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Extracellular biosynthesis of gold nanoparticles using sugar beet pulp

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ABSTRACT

Sugar beet pulp was used as redactor agent for the synthesis of gold nanoparticles. The method developed is environmentally friendly and allows control of nanoparticles shapes by changing the initial pH value of aqueous $HAuCl_4$ solutions. At low initial pH values, polygonal nanoparticles were obtained, mainly triangular and hexagonal shapes. Increasing the pH value, nanorods together with polygonal nanoparticles were produced. At higher initial pH, gold nanowires were formed. Gold biosorption took place at long reaction time, especially at low pH. This procedure could be useful to remove or recover metals from aqueous wastes. The synthesis of other metallic nanostructures such as silver and platinum could be achieved following a similar procedure.

1. Introduction

Gold nanoparticles are interesting due to their applications in optoelectronic, electronic and magnetic devices, and because of their use as catalysts and sensors. These properties strongly depend on size, shape, crystallinity and structure [1]. A variety of shapes have been obtained such as nanospheres [2], nanorods [3], nanowires [4], nanoplates [5], nanocubes [6], nanobelts [7], nanopoles [8] and unusual angled shapes [9]. One- and two-dimensional nanostructures for noble metals are especially attractive [10]. Gold nanowires may be required to connect nanoelectronic devices [11] and have also been used in chemical-sensing devices [12]. Shape is also important in catalysis, Narayanan and El-Sayed [13] reported that platinum tetrapod-shaped catalysed the Suzuki cross-coupling reaction while spherical nanoparticles were unable to catalyse it. Tadpole-shaped gold nanoparticles have unusual optical and electrical properties which may be useful for the assembly of nanodevices or joints biochips [9].

A variety of methods have been developed to achieve control over nanoparticles dimensions. Most of these methods are based on chemical reactions in solution ("wet chemistry"). The Brust–Schiffrin method consists of two-phase synthesis and stabilization by thiols [14]. Gold nanoparticles can be stabilized by other sulfur ligands, such as xantates and disulfides, di- and trithiols and resorcinarene tetrathiols. In addition, other reagents can be used as ligands: phosphine, amine and carboxylate, isocyanide, acetone and iodine [15]. Gold nanoparticles can be synthesized using microemulsion, copolymer micelles, reversed micelles, surfactant, membranes and other amphiphiles [16–18]. The seeding-growth method is very useful in nanorods fabrication [19]. Physical methods include photochemistry (UV, near-IR) [16], sonochemistry [20], radiolysis [21] and thermolysis [22].

Currently, biosynthesis of nanoparticles has attracted scientists' attention because of the necessity to develop new clean, cost-effective and efficient synthesis techniques. There are several organisms capable of synthesizing nanoparticles such as diatoms that produce siliceous materials or magnetostatic bacteria that synthesize magnetite nanoparticles [23]. Biosynthesis of gold nanoparticles has been reported using bacteria, yeasts, actinomycetes, fungi and plants [24], such as the bacteria *Brevibacterium casei* [25], the fungus *Aspergillus oryzae* var. *viridis* [26] or the plants tansy fruit [27] and *Syzygium aromaticum* [28]. Metal nanoparticles can be prepared by intracellular or extracellular reduction. Former experiments were carried out with bacteria. Beveridge and Murray found that gold nanoparticles could be precipitated within bacterial cells [29]. Deplanche and Macaskie reported the biorecovery of gold by *Escherichia coli* and *Desulfovibrio desulfuricans* [30]. In recent years, *Pseudomonas aeruginosa* has been used for the extracellular biosynthesis of gold nanoparticles with different sizes and shapes [31]. However, eukaryotes contain many proteins able to act as reducing agents and have the advantage of easy handling. Several processes have been developed successfully using fungi like *Fusarium semitectum* [32], or plants extracts like *Cinnamomum camphora* [33], due to the great amount of proteins that they can excrete. Moreover, efforts have been made to control the shape and size of gold nanoparticles produced by organisms through changing experimental parameters related with growth mechanism. Recently, Chandran et al. have obtained gold nanotriangles

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using *Aloe vera* plant extract [34]. He et al. have also reported the synthesis of gold nanowires using extract of *Rhodopseudomonas capsulata* [35].

