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Chapter 21

Use of plants in biotechnology: Synthesis of metal nanoparticles by inactivated plant tissues, plant extracts, and living plants

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Abstract

The biological production of metal nanoparticles is becoming a very important field in chemistry, biology, and materials science. Metal nanoparticles have been produced chemically and physically for a long time; however, their biological production has only been investigated very recently. The biological reduction of metals by plant extracts has been known since the early 1900s; however, the reduction products were not studied. Furthermore, the synthesis of nanoparticles using plant materials, for the most part, has only recently been studied within the last three decades, while the production of nanoparticles using living plants has only been studied in the last half decade. The synthesis of metal nanoparticles using biological materials has been shown to produce nanoparticles of the same shapes and sizes as those produced through chemical or physical methods. For example alfalfa, wheat, and oat biomasses are able to reduce Au(III) to Au(0) forming face centered cubic (FCC), tetrahedral, decahedral, hexagonal, icosahedral multitwinned, irregular shape, and rod shape gold nanoparticles. Most of these nanoparticles had sizes ranging from 10 to 50 nm in diameter. Also it has been demonstrated that living alfalfa plants are capable of reducing Au(III) and Ag(I), producing gold and silver nanoparticles. The use of high resolution-TEM showed that the plants formed small silver nanoparticles with sizes averaging from 2 to 20 nm in diameter. These results have proven that biological materials provide an environmentally friendly or green chemistry method to produce invaluable materials because the biosynthesis eliminates the need to use harsh or toxic chemicals. The synthesis of metal nanoparticles using plant-derived materials is a simple yet effective method for the production

of nanoparticles. Finally, the applications of nanoparticles are making the fields of nanoscience and nanotechnologies grow rapidly. Researchers have found uses for nanoparticles in medicine, catalysis, bio-sensors, chemical sensors, environmental remediation, semi-conductors, and photovoltaic devices, among others.

21.1. Introduction

Microscopic particles whose size is measured in nanometers (10^{-9} m) are called nanoparticles. These particles have very special properties which are used for the production and applications in technological devices. This new technology, known as nanotechnology, has applications in catalysis, chemical industry, electronics, and electro-optical devices, among others (Brust et al., 1998; Martin and Mitchell, 1998; Armendariz et al., 2004a,b). In the long term, nanotechnology intends to be able to manipulate individual atoms and molecules for applications in different fields of industry (Tanaka, 1999).

The existence of inorganic nanoparticles was recognized about 435 years ago when Paraselsus described the preparation of *aurum potabile*, which was found to contain very thinly divided gold (Caseri, 2000). Since then, several methods to produce metal nanoparticles have been described. Current techniques for manufacturing nanoparticles have been catalogued as wet and dry methods. Wet methods regularly entail the use of substances such as sodium borohydride, hydroxylamine tetrahydroxymethylphosphonium chloride, and polyvinylpyrrolydone (Westcott et al., 1998; Han et al., 1999; Esumi et al., 2001; Meltzer et al., 2001; Vorobyova et al., 2001; Armendariz et al., 2004a). Dry methods comprise lithography, ultraviolet irradiation, and aerosol technology (Tolles, 1996; Deppert et al., 1998; Zhou et al., 1999; Magnusson et al., 1999a,b; Kammler et al., 2001; Armendariz et al., 2004b).

So far, using wet and dry methods researchers have produced nanoparticles of metals including magnesium, silicon, titanium, vanadium, chromium, manganese, iron, cobalt, nickel, copper, zinc, niobium, barium, cesium, and tungsten (Bae and Oh, 2003; Bunge et al., 2003). Other researches have obtained high-purity metal nanoparticles of gold, silver, platinum, palladium, rhodium, ruthenium, copper, and/or indium (Yanagimoto et al., 2005). Additionally, efforts have been made to control the particle size. Goia and Matijevic (1999) found that by changing the pH of a tetrachloroaurate-isoascorbic acid solution it is possible to keep primary particles or to get much larger and uniform particles due to aggregation. On the other side, Magnusson et al. (1999a,b) produced size-selected gold nanoparticles $\leqslant 30$ nm by passing gold aerosol though a device which uses UV light to create free electrons and positively charged particles. Sau et al. (2001) used UV to irradiate gold particles ranging in size from 5 to 20 nm and they obtained larger particles ranging from 20 to 110 nm. Using ultrasonic field, varying solution temperature and the position of the reactor, Okitsu et al. (2001) were able to form gold nanoparticles of definite size. Other researchers have used size exclusion chromatography to separate gold nanoparticles (Wei and Liu, 1999; Wei et al., 1999). In addition, using surfactant-directed growth Busbee et al. (2003) obtained nanorods from spherical gold nanoparticles used as seeds. Recently, Gardea-Torresdey and coworkers reported the formation of metal nanoparticles by inactivated and living tissues of (*Medicago sativa*) alfalfa and (*Chilopsis linearis*) Desert willow (Gardea-Torresdey et al., 1999, 2002a,b,c,d, 2003, 2005).

