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Green Synthesis of Noble Metal (Au, Ag, Pt) Nanoparticles, Assisted by Plant-Extracts

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1. Introduction

The physicochemical and optoelectronic properties of metallic nanoparticles are strongly dependent on the size and size-distribution, but also nanoparticles shape contributes significantly to the control of their properties. Wide varieties of physical and chemical procedures have been developed in order to synthesize nanoparticles of different compositions, sizes, shapes and controlled polydispersity. Nevertheless, the routinely physicochemical techniques for nanoparticle production such as photochemical reduction [1], laser ablation [2], electrochemistry [3], lithography [4] or high energy irradiation [5], either remain expensive or employ hazardous substances, such as organic solvents, and toxic reducing agents like sodium borohydride and N,N-dimethylformamide. In addition, due to the high surface energy of the nanoparticles, these tend to form aggregates; therefore, surface passivating and capping reagents are frequently added to the reaction systems to avoid coalescence. The development of reliable, eco-friendly processes for the synthesis of nanomaterials is an important aspect of nanotechnology. Nanotechnology also requires the synthesis of nanomaterials of different chemical compositions, sizes and morphology with an excellent control over these characteristics.

With the growing need to minimize or eliminate the use of environmental-risk substances, as the green chemistry principles describe [6], the synthesis of nanoparticles using biological entities has received increasing attention in the last decade [7]. The biosynthetic procedures involve either living organisms such as bacteria [8], fungi [9] and plants [10] or biomass, like plant extracts [11-14]. Biological synthetic processes have emerged as a simple and viable alternative to more complex physicochemical approaches to obtain nanomaterials with adequate control of size and shape [15].

The use of the highly structured physical and biosynthetic activities of microbial cells for the synthesis of nanosized materials has recently emerged as a novel approach for the synthesis of metal nanoparticles. The interactions between microorganisms and metals have been well documented [16] and the ability of microorganisms to extract and/or accumulate metals is already employed in biotechnological processes such as bioleaching and bioremediation [17]. A general scheme for nanoparticles synthesis in microorganisms is illustrated in figure 1, reported by Das-Marsili [18], where is easily observed the scheme

of biomineralization process for nanoparticles synthesis assisted by microorganisms. However more detailed studies are required to fully understand the difference in nanoparticles morphology and size between different metals when the same kind of microorganism is employed. Furthermore, the specific mechanism of reduction, nucleation and grow model of metallic ions and nanoparticles respectively, when interact with metabolic process of the microorganism and biomolecules, remains as a big challenge to be reached.

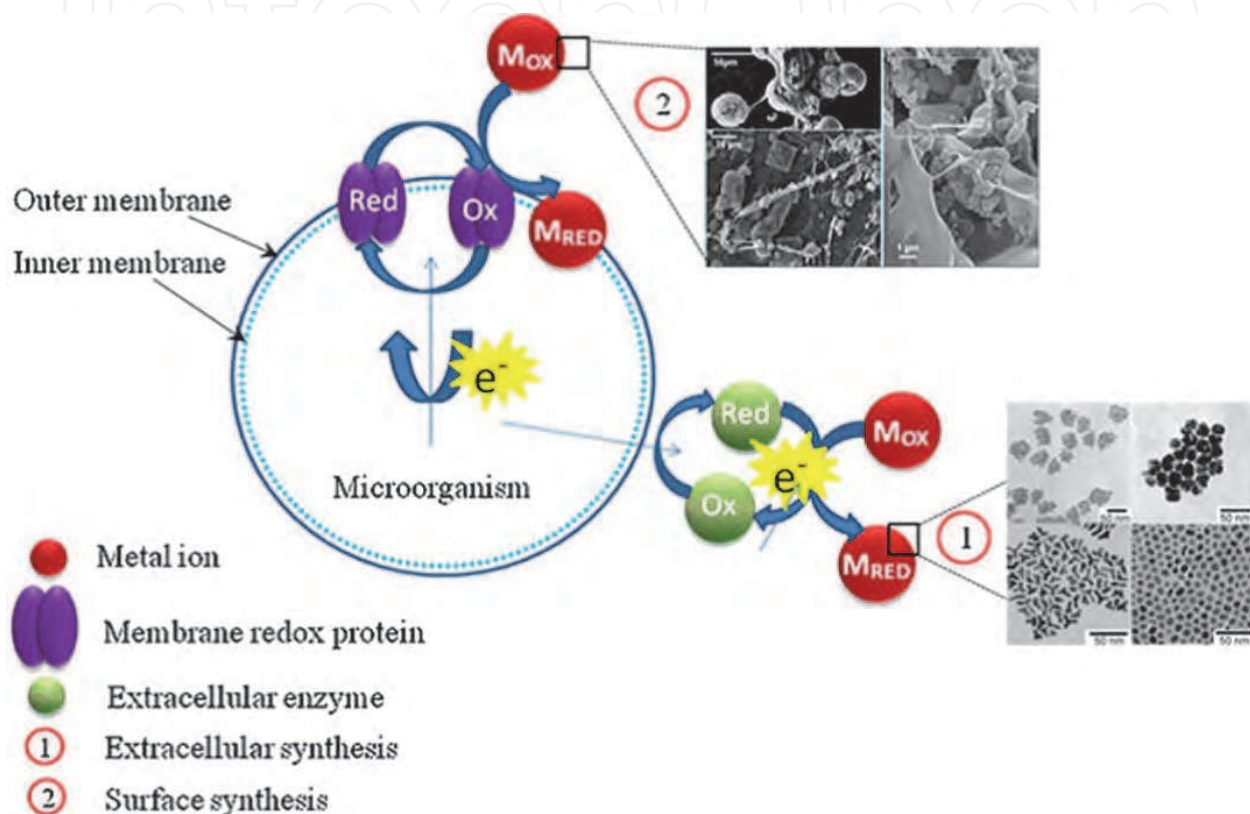


Fig. 1. Scheme of nanoparticles formation by microorganism. (Das-Marsili [18])

1.1 Noble metals nanoparticles synthesis assisted by bacteria

Many organisms, both unicellular and multicellular, are known to produce inorganic materials either intracellularly or extracellularly. One approach that shows immense potential is based on the biosynthesis of nanomaterials using bacteria.

Microorganisms, particularly bacteria, are often exposed to extreme environmental conditions and an ability to resist those stresses is essential for their survival. The specific defense mechanisms help the bacteria to quell such stresses, including the toxicity due to high concentration of foreign metal ions or metals. Such mechanisms include efflux systems, alterations of solubility and toxicity by changes in the redox state of the metal ions, extracellular complexation or precipitation of the metals intracellularly and the lack of specific metal transport systems. [19] One major advantage of having prokaryotes as nanoparticles synthesizers is that they can be easily modified using genetic engineering techniques for overexpression of specific enzymes, apart from the ease of handling.

1.2 Noble metals nanoparticles synthesis assisted by fungus

The use of fungi in the synthesis of nanoparticles is a relatively recent addition and holds promise for large scale nanoparticles production. The use of eukaryotes, especially fungi, is potentially exciting since they secrete large amounts of proteins and enzymes, thus increasing productivity, and are simple to deal with both in the laboratory and at industrial scale. Moreover the process can be easily scaled up, economically viable with the possibility of easily covering large surface areas by suitable growth of mycelia. Furthermore, downstream processing would be much simpler using fungi. [19]

Further information about state of the art of the biosynthesis of metallic nanoparticles assisted by microorganisms, can be revised in some reviews available in literature. [7, 18-20]

1.3 Noble metals nanoparticles synthesis assisted by plants

Among the use of living organisms for nanoparticle synthesis, plants have found application particularly in metal nanoparticle synthesis. Use of plants for synthesis of nanoparticles could be advantageous over other environmentally benign biological processes as this eliminates the elaborate process of maintaining cell cultures. Biosynthetic processes for nanoparticles would be more useful if nanoparticles were produced extracellularly using plants or their extracts and in a controlled manner according to their size, dispersity and shape. Plant use can also be suitably scaled up for large-scale synthesis of nanoparticles. [21] Noble metals, especially Au and Ag, have been extensively tested for the biosynthetic process assisted by plants, in order to obtain metallic nanoparticles with control over shape and size. A list of the metallic nanoparticles obtained by biosynthesis employing plants biomass or extracts can be checked in recent reviews, reported by Yadav *et al.* [21] and Bali *et al.* [22].