Metal biosorption takes place during gold nanoparticles synthesis. Biosorption is a promising process to recover precious metals from wastewaters using biomass of different kind. Certain biomasses are able to bind and concentrate gold and other metals from even very dilute aqueous solutions. Niu and Volesky studied metal biosorption using waste crab shells [36]. Mata et al. obtained gold nanoparticles using the brown alga *Fucus vesiculosus* [37]. This biotechnology involves low operating costs, minimization of reagents, energy and waste products, and high efficiency and biotechnology could be an alternative to conventional metallurgical process [38].

In this work, biosynthesis of gold nanoparticles has been investigated using aqueous chloroaurate ions and sugar beet pulp. This industrial waste of the sugar industry was used as reducing agent. Sugar beet (*Beta vulgaris*) pulp is a residue obtained by heating sugar beet cossettes in water during the extraction of the juice used for the crystallization of sugar. The shape of the nanoparticles produced was controlled varying the initial pH value of the reaction medium: triangular nanoplates at low pH and nanowires at high pH values. Additionally, gold biosorption took place at long reaction time and at low pH values.

2. Materials and methods

2.1. Materials

All chemical reagents including chloroauric acid ($HAuCl_4$), sodium hydroxide flakes and hydrochloric acid (37%) were obtained from Panreac and used as received.

2.2. Sugar beet pulp preparation

The sugar beet pulp was provided by Azucarera Ebro Agrícola plant in Toro (Zamora, Spain). The pulp was collected directly from the final drying line to ensure freshness and ease of use for the experimentation with respect to the pelletized form. The sugar beet pulp was washed repeatedly with tap water and filtered through a cheese-cloth to remove the molasses. The pulp was then dried in a stove at 60 °C and ground with an agate mortar. In batch experiments a pulp particle size lower than 0.5 mm was used.

2.3. Synthesis of gold nanoparticles

Different initial pH values (2–10) of 0.5×10^{-3} M aqueous $HAuCl_4$ solutions were prepared. Synthesis tests were carried out with 0.25 g of sugar beet pulp, 50 ml of $AuCl_4$ solutions under stirring and at 25 °C for 48 h. Several samples were collected at different times for analysis. The biomass was removed from the reaction mixture to analyze the samples at several times and the biomass after the process. The mixture was filtered using nylon membrane filters 0.2 μm from Whatman. After 48 h of reaction, the pulp was separated by centrifugation (4500 rpm) for 10 min and washed four times with deionized water.

2.4. UV–vis absorbance spectroscopy study

The UV–vis spectra of samples at different reaction times were analyzed using a Libra S11 single beam spectrophotometer operated at a resolution of 5 nm with quartz cells. Blanks for each of the sample sets were deionized water.

2.5. TEM observations

TEM samples of the gold nanoparticles synthesized were prepared by placing drops of the product solution onto carbon-coated copper grids and allowing the solvent to evaporate. TEM measurements were performed on a JEOL model JEM-2000FX instrument operated at an accelerating voltage of 200 kV.

2.6. SEM-EDS study

Sugar beet pulp, before and after reduction process, was coated with a thin layer of graphite and examined in a scanning electron microscope (SEM) (JEOL JSM-6400) with an energy-dispersive elemental (EDS) analyzer. The chemical composition of the products was determined by energy-dispersive X-ray spectroscopy (EDS) using a JEOL model JEM-2000FX instrument.

2.7. FTIR analysis

The pellet analyzed was made with 0.5–3 mg of sample (sugar beet pulp plus gold nanoparticles) and approximately 250 mg of KBr. The spectra were recorded with a Nicolet Magna 750 in the region of 500–4000 cm^{-1} at a resolution of 4 cm^{-1}.

2.8. pH and redox potential measurements

pH and redox potential of the gold solution (2 ml) were measured at the end of process using a pHmeter Crison Basic 20.

3. Results and discussion

3.1. Effect of initial pH on the biosynthesis of gold nanoparticles

The initial pH value of the aqueous $HAuCl_4$ solutions for different sets of samples was the main parameter studied in the synthesis of gold nanoparticles using sugar beet pulp at a concentration of 5×10^{-3} g/l. The color of gold solutions changed from pale yellow to dark blue (Fig. 1). This change would be an indication of gold reduction by sugar beet pulp and the formation of nanoparticles. The different color of the solution as a function of pH shows that the shape and size of the nanoparticles produced using this technique could be controlled through pH adjustment. The formation of gold nanoparticles took place in a first stage, since the blue color is characteristic of anisotropic gold nanostructures.