21.2. Metal uptake by plants

The metal uptake by plants has been documented elsewhere (Blaylock and Huang, 2000; Reeves and Baker, 2000). This review will be mainly focused on the uptake of gold and silver by plants. According to Reeves and Baker (2000), the first report on metal accumulating plants date back to 1855. Other reports concerning the unusual high accumulation of certain metals in plant tissues appeared more than 50 years ago (Reeves and Baker, 2000; Blaylock and Huang, 2000). More recently, researchers have focused their attention on the uptake of precious metals and the possibility of using plants for phytomining. Gold has been one of the most studied metals. Starting in the late 1970s, Girling, Peterson, and coworkers published a series of papers describing the gold accumulation by plants (Girling and Peterson, 1978; Girling et al., 1979; Girling and Peterson, 1980). At the beginning of the 1980s appeared a review authored by Brooks (1982), where he reviewed the biological method of prospecting gold. In this review, the author stated the fact that gold can be found in vegetation as product of a mineralization process. The author summarized the number of plants species, origin, gold content, and type of soil where the plants were grown. The data reviewed by the author indicated that the gold content of dry vegetation is usually about 10% of that of the substrate. According to Erdman and Olson (1985), the wood ash of Douglas-fir from Idaho grown in an Au-bearing stockwork contained up to 14 mg kg^{-1} of Au. However, the use of plants for Au prospecting has problems such as the localization of Au in plant tissues and the variation of Au concentrations due to season. Later on, other researchers gave attention to the use of plants for phytomining and phytoremediation of valuable metals.

Researchers from New Zealand have dedicated time and effort to determine the application of plants for metal extraction, especially gold (Anderson et al., 1998; Lamb et al., 2001). The possibility of phytomining of metals such as nickel and thallium has also been studied (Anderson et al., 1999). More recently, Gardea-Torresdey and coworkers have studied the uptake of gold and silver by alfalfa and desert plants (Gardea-Torresdey et al., 2002a,b,c,d, 2003, 2005). Gomez (2002) cultivated alfalfa plants in precious metals-enriched solid media. He found that the plants cultivated for 14 days in medium containing platinum at $10\,\text{mg}\,\text{l}^{-1}$ accumulated more than 100 mg platinum per kg of shoot dry weight. However, the amounts of gold and silver accumulated were lower. For gold the plants exposed to $10\,\text{mg}\,\text{l}^{-1}$ concentrated 56 mg Au per kg of gold in the shoot dry tissues, but the plants exposed to $40\,\text{mg}\,\text{l}^{-1}$ of silver concentrated 11 mg Ag per kg of shoot dry tissue. Attempts have been made to increase the uptake of gold by plants adding naturally occurring chemicals such as thiocyanate or thiosulfate to a gold-rich soil on which plants are growing. It is hypothesized that plants may accumulate the complexed gold as a function of evapotranspiration; however, there is no knowledge about the form of gold distributed through plant tissues. Gardea-Torresdey and coworkers (2005) found that in desert willow (*Chilopsis linearis*), the addition of $10^{-4}\,\text{mol}\,\text{l}^{-1}$ NH_4SCN to 2.5×10^{-5} M Au solution increased the gold concentration by approximately 595%, 396%, and 467% in the roots, stems, and leaves, respectively, compared to the Au concentration obtained without the use of NH_4SCN.

21.3. Formation of metal nanoparticles by inactivated plant biomass

The use of biomass for metal removal from aqueous solutions has been amply documented in the literature. This technology, known as biosorption, emerged in the 1980s and obtained attention because it has shown to be very promising for the removal of contaminants from effluents in an environmentally friendly approach (Gardea-Torresdey et al., 1996a; Volesky, 2001). Biosorbents are generally low-priced because they are either naturally abundant or found as waste material from certain processes (Bailey et al., 1999). Common sources of biosorbents are bacteria, algae, fungi, plant-derived, and animal-derived. Inactivated biomass does not need maintenance and is not sensitive to high concentrations of pollutants. On the other hand, living organisms are frequently affected by high concentrations of contaminants (Gardea-Torresdey et al., 1996b).

Table 21.1. Plant biomaterials studied for the removal of metals from aqueous solutions

Pollutant	Biomaterial	Source
Heavy metals	Pine bark Alfalfa Oat Hops Orange peel Papaya Chickpea Saltbush	Al-Asheh and Duvnjak, 1997; Gardea-Torresdey et al., 2000a, 2002a,b; Ajmal et al., 2000; Saeed et al., 2005a,b; Sawalha et al., 2005
Precious metals	Alfalfa Hops	Gardea-Torresdey et al., 2000b, 2002c; Parsons et al., 2003; Herrera et al., 2003; Lopez et al., 2005
Lanthanides and actinides	Alfalfa	Gardea-Torresdey et al., 2004; Parsons et al., 2005