In the case of the plants and yeast, the possibility to obtain metallic particles with nanometric dimension were explored just after, these organism were employed for the remediation of metal-contaminated water [23] due to a growing necessity to develop environmentally friendly systems to retrieve metals. It has been shown that many plants can actively uptake and bioreduce metal ions from soils and solutions during the detoxification process, thereby forming insoluble complexes with the metal ion in the form of nanoparticles.

The first successfully report of synthesis of nanoparticles assisted by living plants appeared in 2002 when it was shown that gold nanoparticles, ranging in size from 2 to 20 nm, could form inside alfalfa seedlings [10]. Subsequently it was shown that alfalfa also could form silver nanoparticles when exposed to a silver rich solid medium. [24]

The research group of Gardea-Torresdey from the University of Texas at El Paso, is the major responsible of the experiments that involve the formation of metallic nanoparticles (primarily gold and silver) by different living plant systems as can be observed in table 1.

A virtual circle has been achieved following the biomass method when the catalytic function of the nanoparticles rich biomass was substantiated by the reduction of aqueous 4-nitrophenol, the first report of gold nanoparticle-bearing biomatrix directly reducing a toxic pollutant [25].

The use of plants in metal extraction (phytoremediation) has appeared as a promising alternative in the removal of heavy metal excess from soil and water, and in the process a new method to produce metallic nanoparticles was developed. In order to understand how

the phytoremediation technology works, researchers have used X-ray absorption spectroscopy. X-ray absorption spectroscopy (XAS) consists of two complimentary techniques X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS), which provide invaluable information about the coordination chemistry of metals and toxic element interactions with phytoremediation systems [27].

Using X-ray absorption spectroscopy (XAS) analysis, XANES, and EXAFS, Gardea-Torresdey group has tried to elucidate the process involved during the nanoparticles formation inside living plants and the biomolecules associated with the particles in different parts of the plant. Actually it can be determined the oxidation state, coordination environment, and the average radii of the nanoparticles bound to the hops biomass [28]. The studies suggest that the carboxyl or other oxygen containing ligands on the biomass are the functional groups responsible for the binding and the reduction site for gold on the biomass.

| Plant | Metal nanoparticle | Shape | Size | Year/Reference |
|--|--------------------|---|---------------------------------------|----------------|
| <i>Sesbania drummondii</i> | Gold | Spherical | 6-20 nm | 2007-[25] |
| <i>Avena sativa</i> | Gold | Fcc: tetrahedral, decahedral, hexagonal, icosahedral multitwinned, irregular, and rod shape | 5-20 nm and 25-85 nm, depending on pH | 2004-[26] |
| <i>Medicago sativa</i> (alfalfa sprouts) | Silver | Mostly spherical | 2-20 nm | 2003-[24] |
| <i>Medicago sativa</i> | Gold | fcc twinned and icosahedron structure | 2-20 nm | 2002-[23] |

Table 1. Nanoparticles obtained by bioreduction process, assisted by living plants.

From the first reports on the formation of gold and silver nanoparticles by living plants, it was opened up new and exciting ways to fabricate nanoparticles. It showed how it is possible to link materials science and biotechnology in the new emerging field of nanobiotechnology.

The next methodology associated with plants to produce metallic nanoparticles employs the dried biomass of the plants and a metallic salt, as bioreducing agent and precursor, respectively. The general procedure can be described in a general way as follow, the plant is dried (typically sun-dried), then is suspended in water and placed in an ultrasonic bath to homogenize the suspension. Finally the suspension is allowed to rest with the metallic ion aqueous solutions followed by a homogenization process.

Silver or gold precursors at ambient temperature produces both silver nanoparticles (55–80 nm) and triangular or spherical gold nanoparticles, from sun-dried biomass of *Cinnamomum camphora* leaf when are incubated together [13]. This report evidence that the mechanism concerned to the gold and silver nanoparticles formation is different despite of the same reducing agent employed. For gold nanoparticles there is strongly evidence that suggests that these particles are the result of coalescence of smaller particles, because there is no reason to expect a rapid growth in the gold particles and the formation of nanotriangles. The author's

indicate the marked difference of shape control between gold and silver nanoparticles was attributed to the comparative advantage of protective biomolecules. The polyol components and the water-soluble heterocyclic components were mainly responsible for the reduction of silver ions or chloroaurate ions and the stabilization of the nanoparticles, respectively. The process were scaled-up successfully for biological production of silver nanoparticles by lixivium of sundried *Cinnamomum camphora* leaf in continuous-flow tubular microreactors [29]

Silver nanoparticles (NPs) were rapidly synthesized by treating silver ions with a *Capsicum annuum* L. extract [14]. The reaction process was simple and convenient to handle, and was monitored using ultraviolet-visible spectroscopy (UV-vis). The reduction of silver ions and stabilization of the silver NPs was thought to occur through the participation of proteins.

From the bioreduction method, originally proposed by Gardea-Torresday [30], where bionanotechnology shows a huge potencial to produce metallic nanoparticles with different shapes (figure 2), nevertheless the most important results employing biomass have been reached by J. Ascencio research group, who have developed a procedure based on the use of the tannins of the biomass of *Medicago sativa* (alfalfa) to obtain Au nanorods [31], bimetallic nanoparticles [32, 33] and even lanthanide clusters [34, 35], and lately has also been demonstrated effective for the synthesis Zn nanoparticles [36], and iron oxide [wuestite ($\text{Fe}_{0.902}\text{O}$) and magnetite (Fe_3O_4)] clusters [37]. The method is based on the reduction of metal ions through biomass at controlled pH conditions to improve the size control of nanoparticles. (See table 2)

| Plant | Metal nanoparticle | Shape | Size | Year/Reference |
|---------------------|--------------------|--|---------------------------------------|----------------|
| Medicago sativa | Gold | decahedral multiple twinned, icosahedral multiple twinned particles, irregular shaped particles, Fcc tetrahedral particles, and hexagonal platelet particles | From 20-100 nm depending on pH | 1999-[30] |
| Cinnamomum camphora | Gold and Silver | Triangular or spherical | 55-80 nm | 2007-[13] |
| Capsicum annuum L | Silver | Spherical | 10-40 nm. Depending on reduction time | 2007-[14] |
| Medicago sativa | gold | nanorods | 20 nm diameter | 2001-[31] |
| Medicago sativa | Eu-Au bimetallic | spherical | From 2-30 nm, depending on pH | 2003-[32] |

| Plant | Metal nanoparticle | Shape | Size | Year/Reference |
|-----------------|--|------------------|------------------------------|----------------|
| Medicago sativa | Ti/Ni bimetallic, core-shell structure with the Ti covering a Ni core | Mainly spherical | From 2-6 nm, depending on pH | 2006-[33] |
| Medicago sativa | Sm | spherical | From 2-8 nm at pH 4 | 2005-[35] |
| Medicago sativa | Zn | Spherical | 2-5.6 nm depending on pH | 2006-[36] |
| Medicago sativa | Yb | Spherical | 2-10 nm | 2004-[34] |
| Medicago sativa | wuestite (Fe _{0.902} O) and magnetite (Fe ₃ O ₄) | spherical | 3.1 nm average size | 2007-[37] |

Table 2. Nanoparticles obtained by bioreduction process, assisted by plant biomass.