Moreover, sugar beet pulp is able to bind and concentrate gold from aqueous solutions in a second stage. In general, biosorption mechanisms are based on physico-chemical interactions between Au^{3+} ions and the functional groups present on the biomass surface, commonly carboxylate, hydroxyl, amine and phosphoryl groups present in polysaccharides, lipids and proteins. The pH of the gold aqueous solution is one of the most influential variables in the biosorption process. Gold is present in solution in anionic form and sorption of gold shows a maximum value under acidic pH. The blue color of the solution disappeared at acid pH values (2 and 4) after 24 h and no analytical evidence of nanoparticles was found by UV–vis spectroscopy and TEM. The color disappearance suggested the absence of nanoparticles in solution due to its sorption on the sugar beet pulp. These nuclei grew when the biomass and the gold solution were kept in contact for 24 h.

The variation of pH and redox potential after 48 h of gold reduction is shown in Table 1. The sharp decrease of these parameters is another evidence of gold reduction. The decrease of pH would be related to protons release during gold reduction. At low pH values, cell wall functional groups become highly protonated, resulting in an overall positive charge that attract electrostatically negatively

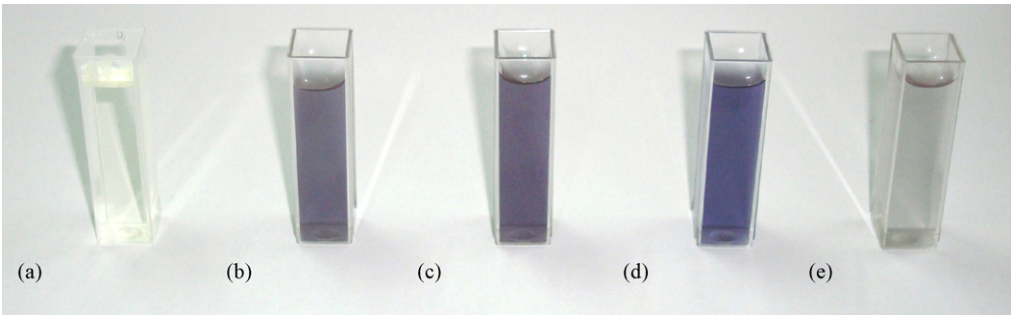

Fig. 1. Color changes of gold nanoparticle solutions after 7 h at different pH values: (a) control $HAuCl_4$ solution, (b) pH 2, (c) pH 4, (d) pH 7 and (e) pH 10.

Table 1
Variation of pH and redox potential in solution after gold reduction with sugar beet pulp at different initial pH values.

$pH_{initial}$	2	4	7	10
$E_{initial}$ (mV vs. Ag/AgCl)	741	727	620	476
48 h				
pH_{final}	1.89	3.78	4.31	5.82
E_{final} (mV vs. Ag/AgCl)	377	249	266	374

charged ions $AuCl_4^-$. Kuyucak and Volesky [38] have suggested that the following reaction occurs:

$$AuCl_4^- + 3R\text{–}OH \rightarrow Au^0 + 3R{=}O + 3H^+ + 4Cl^- \quad (1)$$

Reaction (Eq. (1)) indicates that gold reduction is accompanied by the oxidation of hydroxyl to carbonyl groups present in the sugar beet pulp. In fact, hydroxyl groups are very abundant in polysaccharides of the sugar beet pulp and could participate in the gold recovery.

At higher initial pH values (7 and 10), the color of the solution did not disappear after 24 h and the gold sorption was not observed. However, the color changed from blue to reddish suggesting a morphological change of the gold nanoparticles from nanorods and nanowires to spheres.