Several researchers have studied plant-derived materials to remove a wide variety of elements from aqueous solutions. Examples of biomaterials that have been successfully used in the removal of heavy metals are shown in Table 21.1. As shown in this table, plant-derived materials have been extensively studied for the removal toxic heavy metals. Less attention has been given to the use of plant biomass for recuperating precious metals and actinides and lanthanides elements. However, the earliest reports of silver and gold reduction by non-living plant tissues occurred in the 1920s and 1930s. In 1921, a researcher by the name of Molisch reported on the microchemistry of plants and the reduction of silver by chlorophyll (Molisch, 1921). Later, Iwase (1928) reported on the production of gold sols produced by the aqueous extract of fresh leaves. He noted that the color of the solution was not as vivid red as particles obtained by the Veimarn tartrate method for the reduction of gold salts. In the 1950s, the reduction of silver nitrate by plant cells was investigated (Nagai, 1951). The study was aimed at determining the chemical species in cells of leaf extracts responsible for the reduction of the silver nitrate. It was determined that ascorbic acid was responsible for silver nitrate in spinach, white clover, sorrel, gladiolus, *Vicia sativa*, broad bean, *Acuba japonica*, normal and elongated seedlings of barley, and the fruit of garden pepper. Nagai also noted that 3,4-dihydroxyphenylalanine in *V. faba* has a strong reducing capacity. Dalal (1979) investigated the reduction of silver ions on three plant materials and concluded that the ascorbic acid was responsible for the reduction. In addition, he concluded that silver nitrate was a specific reagent for localizing ascorbic acid in plant tissues. For the most part, with the exception of the gold sols production using plant extract, the aforementioned studies only report on the reduction of silver ions by plant materials as a tool to determine ascorbic acid. However, these studies are the first indications that plant materials have the ability to reduce metal ions to form particles either nanoparticles or microparticles.

Gardea-Torresdey et al. (1999) reported for the first time the production of gold nanoparticles by a plant biomass. These researchers reacted a 0.1 M Au(III) solution (from potassium tetrachloroaurate) with 10 mg of ground alfalfa biomass at various pH values. The decanted biomass was observed by using a high resolution JEOL-4000 Fx microscope and a JEOL 2010 microscope fitted with EDS analysis. The results demonstrated that the biomass was effective at binding and reducing the Au(III) to Au(0) forming nanoparticles of different forms and sizes. The particles found had tetrahedral, face centered cubic (FCC), hexagonal, irregular, decahedral, and icosahedral forms. The results also suggested that the most frequent shape for the smaller particles was the icosahedral, while for the largest the decahedral and tetrahedral were most abundant shapes. The authors concluded that the particles formed by alfalfa biomass were similar in structure to the particles obtained by chemical methods. As for the mechanisms involved in the nanoparticle formation by the biomass, the authors concluded that three moles of chloride ions are released per mole of gold adsorbed. In addition, they found that both amino and carboxyl functional groups on the alfalfa biomass are involved in the reduction process. The X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) spectroscopy suggested that the Au(III) reduction goes through Au(I) to Au(0) (Gardea-Torresdey et al., 2002c).

The formation of gold nanoparticles by other biomasses has also been studied by Gardea-Torresdey's research group. Armendariz et al. (2004a,b) characterized the gold nanoparticles formed by wheat biomass exposed to a 0.3 mM potassium tetrachloroaurate solution at pH values of 2–6 for three and a half hours at room temperature. Through the observation of the reacted biomass with a JEOL-400 EX microscope, the researchers concluded that wheat biomass was able to reduce Au(III) to Au(0) forming FCC tetrahedral, decahedral, hexagonal, icosahedral multitwinned, irregular shape, and rod shape nanoparticles. This was the first report about the formation of rod shape nanoparticles by biomaterials. Most of the observed particles were 1030 nm in diameter. The stem biomass of oat (*Avena sativa*) was also studied as a reducing agent for Au(III). A 0.1 mM solution of Au(III) (from tetrachloroaurate) was reacted for 1 h with powdered oat biomass at pH values of 2–6. As in the case of wheat, oat biomass formed FCC tetrahedral, decahedral, hexagonal, icosahedral multitwinned, irregular shape, and rod shape nanoparticles. This is the second report about the formation of rod shape nanoparticles by biomaterials. Fig. 21.1 shows TEM micrographs to provide a visualization of some of the typical nanoparticles created using biomass (in this case hops biomass) in aqueous solution. Fig. 21.2A shows the TEM micrograph of a triangular (twinned) nanoparticle while Fig. 21.2B shows the structure of a rod-shaped nanoparticle, Fig. 21.2C shows an icosahedral nanoparticle, and Fig. 21.2D shows a decahedral nanoparticle. On the other hand, Table 21.2 shows that pH controls the size of the nanoparticle formed by the biomasses. At pH values of 3 and 4, oat and wheat biomasses formed nanoparticles whose diameter varied from 10 to 20 nanometers. In addition, pH controlled the shape of the