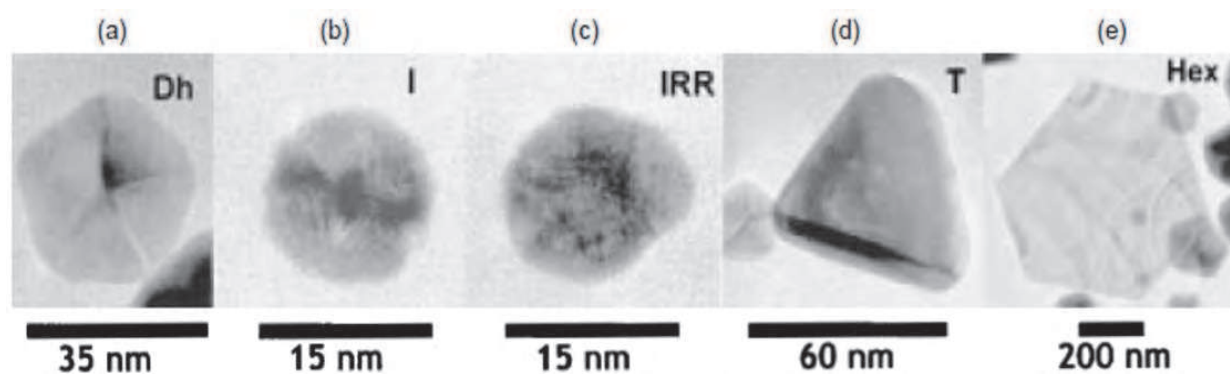


Fig. 2. Morphologies of gold nanoparticles obtained with *Medicago sativa* biomass. Enlargement showing the different kinds of gold particles observed. (a) decahedral multiple twinned; (b) icosahedral multiple twinned; (c) irregular shaped; (d) FCC tetrahedral; (e) FCC hexagonal platelets. *Yacaman et al.* [30]

Here we present a simple green synthetic methodology of silver, gold and platinum nanoparticles, which involves the in-situ reduction of aqueous Ag(I), Au(III) and Pt(IV) ions employing *Camellia sinensis*, and *Opuntia ficus indica* aqueous extract as a reducing and capping agents.

2. Experimental section

2.1 Materials

For the green synthesis, water soluble salts (HAuCl₄, AgNO₃ and H₂PtCl₆) were employed as precursor of nanoparticles, all purchased from Sigma-Aldrich Chemicals. The above reagents were of analytical purity and were used without further purification.

2.2 Extract preparation

In general manner, different portions of plants: 30g of fresh cladodes of *Opuntia ficus indica* were rinsed with de-ionized water and finely cut. In the case of *Camellia sinensis* 1.5 g of dried leaves were employed to prepare the extract. Afterwards, it was boiled in 100 mL of de-ionized water for five minutes. The mixture was cooled and vacuum filtered. The resulting extract was used for further experiments.

2.3 Synthesis of metallic nanoparticles

Noble metals (Ag, Au and Pt) nanoparticles were prepared by adding different volumes of the plants extracts in a range between 1- 10 mL to 5 mL of 10^{-3} M AgNO_3 , HAuCl_4 and H_2PtCl_6 solutions, respectively. Then, the volume was mixed with de-ionized water until to reach a final volume of 20 mL. This mixture was allowed to stand for 24 h. No additional reducing agent or surfactants were needed for the synthesis of gold, silver or platinum nanoparticles.

2.4 UV-Vis absorbance spectroscopy

The bioreduction of Ag(I), Au (III), and Pt(IV) in aqueous solution was monitored by following the UV-Vis absorbance of the reaction mixture during 4 hours as a function of time, and after 24 hours of reaction. UV-Vis analysis was performed on a CARY 5000 spectrophotometer operated at a resolution of 1 nm at room temperature.

2.5 Transmission electron microscopy (TEM)

Samples for TEM studies were prepared by placing a drop of the silver, gold or platinum nanoparticles colloidal suspension obtained by bioreduction on lacy carbon-coated grids. TEM observations were performed on a transmission electron microscope JEOL 2010.

3. Results

3.1 *Camellia sinensis* system

It is well known that *Camellia sinensis* contains polyphenols and terpenoids, such as β -cariophyllene, linalool, cis-jasmone, α -terpineol, δ -cadinene, indole, geraniol, among the major bio-components, which have bactericidal and antioxidant activity, and several other useful properties. [38] As stated in previously reported bio-reduction methods, [12, 13, 14] these type of compounds contribute to the metal ion reduction processes, and can also control the size and stabilize the nanostructures formed. For instance, gallic acid, a secondary metabolite present in plants like green tea that also has powerful antioxidant properties, has been successfully used to obtain water soluble Au and Ag nanostructures, and has proved to be an efficient capping agent of these noble-metal nanoparticles.[38, 39]

Addition of *Camellia sinensis* extract to aqueous HAuCl_4 solutions, at ambient temperature, quickly turned the initial yellowish solution into pink, grey-blue and pale violet, respectively (inset of figure 3a). In case of formation of silver nanoparticles, the solution turned from yellowish to bright yellow and to dark brown (inset of figure 3b). In the case of

platinum nanoparticles, when the time reaction increased, the color of the solution gradually changed from yellow brown to dark brown.

UV-Vis spectra of Au and Ag nanoparticles in aqueous solution are shown in Figure 3a and 3b, respectively. [11] The absorption peaks at around 550 nm for Au and around 430 nm for Ag are characteristic of these noble-metal particles. Colloidal solutions of gold and silver nanoparticles show bright colors, as mentioned before, their origin is attributed to the collective oscillation of the free conduction electrons induced by an electromagnetic field. These resonances are also denoted as surface plasmons. These oscillations depend on the particle size, and with increasing size the plasmon absorption maximum is shifted to longer wavelength and the bandwidth increases. Red shift are observed in both spectra (figure 3), which could be due to an increment in the particle size. In other words, the wavelength shift observed in the plasmon bands is a consequence of the different volume of *Camellia sinensis* extract added to the metal ions solution; however, the initial metal ion concentrations and the reaction time play also a crucial role in the optical properties and size obtained for these nanostructures. Meanwhile, stable gold nanoparticles are obtained until 24 h of reaction (figure 3a). A good control of optical properties of gold nanotriangles, synthesized with lemongrass extract, was also achieved with a simple variation of the extract concentrations. [48]