3.2. UV–vis spectral study

The UV–vis absorption spectra recorded from the solutions at different initial pH values after 7 h of reaction are shown in Fig. 2. In all cases, a surface plasmon resonance (SPR) band absorption peak appears centered at approximately 560 nm, which is characteristic of gold nanoparticles. At a longer wavelength, a second band related to aggregates of spherical nanoparticles [39] or anisotropic nanostructures [1] is shown in solutions at pH 2, 4 and 7. The nanoparticles solutions exhibit two absorbance bands. The relative intensity and position of the second band occurs in the near-IR region and is a function of the initial pH value. This band corresponds to the longitudinal surface plasmon absorption of rod-shaped and flat gold nanoparticles. At pH 10, the absorbance curve is practically flat in the range of 500–825 nm and corresponds to the light blue sample. Generally, one-dimensional nanostructures exhibit two plasmon absorption peaks with energies characteristic of the longitudinal and the transversal axes of these particles. In this case, the two peaks cannot be observed due to the overlap of the longitudinal absorption of the nanowires with different aspect ratios at relevant wavelengths [35].

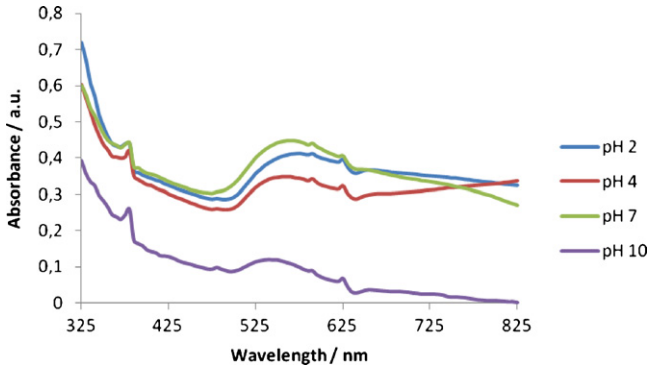

Fig. 2. UV–vis spectra of gold nanoparticles solutions after 7 h shown in Fig. 1.

Triangular nanoparticles, nanorods and nanowires of gold display two distinct SPR bands referred to as transverse and longitudinal electron oscillations. The transverse SPR band coincides with the longitudinal SPR band of spherical gold nanoparticles. However, the longitudinal oscillation is very sensitive to the nanoparticle shape. In consequence, slight deviations from spherical shape can lead to dramatic color changes. Longitudinal SPR band is a strong function of the edge length of the triangles [34]. Gold nanorods and nanowires exhibit a band corresponding to the short axis and another corresponding to the long axis at a longer wavelength [10].

3.3. Characterization of gold nanoparticles

The morphology of the gold nanoparticles was observed by transmission electron microscopy. Fig. 3 shows representative TEM images of the nanoparticles synthesized using sugar beet pulp at different pH values. TEM observations revealed that gold nanoparticles formed at acidic medium were mainly triangular and spherical (Fig. 3a and b). The edge length of the triangles can reach 200 nm at pH 2. When the pH was increased to 4, the edge of the triangles was not well defined and the average size was 160 nm, and spherical nanoparticles (~20 nm) were formed. An increase of initial solution pH favored the formation of one-dimensional nanostructures. At neutral pH, gold nanorods together with spherical and triangular nanoparticles were formed (Fig. 3c). The analysis shows that the average diameter of the nanorods is about 25 nm and the length is very variable from 40 to 290 nm. Gold nanowires were also obtained at alkaline pH (Fig. 3d). The diameter of the nanowires is approximately 30 nm.

The synthesis of gold nanotriangles under acidic conditions could be produced by slow reduction and slow crystallization leads to the formation of stable multiply twinned particles which evolve into gold nanotriangles due to the shape-directing effect of the constituents of the sugar beet pulp. Moreover, the difference in the growth rates of the various crystallographic planes could lead to the changes of the morphology of the nanoparticles [40].

Our results show that one-dimensional nanostructures were produced increasing solution pH. The explanation for this probably involves Ostwald ripening and the capping action of the biomolecules. In spite that molecules of the biomass were available, there may be competition from the hydroxide ion for the