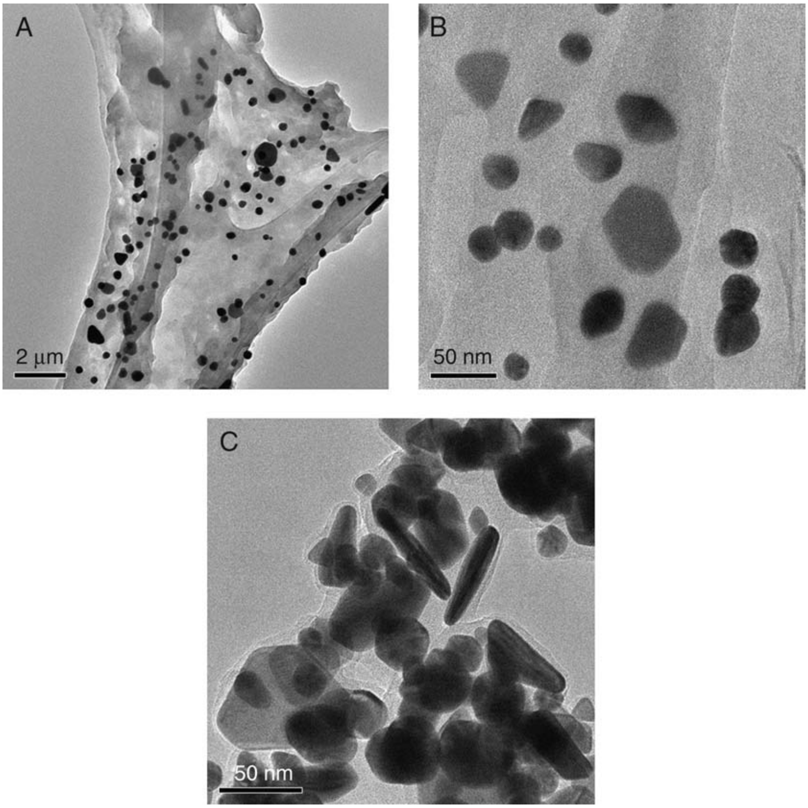

Figure 21.1. Low-resolution TEM of gold nanoparticles formed on hops biomass and in the aqueous reaction solution. A. Gold nanoparticles immobilized on the inactivated hops biomass, B. Magnified view of gold nanoparticles immobilized on the biomass showing a large hexagonal platelet, and C. Gold nanoparticles formed in solution during the reaction of hops biomass with tetrachloroaurate.

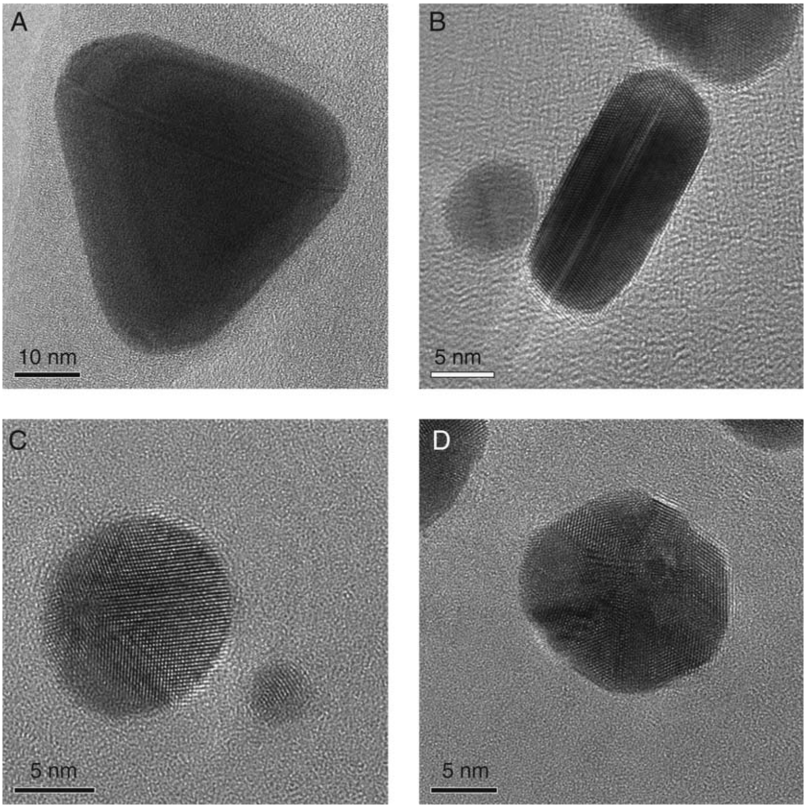

Figure 21.2. TEM micrographs of typical gold precipitated by hops biomass in aqueous solution at room temperature. A. A triangular nanoparticle (size bar indicates 10 nm), B. Rod-shaped gold nanoparticle (size bar indicates 5 nm), C. Icosahedral gold nanoparticle (size bar indicates 5 nm), and D. Decahedral shaped gold nanoparticle (size bar indicates 5 nm).

nanoparticles formed. In alfalfa, oat, and wheat, most of the nanoparticles formed at pH 2 had an irregular shape (Gardea-Torresdey et al., 1999; Armendariz et al., 2004a). However, pH has a major impact on the size rather than on the shape of the nanoparticle formed.

