, *Langmuir* 16 (2000) 2978.

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19. J.L. Gardea-Torresdey et al., J. Nanopart. Res. 1 (1999) 397.
20. J.A. Ascencio, M. Perez, and M. Jose-Yacaman, Surf. Sci. 447 (2000) 73.
21. B.M.I. Van der Zande, M.R. Bohomer, L.G.J Fokkink, and C. Schoneberg, Langmuir 16 (2000) 451.
22. B.M.I Van der Zande, M.R. Bohomer, L.G.J. Fokkink, and C.J Schoneberg, J. Phys. Chem. B 101 (1997) 852.
23. G. Berhault et al., J. Catal. 198 (2001) 9.
24. M.K. Chow and C.F. Zukoski, J. Colloid Interface Sci. 165 (1994) 97.