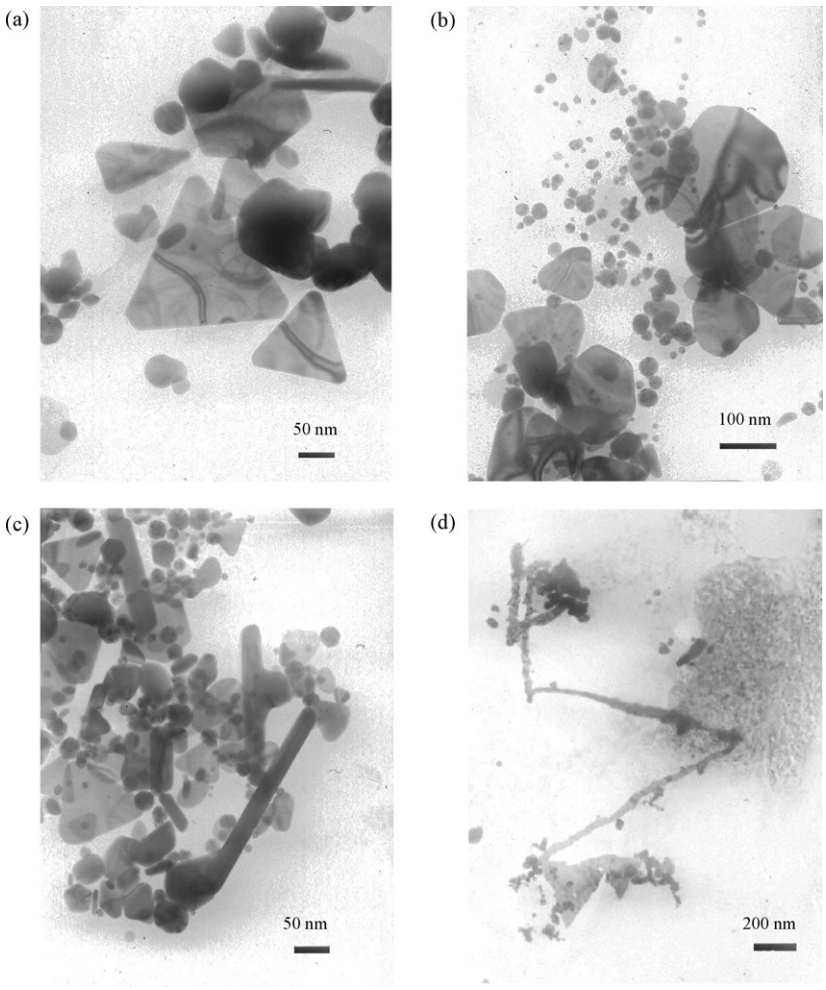

Fig. 3. TEM images of gold nanostructures synthesized using sugar beet pulp at different initial pH values: (a) pH 2, (b) pH 4, (c) pH 7 and (d) pH 10.

gold ion. In fact, hydroxide is a strong complexing agent of gold ion ($\log K_3 = 38.6$) and could interfere with the capping ability of molecules present in the sugar beet pulp [41].

Furthermore, sugar beet pulp, before and after being in contact with the gold aqueous solution for 48 h, was examined by SEM to confirm the biosorption mechanism (Fig. 4a). Gold particles were microprecipitated on the surface of the sugar beet pulp at low pH. These precipitates were formed in a second stage which was characterized by a decrease of gold ion concentration in solution and the absence of color in the solutions after more than 24 h. The brighter areas of the backscattered electron images correspond to metallic gold, as identified by EDS analysis (Fig. 4b) giving an evidence of the gold presence on the pulp. The precipitates had different sizes and reached 6 μm.

3.4. Functional groups involved in the biosynthesis of gold nanoparticles

The nature of the biomolecules involved in the reduction and formation of gold nanoparticles was studied by FTIR analysis of

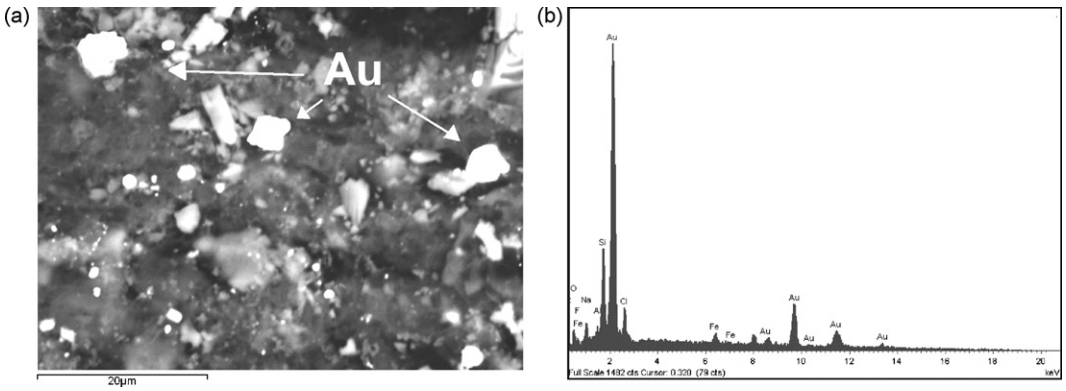

Fig. 4. Backscattered electron SEM micrograph of gold microparticles biosorbed onto sugar beet pulp at pH 4 after 48 h (a) and its corresponding EDS spectrum (b).