Lopez et al. (2005) studied the effect of chemical modification on the Au(III) reduction capacity of hops biomass. Using X-ray absorption spectroscopy (XAS) analysis, XANES (X-ray absorption near edge structure), and EXAFS (extended X-ray absorption fine structure), these researchers determined that Au(III) (from potassium tetrachloroaurate) was reduced to Au(0) at approximately 81%, 70%, and 83% by native,

Table 21.2. Gold nanoparticles formed by alfalfa, wheat, and oat biomasses reacted with Au(III) solution at various pH values

pH	Biomass/nanoparticle size		
	Alfalfa[a]	Wheat[b]	Oat[c]
2	15 nm (60%)	20–50 nm (75%)	20–40 nm (60%)
3	–	10–20 nm (72%)	10–20 nm (65%)
4	–	10–15 nm (65%)	10 nm (75%)
5	–	10–20 nm (70%)	10–30 nm (nd)
6	–	10–30 nm (90%)	–

[a] Gardea-Torresdey et al., 1999.
[b] Armendariz et al., 2004a.
[c] Armendariz et al., 2004b.

esterified, and hydrolyzed hop biomass, respectively. The average particle size for the native and esterified hops biomass showed particle radii of 17.3 Å and 9.2 Å, respectively.

Researchers are looking for new method for nanoparticle formation using plant extracts. Egorova and Revina (2000) obtained stable silver and copper nanoparticles with quercetin, a natural plant pigment, in the presence of air–oxygen in water by the reduction of silver and copper salts. These researchers obtained particle size ranging between 1 and 1.5 nm. Shankar et al. (2003a) reported that the leaf biomass of *Pelargonium graveolens* reacted with a 10^{-3} M $HAuCl_4$ solution formed gold nanoparticles of a variety of shapes including rods, flat sheet, and triangles. Shankar et al. (2005) have explored the use of lemon grass extract for the Au(III) reduction and the formation of gold nanoparticles. These researchers added different amounts of lemongrass extract to the Au solution. The results have shown that increasing the amount of the extract reduces the average size of the triangular and hexagonal particles. However, the ratio of the number of spherical particles to triangular/hexagonal particles increased as the amount of extract increased. According to the authors, the nanoparticles formed can be extended on a glass substrate in the form of films which absorb IR radiation. In addition, Shankar et al. (2004a) have shown that the particle size changes with time. After two minutes the particles had an average size of approximately 1 micron, at 90 min particles of a 0.1 micron started to appear, and at 360 min the distribution of the particle size was bimodal with 0.1 and 1.0 micron particles. It has also been shown by Ankamwar et al. (2005) that tamarind leaf extract is also capable of forming gold nanotriangles in aqueous solution. These authors showed that the reduction process was rapid resulting in thin flat single crystal gold nanotriangles ranging in thickness from 20 to 40 nm. The authors also tested the effects of different organic solvent vapors on the conductivity of the nanotriangles and suggested the application of these nanoparticles in future chemical sensors. In another study by Shankar et al. (2003b), silver nanoparticles were created using a crude extract from geranium leaves. The authors boiled cleaned and finely cut geranium leaves for 5 min in distilled water and added the extract to a 10^{-3} M solution of Ag(I) ions and produced silver nanoparticles ranging in size from 16 to 40 nm with an average size of 27 nm.

Ascencio et al. (2004) have shown the production of ytterbium nanoparticles using ground alfalfa biomass in aqueous solution. The ytterbium nanoparticles were produced by alfalfa biomass in solution at pH values ranging from 2 to 10. The analysis performed using TEM showed the presence of FCC nanoparticles. Another study by Ascencio et al. (2005) demonstrated that alfalfa biomass reacted with a samarium solution is able to produce samarium nanoparticles. In this study, the author reported that at pH 4 a larger number of small nanoparticles ranging from 1 to 3 nm were formed; however, at pH 6 the majority of the nanoparticles had sizes ranging from 2 to 8 nm.

The production of core-shell nanoparticles has also been performed using plant extracts. Shankar et al. (2004b) used an extract from Neem (*Azadirachta indica*) leaves and a mixture of tetrachloroaurate and silver nitrate and produced gold core-silver shell nanoparticles. In this study, the authors showed the production of monometallic silver and gold nanoparticles by the plant extracts. The particle sizes and shape for the gold nanoparticles produced using this plant extract were poly-dispersed both in size and shape; however, the silver nanoparticles were spherical in shape and ranged in size from 5 to 35 nm. The authors also noted that the particles were stable in solution up to four weeks after synthesis. The bimetallic core-shell nanoparticles had sizes ranging from 50 to 100 nm, but did not have a continuous shell of silver over the gold. Instead the silver layer is a compilation of silver nanoparticles. In another study, investigating the effects of plant extracts on metal ions, Mallikarjuna et al. (2005) showed the reduction of palladium and silver ions by coffee and tea extracts. They observed a surface plasmon peak at approximately 430 nm, using a UV-Vis instrument that indicates the production of silver nanoparticles. In addition, in the palladium reduction they observed a continuous absorption in the UV region, indicative of colloidal palladium. Further investigation using TEM showed that the silver nanoparticles were poly-dispersed and the palladium particles showed a layered structure. The structures obtained from this study indicate that the particles were capped with an organic molecule from the parent solution.

In another study performed with ground alfalfa, Ascencio et al. (2000) using TEM analysis showed the production of a new type of gold nanoparticle, a truncated icosahedron. The new particle found through the bioreduction of tetrachloroaurate on alfalfa biomass was thought to be formed through slow growth or equilibrium processes. Ascencio et al. (2003) have also prepared europium–gold nanoparticles. In this study, it was shown that the size and shape was dependent on the pH of the solution. The authors used TEM to perform the particle analysis and showed that the highest distribution of small nanoparticles occurred at pH 8; whereas the larger bimetallic nanoparticles were formed at 6. Furthermore, the authors showed that the structure of the Eu–Au nanoparticles were multitwinned with a gold core and a thin layer of Eu atoms over the gold core.