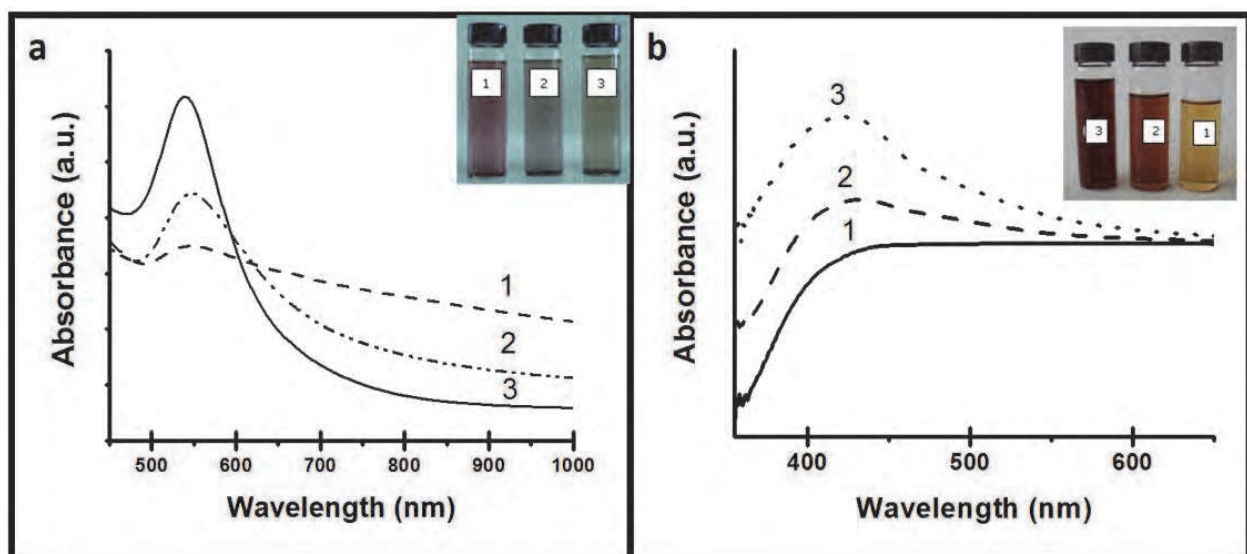


Fig. 3. a) UV-Vis-NIR absorption spectra of gold nanoparticles formed after 24 hours of the reaction of different amounts of *Camellia sinensis* extract with 5 mL of 10^{-3} M aqueous solution $\text{H[AuCl}_4\text{]}$ (4, 2 and 1 mL of *Camellia sinensis* extract, curves 1-3 respectively). b) UV-Vis absorption spectra of silver nanostructures formed after 4 hours of the reaction of different amounts of *Camellia sinensis* extract with 5 mL of 10^{-3} M aqueous solution AgNO_3 (1, 5 and 10 mL of *Camellia sinensis* extract, curves 1-3 respectively).

One of the most convenient techniques for characterization of Pt nanoparticles was UV-vis spectroscopy. Due to the ligand-to-metal charge transfer transition of the $[\text{PtCl}_4]^{2-}$, it exhibited a peak at 215 nm in its UV-Vis spectrum. The peak at 215 nm disappeared after

the reaction, indicating that the $[\text{PtCl}_4]^{-2}$ ions were completely reduced. The Pt nanoparticles had absorption in all ranges of the UV-Vis spectrum and the absorption increased with the decrease of wavelength [40]. Unfortunately, the remnant biomolecules that act as capping and reducing agents, present a strong absorption band in the region between 210 and 260 nm, causing interference with the UV-Vis band of the $[\text{PtCl}_4]^{-2}$.

TEM images of poly-disperse gold nanoparticles are shown in figure 4 depending on the volume extract used during the synthesis. Some anisotropic nanoparticles with irregular contours could be observed in figure 4b, with an average particle size of around 25 nm, in contrast with the smaller average size (2.5 nm) of the gold nanoparticles obtained from reaction that employs 0.2 mL of *Camellia sinensis* extract. TEM studies also revealed that the concentration of tea extract plays the main role in the morphology of the metal nanoparticles. When 0.2 mL of green tea extract was used for formation of Au nanoparticles, more anisotropic particles were obtained (figure 4a). However, by increasing the amount of *Camellia sinensis* extract from 0.2 to 1 mL, the resulted nanoparticles are slightly bigger and more spherical. It is believed that, when a larger concentration of bio-reducing agent is used, a relatively fast nucleation process occurs, which is followed by a slower growing stage due to stronger interactions between protective bio-molecules and growing Au nanocrystals, leading to the formation of more isotropic particles. [13]

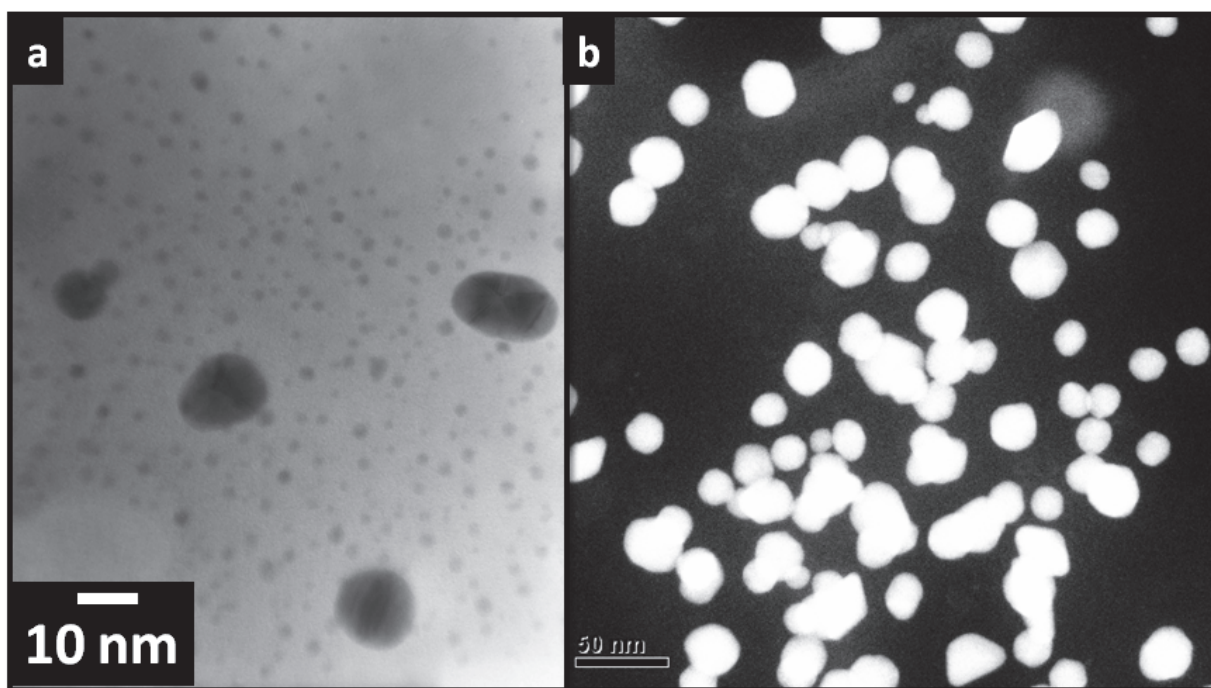


Fig. 4. a) Bright-field TEM micrograph of gold nanoparticles formed after 24 hours of the reaction, using 0.2 mL of *Camellia sinensis* extract; and b) Dark-field TEM micrograph of gold nanoparticles formed after 24 hours of the reaction 1 mL of *Camellia sinensis* extract, respectively. In both cases 5 mL of 10^{-3} M aqueous solution HAuCl_4 were employed for the synthesis.

Typical TEM image of silver nanoparticles can be observed in figure 5. The inset in figure 5 corresponds to SAED pattern, associate to face-centered cubic (FCC) silver. The diffraction spots suggest that grow as a single crystal. On the contrary, when a larger volume of *Camellia sinensis* extract is added to a silver ions solution, the resultant nanocrystals exhibit anisotropy, which is mainly attributed to both, a rapid reduction of the Ag ions and fast sinter of growing crystals into anisotropic nanostructures (figure 5). This last outcome can be explained by weaker interactions of Ag growing nanoparticles and protective bio-molecules compared to those with Au nanoparticles. This also explains the different rate of formation of stable Au and Ag nanoparticles using this methodology.