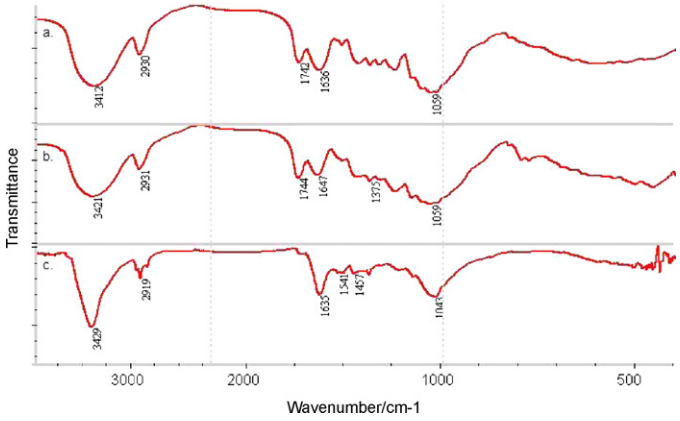

Fig. 5. FTIR spectra of (a) sugar beet pulp before and (b) after gold reduction and (c) gold nanoparticles synthesized.

the biomass before and after reduction and of the nanoparticles (Fig. 5). The FTIR spectrum of the unreacted sugar beet pulp shows bands at 1742 and 1636 cm^{-1} (Fig. 5a). The first band is characteristic of stretching vibrations of the carbonyl functional group in ketones, aldehydes and carboxylic acids. The second absorption at 1636 cm^{-1} corresponds to the amide I band. The intense broad absorbance at 3412 cm^{-1} is attributed to the O–H stretching modes of vibration in hydroxyl functional group in alcohols and N–H stretching vibrations in amides and amines. Moreover, the 1059 cm^{-1} band can be assigned to C–O stretching vibrations. The absorption peak at 2930 cm^{-1} corresponds to C–H stretching vibration modes in the hydrocarbon chains. The spectrum of the biomass after gold reduction shows the same bands that in the untreated biomass. The main difference between both spectra is that the treated biomass exhibits peaks of less intensity for the amide I band. This would suggest that proteins are responsible for Au(III) reduction and gold nanoparticles stabilization. The particles would have been stabilized in solution by the capping agent provided by proteins of the sugar beet pulp. FTIR analysis of gold nanoparticles shows the presence of three bands at 1635, 1541 and 1457 cm^{-1} (Fig. 5c). The two first absorptions are characteristic of amide I and II bands, respectively. The other band at 1457 cm^{-1} is assigned to the methylene scissoring vibrations of proteins. Another band at 1043 cm^{-1} can be related to S=O stretching vibrations. Sugar beet pulp may contain proteins and it is well-known that gold nanoparticles can be capped and stabilized by them. The surface-bound is established through free amine groups or cysteine residues in the proteins [34,42].

4. Conclusions

Reduction of tetrachloroaurate with sugar beet pulp is a simple, room temperature and efficient biological method to synthesize gold nanostructures from dilute solutions that can reuse industry wastes. This could be an alternative method for the nanoparticles synthesis from dilute hydrometallurgical solutions.

The nanoparticle shape can be controlled by the initial pH of the aqueous $HAuCl_4$ solution. Proteins are the principal biomolecules involved in the biosynthesis.

Optimum gold biorecovery requires control of both pH solution and time reaction. Gold biosorption took place at low initial pH values after 24 h due to the presence of hydroxyl groups in the biomass.