21.4. Formation of metal nanoparticles by living plants

The production of nanoparticles by living systems dates back to the early 1900s where it was shown that colloidal silver was deposited in organs of living organisms (Voigt, 1914). Around the same time it was shown that fungi could remove colloidal gold from solution through adsorption (Williams, 1918). It was shown in the early 1970s that bacteria could adsorb colloidal iron particles from solution (Macrae and Edwards, 1972). However, the actual formation of metal nanoparticles by both fungi and bacteria was not known until the 1990s (Karamushka, et al., 1990; Moiseenko et al., 1999). As cited above, the characterization of gold nanoparticles by plant extracts has only been performed in the last few years. However, the reduction of silver by plant roots has been noted in the literature since 1935. Gautheret (1935) reported the production of a green color when plant roots were treated with silver nitrate. The color indicates the reduction of silver and the production of nanoparticles; green-colored silver nanoparticles have been observed with the reduction of silver nitrate in the presence of ascorbic acid and light (Jiang et al., 2001).

Although the reduction of silver by living plants was previously reported, the products of the reduction were not characterized. The nanoparticle production by living plants and their characterization has only recently reported by Gardea-Torresdey and coworkers (2002a,b,c,d). Gardea-Torresdey et al. (2002d) showed the production of gold nanoparticles by alfalfa plants. In this study the authors showed the accumulation of Au(0) nanoparticles inside living alfalfa plants using XAS and TEM analytical techniques to characterize the gold particles. The XAS studies showed that the nanoparticles consisted of Au(0) with no oxidized gold present. To complement the XAS data, TEM images of the plants containing the gold nanoparticles were taken. The images showed that the particles were in the FCC configuration, and were multi-twinned and the lattice parameter calculated was 0.23, which is approximately the spacing between the 111 planes of Au(0). It was further shown in this study that the gold was present in an icosahedral structure, a low-energy configuration for Au(0), indicating that the reduction was performed slowly or under equilibrium conditions. The same researchers, Gardea-Torresdey et al. (2003), again using alfalfa, showed for the first time the production of Ag(0) nanostructures inside a living plant. In this study a combination of XAS and TEM was used to characterize the silver nanoparticles. The XANES spectroscopy showed that silver was present as Ag(0) in the plants. From the EXAFS of the root sample, Ag(0) in the plant had a coordination of approximately four Ag atoms. The low coordination found in the EXAFS is indicative of colloidal silver or silver nanoparticles because of the incomplete first shell coordination. An example of the EXAFS obtained from silver nanoparticles is represented in Fig. 21.3. Fig. 21.3A shows the reduced amplitude in the raw EXAFS of the nanoparticle compared to the bulk silver. Fig. 21.3B shows the Fourier-transformed EXAFS of the samples shown in Fig. 21.3A. It is noticeable that the Fourier-transformed EXAFS of the silver nanoparticle have less amplitude than the bulk silver. Bulk silver or large particles of silver have a first shell coordination of 12 nearest neighboring Ag atoms. Fig. 21.3C shows the XANES of the Ag(I) model compound ($AgNO_3$), Ag(0) metal foil, and Ag bound to the alfalfa biomass. From the energy position and the shape of the Ag bound to the alfalfa biomass it is clear that the silver present on the biomass is present as Ag(0). It was also shown using EXAFS that the estimated average particle size of the silver nanoparticles was about 9 Å. Furthermore, the dark-filed imaging TEM investigation showed that the nanoparticles or nanostructures were dispersed throughout the plant in small assemblies like nanowires. The use of high-resolution TEM showed small silver nanoparticles with sizes averaging from 2 to 20 nm in diameter.

Yates et al. (2005) attempted to synthesize pure metal nanoparticles of silver, gold, titanium, chromium, zinc, and cobalt using the metabolic pathways of plants. More specifically, they studied the possible reduction of the aforementioned metals using morning glory (*Ipomoea lacunosa*) and alfalfa (*Medicago sativa*) followed by deposition of the particles on stainless steel supports. The metals were prepared in a hydroponics growth solution and supplied to the plants to investigate the natural process of bio-precipitation or bio-mineralization.