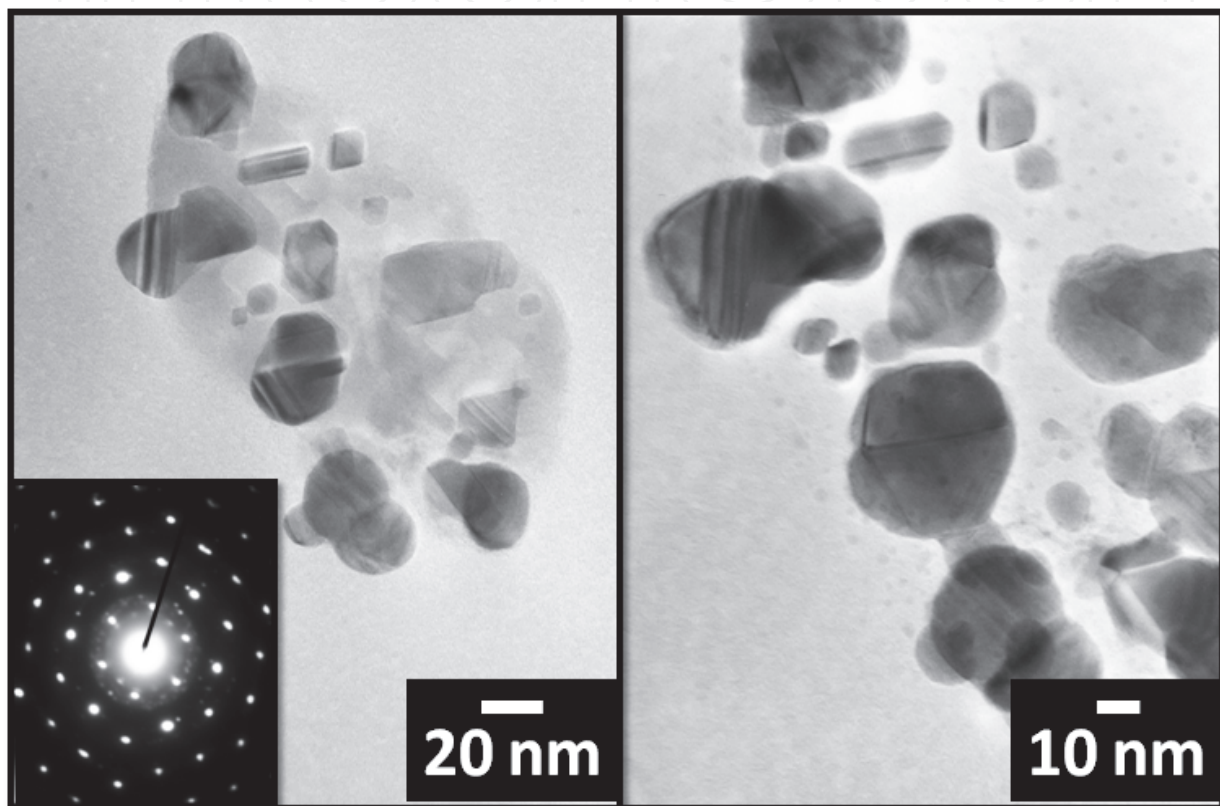


Fig. 5. Typical TEM images of silver nanostructures formed after 24 hours of the reaction, using 2 mL of *Camellia sinensis* extract with 5 mL of 10^{-3} M aqueous solution AgNO_3 . The inset shows the SAED pattern which correspond to a FCC structure.

In case of platinum, the nanoparticles obtained by bioreduction with *Camellia sinensis* aqueous extract, are shown in the micrographs of figure 6. The morphology of the nanoparticles was mainly spherical with a size between 2-10 nm.

Control of the size and morphology of the resultant nanostructures can be related to the interactions between biomolecules (e.g., terpenoids, polyphenols and phenolic acids) and metal atoms. Therefore, it is thought that phenolic acid type biomolecules present in *Camellia sinensis* extract, are responsible for the reduction of silver, chloroaurate and chloroplatinate ions, and also for the stabilization of the nanoparticles throughout electrostatic interactions. Although good efforts have been done to elucidate these reduction and stabilization mechanisms, more studies are required.

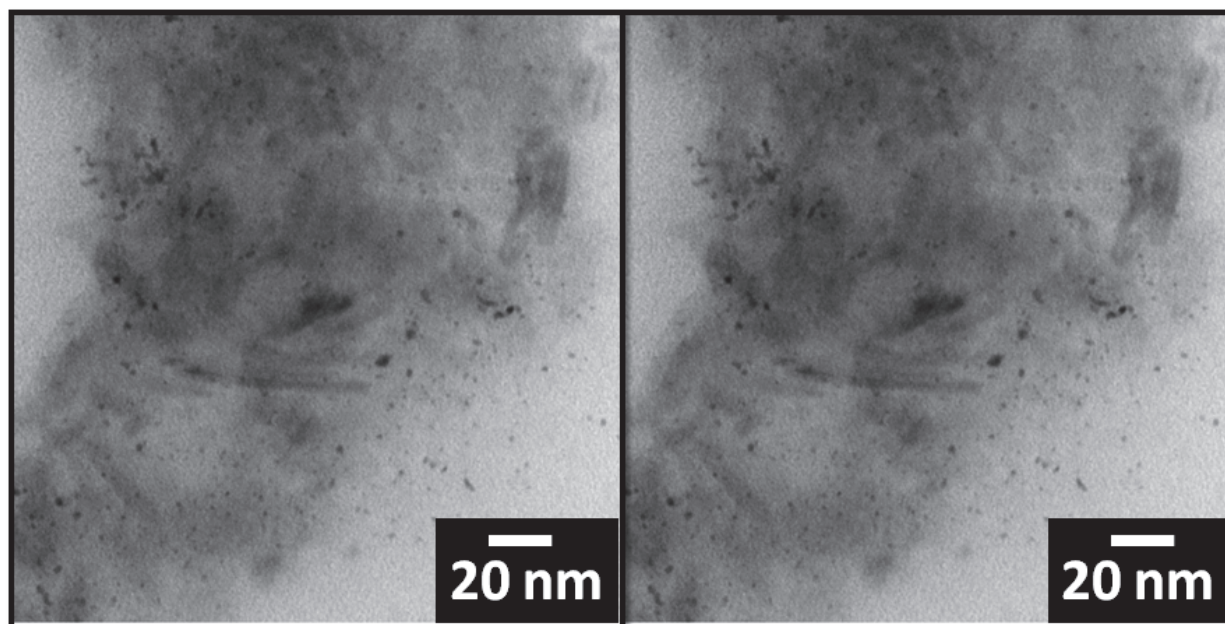


Fig. 6. Typical TEM images of platinum nanoparticles formed after 24 hours of the reaction, using 5 mL of *Camellia sinensis* extract with 5 mL of 10^{-3} M aqueous solution H_2PtCl_6 .

3.2 *Opuntia ficus indica* system

Chemical composition of *Opuntia ficus indica* cladodes are mainly water (92%), carbohydrates (~4-6%), proteins (~1%), vegetable fats (~0.2%), minerals (~1%) such as calcium and iron predominantly, and vitamins mainly ascorbic acid (vitamin C) [41,42]. On another hand, it has been demonstrated by Sun et al. [43] that gold nanoparticles can be obtained directly and simply by reduction of Au(III) ions with ascorbic acid as reducing agent.

The carbohydrate fraction of the *Opuntia ficus indica* can be attributed mainly to the starch and soluble sugars contents. The cladodes showed higher starch contents (from 7 to 13/100 g of dry weight) than soluble sugars (from 6 to 2/100 g of dry weight), in contrast, protein and fats contents showed poorer quantities. Besides, cladodes exhibited also low pH values due to the presence of many organic acids such as: malic, citric and oxalic acids [44]. Carboxylic moieties show a great affinity towards the surface of the nanoparticles, for this reason nanoparticles can be stabilized through electrostatic interactions with carboxylic groups, as reported previously by K Yoosaf et al. [38].

Opuntia ficus indica is considered as a great source of natural antioxidant compounds due to the content of polyphenols, higher than 900 mg/100g of dry matter, which are mainly responsible for an antioxidant activity [44]. This type of compounds play an important role during metal ion reduction processes in biosynthetic methods, as stated in previously reported [13]. Although a more detailed study is required to establish a detailed mechanism of formation and stabilization of the metallic nanoparticles, we can assumed that hydroxyl and carboxylic groups present in the biomolecules of the *Opuntia ficus indica* extract play an important role in the Ag(I) and Au(III) ions reduction and can also control the size and the stability of the nanostructures formed.