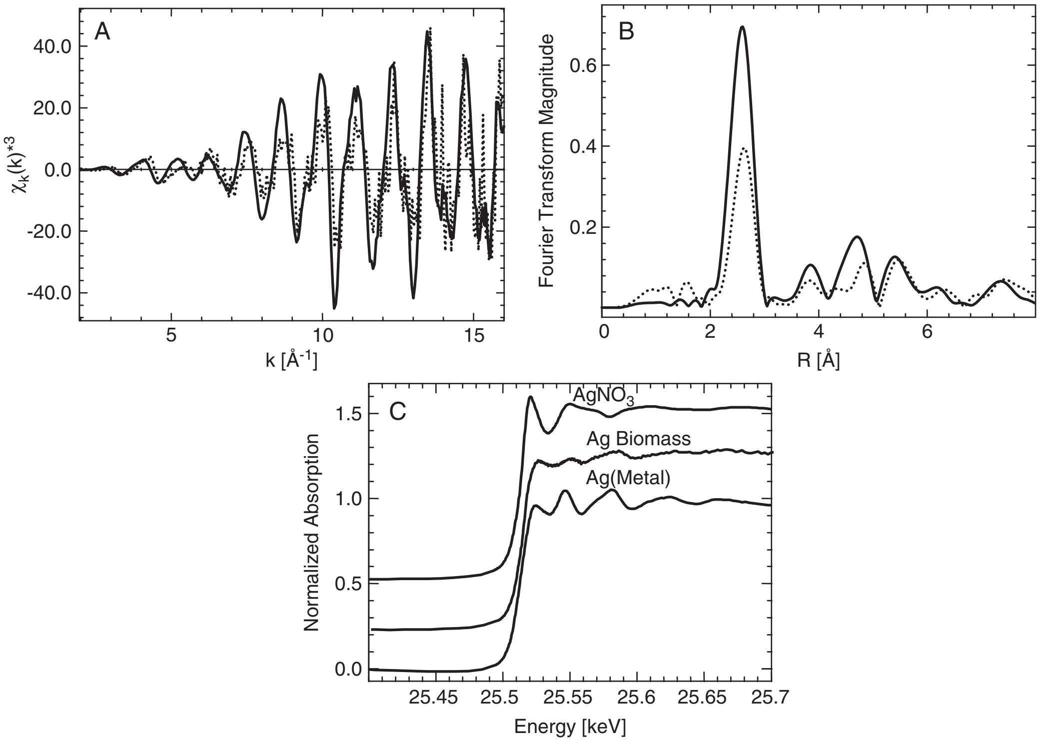

Figure 21.3. A. Raw EXAFS of silver nanoparticles formed on inactivated tissues of alfalfa biomass (dotted line) and the EXAFS of a metallic silver standard (solid line), B. Fourier-transformed EXAFS of silver nanoparticles formed on inactivated tissues of alfalfa biomass (dotted line) and the EXAFS of a metallic silver standard (solid line),and C. XANES spectra from 25.40 to 25.70 keV showing the change in the energy and the reduction from Ag(I) to Ag(0) on the biomass.

In another study, Gardea-Torresdey et al. (2005) investigated the effects of using thiocyanate as a complexing agent for the enhancement of gold uptake by desert willow (*Chilopsis linearis*). These researchers, using ICP-OES, showed that thiocyanate does increase the uptake of gold from a gold enriched media. In addition, through the use of XAS the authors showed that the Au in the plants was present as Au(0) forming Au nanoparticles.

21.5. Nanoparticle extraction

The synthesis of metal nanoparticles using chemical and physical methods is well documented in the literature, and the extraction of nanoparticles from inorganic materials is as well (Praharaj et al., 2004; Abed et al., 2005). Also, the phase transfer of nanoparticles from organic solvents of aqueous solvents and micelles has been shown in the literature (Zhang et al., 2001; Zhang et al., 2002; Wei et al., 2004). In the solvent extraction or phase transfer of nanoparticles, generally a micelle or a non-ionic liquid is used to transport the nanoparticles from the organic phase to a polar phase. Finally, the extraction of nanoparticles from micelles is performed through the dissolution of an antisolvent into solution that disrupts the micelles, thus releasing the nanoparticles into solution.

The synthesis of both monometallic and bimetallic nanoparticles by living and non-living biological materials has been reported in the literature as shown above. However, the extraction of biologically synthesized nanoparticles for further application is not well studied or well understood. In fact, there are only two references about the extraction of nanoparticles from either living or non-living plant materials (Yates et al., 2005; Armendariz, 2005). Yates et al. (2005) mentioned the solventless extraction of titanium nanoparticles and the subsequent deposition onto a stainless steel support. The deposition of the titanium nanoparticles was performed by grinding the biomass sample and preparing it in 2.0 ml of water and coating the stainless steel plate with the solution. Armendariz (2005) extracted gold nanoparticles from inactivated tissues of oat and wheat biomasses. Studies using different instrumental techniques were performed to extract the nanoparticles from the biological materials. Primarily, the extraction process involved the use of CTAB and citrate combined with sonication to transfer the nanoparticles from the biomass samples into aqueous solution. The UV-Vis spectroscopy showed that some of the gold was extracted from the plant material. In the extraction solutions using either CTAB or citrate the 540 nm plasmon resonance peak was present. However, it should be noted that the citrate extractions were more successful than the CTAB extractions. The combination of XAS and TEM data showed that a higher number of smaller nanoparticles were extracted from the biomass in the first extraction, and by the fourth extraction of the same biomass, larger nanoparticles were being extracted. The XAS analysis demonstrated that the effective radius of the nanoparticles left on the biomass was increasing after the first extraction. While the TEM analysis of the extraction solutions revealed the smaller radius of the nanoparticles extracted at first.

21.6. Applications of nanoparticles

Nanoparticles whether chemically, physically, or biologically synthesized have a number of different potential applications which make them an invaluable material. A broad overview of the different applications of metal nanoparticles includes the following: medical, bioanalysis, catalysis, environmental remediation, sensors, semi-conductors, among other applications.

Recently, Paciottie et al. (2005) showed the ability of gold nanoparticles to be used for tumor-targeted drug delivery systems. The authors showed the ability to attach a very powerful yet very toxic anticancer protein tumor necrosis factor. The study showed that the mice treated with this had a 10-fold increase in concentrations of the anticancer protein tumor necrosis factor as compared with mice treated with just the anticancer protein tumor necrosis factor. The attachment of this antitumor treatment to gold nanoparticles increased the efficiency of the factor. In another study by Hainfeld et al. (2004), 1.9 nm gold nanoparticles were injected into mice with mammary carcinomas to investigate the enhancement of radiotherapy. The authors found that 86% of the mice injected with the gold nanoparticles survived compared with 20% treated with the X-rays alone. The use of the gold nanoparticles in this study allowed for high Z-radioenhancement. Carpenter et al. (2005) showed that iron nanoparticles could be used for magnetodynamic therapy for cancer patients. A combination of the magnetic nanoparticles and 100 MHz generated localized heating of the nanoparticles facilitated cellular destruction or targeted drug delivery. In addition, Nie (2003) talked about nanotechnology applications with regard to nanoprobes for molecular imaging and nanoscaffolds for tissue engineering. This author discusses the applications of pure metal and metal oxide nanoparticles in imaging and sensing, luminescence for cancer cell identification and profiling, drug delivery, and tissue engineering properties of nanoparticles.

In medicine, nanoparticles can be used in bioanalysis and as biosensors. The bioanalysis can have a variety of applications. For example, nanoparticles can be used to induce signal transduction, as quantitation identifiers, in bioassays, and finally nanoparticles can be used for specific functions in biological systems (Penn et al., 2003). Maxwell et al. (2002) showed that colloidal gold could be used to create biosensors to identify specific DNA sequences and base mutations. It has also been shown that copper–gold bimetallic nanoparticles can be used as oligonucleotides labels for the electrochemical stripping detection of DNA hybridization (Cai et al., 2003).

Related to health and environmental issues it has been shown that nanoparticles can be used in the remediation of organic pollutants in the environment (Obare and Meyer, 2004). Iron nanoparticles have been proven to be effective in the dechlorination of polychlorinated biphenyls (Paciottie et al., 2005; Johnson and Lowry, 2003). It is also shown in the literature that bimetallic nanoparticles can be used for groundwater treatment (Elliott and Zhang, 2001). This study looked at the destruction of tricholorethene (TEC) and other chlorinated hydrocarbons using bimetallic nanoparticles. The results of this study showed that 96% of the TCE was eliminated within four weeks of injecting the nanoparticles.

The environmental applications of nanoparticles for the most part concern the catalysis of environmental reactions resulting in the destruction of a contaminant. However, from an industrial/chemical stand point nanoparticles are applicable in the catalysis of different reactions. For example, supported gold nanoparticles have been shown to be useful in hydrogenation and oxidation reactions (Schimpf et al., 2002). Another example of catalysis using nanoparticles is the three-way catalysis (Baker et al., 2001). In the three-way catalysis application, the authors showed that platinum, rhodium, and palladium nanoparticles supported on a cesium–zirconium mixed oxide was an excellent material for the three-way catalysis in automobiles.

Another application of nanoparticles is in sensors. For example, Krasteva et al. (2002) showed that thin film resistors composing of gold and different organic-based dendrimers could be used to detect different organic vapors. Ishibashi (2002) showed that noble metal nanoparticles with diameters ranging between 5 and 20 nm with a tertiary amine-protecting group could be used in paints. The nanoparticles in this range for silver and gold exhibit yellow and red colors, respectively, which could be used as unique colorants. Finally, Thomas and Kamat (2003) investigated chromophore-functionalized metal nanoparticles from the ground- and excited-state interactions of the nanoparticles and the chromophores. They concluded that these functionalized nanoparticles could be used in photovoltaics, for the light mediated binding of biologically important molecules, and fluorescence applications in fluorescence display devices.

21.7. Conclusions

The field of nanoscience is growing rapidly with regard to the synthesis, characterization, and applications of metallic nanoparticles. In conjunction with this rapid growth, the field of bio-nanotechnology is also growing rapidly in all areas. The newest subcategory of bio-nanotechnology is the use of plants and plant-derived materials for the synthesis of metallic nanoparticles as has been shown in this brief review. The use of plants and plant-derived materials for the synthesis of nanoparticles has shown to be effective in producing size and shape-controlled nanoparticles. In addition, the bio-synthesized nanoparticles have the same defects, structures and properties of nanoparticles that have been synthesized through chemical and physical methods. The only problem with using plant material and living plant-derived nanoparticles is the extraction of these nanoparticles for future applications. However, studies are being performed to solve the problems of extracting nanoparticles from these biologically derived materials for further application. As mentioned earlier, the potential uses for nanoparticles include medicine, catalysis, bio-sensors, chemical sensors, environmental remediation, semi-conductors, and photovoltaic devices, among others.

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