When *Opuntia ficus indica* aqueous extract is combined with 10^{-3} M aqueous AgNO_3 and HAuCl_4 , solutions color changes from pale yellow to dark yellow and from yellowish to red due to the formation of silver and gold nanoparticles respectively, as a consequence of the excitation of surface plasmon vibrations.

The UV-vis absorption spectra of silver nanoparticles, formed after 1 hour of reaction using different quantities of *Opuntia ficus indica* extract, are shown in Fig. 7(a) Spectra 1, 2 and 3 correspond respectively to 10, 5 and 1 ml of *Opuntia ficus indica* extract used as bioreducing agent. Spectra 2 and 3 show a single absorption band centered at 398 nm. In contrast, spectra 1 exhibits an insignificant intensity band at 404 nm width, which can be attributable to an insufficient amount of reductive biomolecules for the Ag^{+1} reduction ; consequently fewer silver nanoparticles are formed.

As described by Huang et al. [13], weaker binding of biomolecules with the nascent silver nanoparticles could lead to isotropic growth of the crystals and further formation of spherical nanoparticles.

In plant-mediated synthesis, the control of the size of silver nanoparticles has been proposed to be time-reaction dependent [45]. Basically, the longer the reaction time, the larger the sizes and the nanoparticles change from polycrystalline to single crystalline. Fig. 7(b) shows UV-vis spectra after 1 and 65 hours or reaction time. The fact that the spectra are very similar indicates that the particles have essentially the same size and shape (spheroids). This behavior takes place only when 5 ml of *Opuntia ficus indica* extract are used as the reducing agent. However, when this quantity is doubled, the corresponding UV-Vis band disappears after 65 hours, and silver micro-particles are deposited in the reaction solution as a result of a coalescence process of nanoparticles and probably due to the poor efficacy of *Opuntia ficus indica* extract capping biomolecules in stabilizing the silver nanoparticles through time, thus increasing the size of Ag crystals.

Addition of *Opuntia ficus indica* extract to 10^{-3} M aqueous HAuCl_4 solution led to the appearance of a blue color in solution after about 1 h of reaction, indicating the formation of gold nanoparticles (inset in figure 9). The UV-vis absorption spectrum recorded from this solution shows the characteristic surface plasmon resonance (SPR) band of gold nanoparticles centered at 540 nm (Figure 8). The kinetics of formation of gold nanoparticles was followed by UV-Vis spectroscopy, and the spectra obtained are shown in Figure 8. It is observed that with the progress of the reaction the absorbance intensity at 540 nm increases monotonically with time when 1 mL of *Opuntia ficus indica* extract is employed, while with time, the band centered at 560 nm for the system that used 2 mL of *Opuntia ficus indica* extract for the reduction undergoes a further red shift before stabilizing at 640 nm after completion of reaction. These time-dependent features in the UV-Vis spectra are characteristic of aggregated spherical nanoparticles or anisotropic nanostructures whose dimensions change with time. Figure 8b shows the UV-Vis absorbance spectra of gold nanoparticles synthesized 2 mL of *Opuntia ficus indica* extract recorded from 05 to 4 h of the reaction. It can be observed in figure 9 a clearly band shift to longer wavelengths and strong intensity with the time. It is well known that rod-shaped and flat gold nanoparticles absorb in the NIR region of the electromagnetic spectrum [12, 46]. Such nanostructures exhibit two well-separated absorption bands wherein the low wavelength band centered at ca. 540 nm corresponds to the transverse

surface plasmon vibration while the long wavelength component corresponds to the longitudinal surface plasmon absorption. [47] The first signal could be enclosed by the second one, causing that the spectra profile non symmetric of figure 8b.

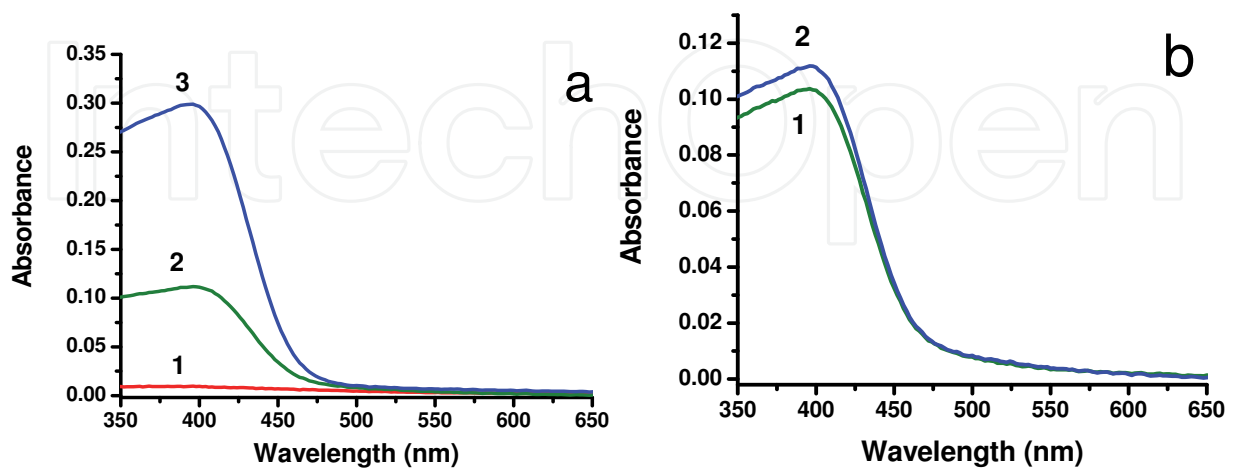


Fig. 7. **a)** UV-Vis absorption spectra of silver nanoparticles formed after 1 hour of the reaction of different amounts (1, 5 and 10 ml, curves 1-3 respectively) of *Opuntia ficus indica* extract with 5 ml of 10^{-3} M aqueous solution of AgNO_3 . **b)** UV-Vis absorption spectra of silver nanostructures formed with 5 ml of *Opuntia ficus indica* extract and 5 ml of 10^{-3} M aqueous solution of AgNO_3 after 1 and 65 hours of the reaction (curves 1 and 2, respectively).

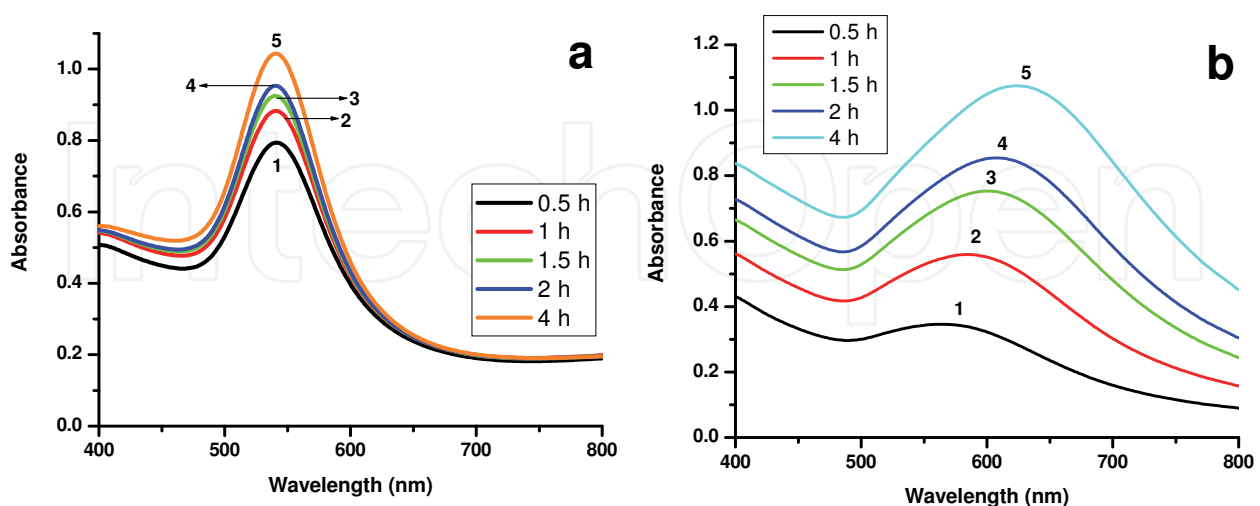


Fig. 8. UV-Vis absorption spectra of gold nanoparticles measured during the reaction of **a)** 1 mL and **b)** 2 mL of *Opuntia ficus indica* aqueous extract with 5 ml of 10^{-3} M solution of HAuCl_4 , respectively (final volume of reaction mixture adjuste to 10 mL using deionized water); after 0.5, 1, 1.5, 2 and 4 h of reaction (curves 1-5, respectively)

Figure 9 presents a plot of the plasmon intensity at 540 nm against reaction time, from the graph in figure 8a. It can be seen easily that the plasmon intensity at the reaction time of 2 h is near to that at 4 h, meaning completion of the reaction. The inset of figure 9 presents the final color in the mixture solution after 4 h of reaction time. The extract was light green before reaction with gold ions and changed to pale blue and blue after 4 hours of reaction time, with 1 mL and 2 mL of *Opuntia ficus indica* extract, respectively, and then the color did not change any more with reaction time. The characteristic blue of gold nanoparticles solutions provided a convenient spectroscopic signature to indicate their formation.

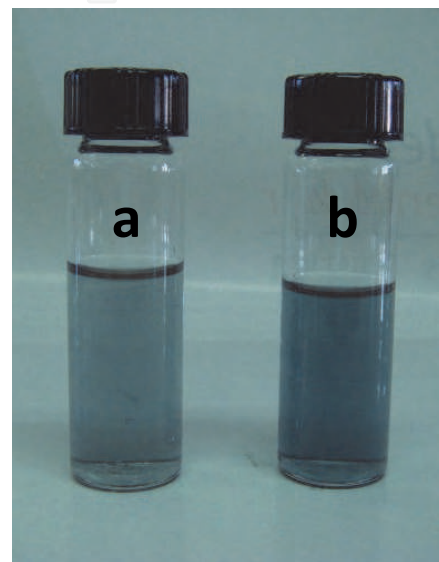
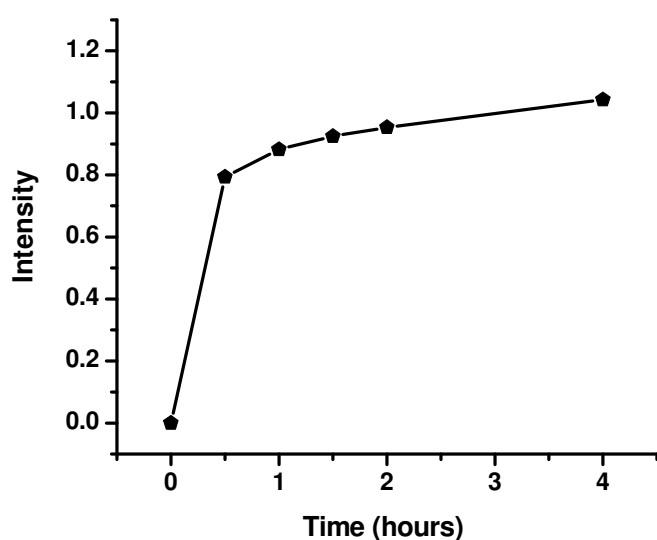


Fig. 9. Plot of the intensity of surface plasmon resonance at 540 nm against the reaction time, for gold nanoparticles obtained from 1 mL of *Opuntia ficus indica* aqueous extract with 5 ml of 10^{-3} M solution of HAuCl_4 . The inset shows photos of the different nanoparticle solutions after 4 h of the reaction whose labels correspond to spectra **a**) and **b**) shown in the figure 8.

TEM analysis reveals that silver nanoparticles are predominately ellipsoids, as can be observed in Fig. 10(a). Micrograph 10b and histogram 10b correspond to silver nanoparticles formed after 24 hours of reaction, using 5 ml of 10^{-3} M of aqueous solution AgNO_3 . Nanoparticles sizes are between 8 and 50 nm, with an average of $23.5 \text{ nm} \pm 5 \text{ nm}$. A typical selected area diffraction pattern is shown in the inset of Fig. 10a. Diffraction rings can be indexed as (200), (220), (311) and (222) reflections (indicated by numbers 1, 2, 3 and 4 respectively), corresponding to a FCC structure of silver. For the 1 and 10 ml of biomass extract, the average particle size was 8.6 and 53 nm, respectively. Figure 11(a) shows silver nanoparticles after 24 hours of the bioreduction process, with the same amount of silver ions and volume of reducing agent used previously in Figure 10(a) but kept at 60°C instead of at room temperature. Average particle size is reduced to 8.1 nm, and the particles are quite spherical.

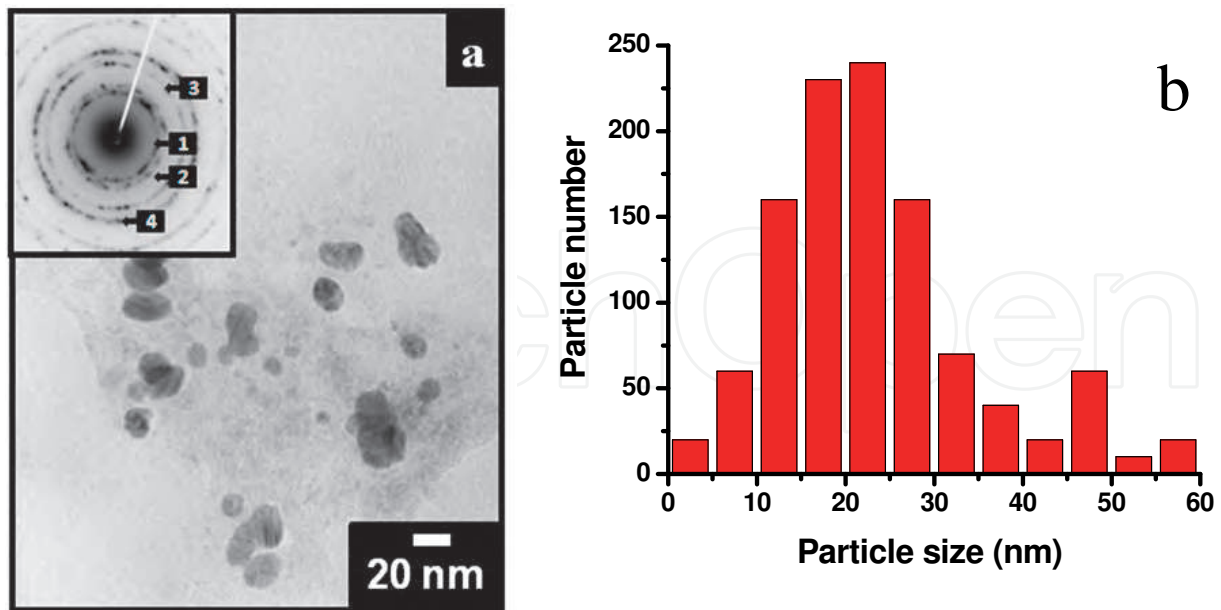


Fig. 10. **a)** Representative TEM image of silver nanoparticles synthesized with 5 ml of *Opuntia ficus indica* extract when reacting with 5 ml of 10^{-3} M aqueous solution of AgNO_3 . **Inset 10 a)** Electron diffraction pattern of (a), which can be indexed on the basis of the FCC structures of silver. **b)** Size distribution of Ag nanoparticles synthesized with 5 ml of *Opuntia ficus indica* extract when reacting with 5 ml of 10^{-3} M aqueous solution of AgNO_3 .

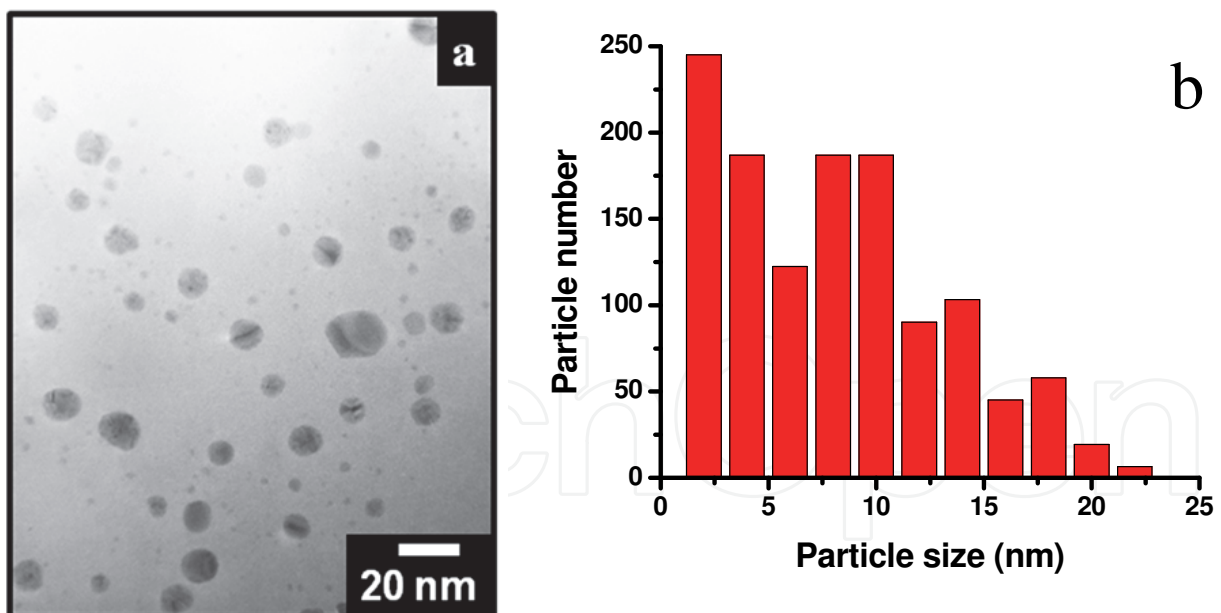


Fig. 11. **a)** Representative TEM image of Ag nanoparticles formed after 24 hours of the bioreduction, with 5 ml of *Opuntia ficus indica* extract and 5 ml of 10^{-3} M aqueous solution of AgNO_3 at 60°C . **b)** Histogram showing the Ag nanoparticles size distribution obtained at 60°C .

Figure 12 shows typical TEM micrograph of gold nanoparticles synthesized using of *Opuntia ficus indica* extract. The morphology of the nanoparticles observed was icosahedral,

multiple-twined particles, but also irregular shapes were formed, with an average size of 40 nm. The inset SAED pattern revealed that the diffraction rings from inner to outer, could be indexed as (111), (200), (220), and (311) reflections, respectively, corresponding to face-centered cubic (FCC) gold. The diffraction rings also suggested the NPs were polycrystalline.

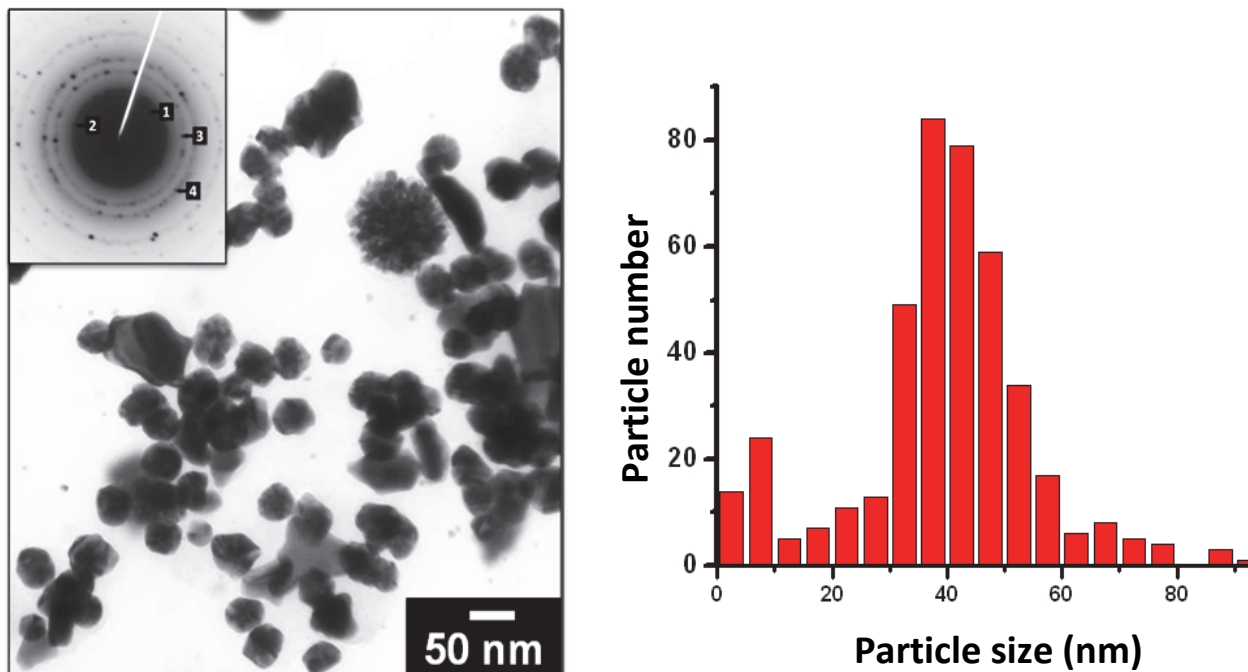


Fig. 12. **a)** Transmission electron micrograph of gold nanoparticles after bioreduction. Gold nanoparticles were obtained by exposing 2 mL of *Opuntia ficus indica* extract to 5 ml of 10^{-3} M solution of HAuCl_4 . The inset shows the electron diffraction pattern of the gold particles in the main part of the image. Rings 1, 2, and 3 arise due to reflections from the (111), (200), (220) and (311) lattice planes of FCC gold. **b)** Histogram of size distribution of gold nanoparticles synthesized by the experiment of figure 12a. The average particle size is 40 nm.

4. Summary

If nanotechnology is to realize its full promise and potential, it is essential that these next-generation materials be designed from the outset to be benign to human health and the environment.

Nanoparticles of gold, silver and platinum have been successfully prepared using a simple and efficient green nanochemistry methodology. Furthermore, we have demonstrated that use of natural, renewable and low cost biological reducing agents, such as *Camellia sinensis* and *Opuntia ficus indica* can produce noble metal nanostructures in aqueous solution at ambient conditions, avoiding, in consequence, the presence of hazardous and toxic solvents and waste.

The colloidal systems of silver and gold nanoparticles, stabilized by the bio-molecules present in the *Camellia sinensis* and *Opuntia ficus indica* aqueous solutions, are currently under evaluation as potential useful bio-imaging agents for medical applications due to their characteristic optical properties exhibited.

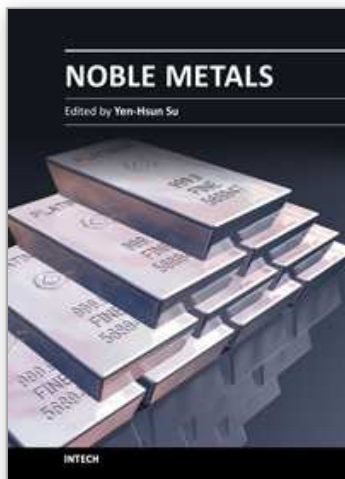
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