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References

[1] K.L. Kelly, E. Coronado, L.L. Zhao, G.C. Schatz, The optical properties of metal nanoparticles: The influence of size, shape, and dielectric environment, J. Phys. Chem. B 107 (2003) 668–677.
[2] J. Zhang, B. Zhao, L. Meng, H. Wu, X. Wang, C. Li, Controlled synthesis of gold nanospheres and single crystals in hydrogel, J. Nano Res. 9 (2007) 1167–1171.
[3] A.V. Alekseeva, V.A. Bogatyrev, B.N. Khlebtsov, A.G. Mel'nikov, L.A. Dykman, N.G. Khlebtsov, Gold nanorods: synthesis and optical properties, Colloid J. 68 (2006) 661–678.
[4] L.H. Pei, K. Mori, M. Adachi, Formation process of two-dimensional networked gold nanowires by citrate reduction of $AuCl_4^-$ and the shape stabilization, Langmuir 20 (2004) 7837–7843.
[5] L. Wang, X. Chen, J. Zhang, Y. Chai, C. Yang, L. Xu, W. Zhuang, B. Jing, Synthesis of gold nano- and microplates in hexagonal liquid crystals, J. Phys. Chem. B 109 (2005) 3189–3194.
[6] T.K. Sau, C.J. Murphy, Room temperature, high-yield synthesis of multiple shapes of gold nanoparticles in aqueous solution, J. Am. Chem. Soc. 126 (2004) 8648–8649.
[7] Y. Chen, C. Somsen, S. Milenkovic, A.W. Hassel, Fabrication of single crystalline gold nanobelts, J. Mater. Chem. 19 (2009) 924–927.
[8] J.Q. Hu, Y. Zhang, B. Liu, J.X. Liu, H.H. Zhou, Y.F. Xu, Y.X. Jiang, Z.L. Yang, Z.Q. Tian, Synthesis and properties of tadpole-shaped gold nanoparticles, J. Am. Chem. Soc. 126 (2006) 9470–9471.
[9] A. Sanchez-Iglesias, M. Grzelczak, B. Rodríguez-González, R.A. Alvarez-Puebla, L.M. Liz-Marzán, N.A. Kotov, Gold colloids with unconventional angled shapes, Langmuir 25 (2009) 11431–11435.
[10] C.J. Murphy, A.M. Gole, S.E. Hunyadi, C. Orendorff, One-dimensional colloidal gold and silver nanostructures, J. Inorg. Chem. 45 (2006) 7544–7554.
[11] N.A. Melosh, A. Boukai, F. Diana, B. Gerardot, A. Badolato, P.M. Petroff, J.R. Heath, Ultrahigh-density nanowire lattices and circuits, Science 300 (2003) 112–115.
[12] C.Z. Li, H.X. He, A. Bogozi, J.S. Bunch, N. Tao, Molecular detection based on conductance quantization of nanowires, J. Appl. Phys. Lett. 76 (2000) 1333–1336.
[13] R. Narayanan, M.A. El-Sayed, Effect of colloidal nanocatalysis on the metallic nanoparticle shape: the Suzuki reaction, Langmuir 21 (2005) 2027–2033.
[14] M. Brust, J. Fink, D. Bethell, D.J. Schiffrin, C. Kiely, Synthesis and reactions of functionalized gold nanoparticles, Chem. Commun. (1995) 1655–1656.
[15] M.C. Daniel, D. Astruc, Gold nanoparticles: assembly, supramolecular chemistry, quantum-size-related properties, and applications toward biology, catalysis, and nanotechnology, Chem. Rev. 104 (2004) 293–346.
[16] S Kundu, S. Panigrahi, S. Praharaj, S. Basu, S.K. Ghosh, A. Pal, T. Pal, Anisotropic growth of gold clusters to gold nanocubes under UV irradiation, Nanotechnology 18 (2007) 075712–075719.
[17] Z. Yang, Z.H. Lin, C.Y. Tang, H.T. Chang, Preparation and characterization of flower-like gold nanomaterials and iron oxide/gold composite nanomaterials, Nanotechnology 18 (2007) 255606–255613.
[18] D.W. Chang, L. Dai, Photo-induced formation and self-assembling of gold nanoparticles in aqueous solution of amphiphilic dendrimers with oligo(*p*-phenylene vinylene) core branches and oligo(ethylene oxide) terminal chains, Nanotechnology 18 (2007) 365605–365612.
[19] P.H. Qiu, C.B. Mao, Seed-mediated shape evolution of gold nanomaterials: from spherical nanoparticles to polycrystalline nanochains and single-crystalline nanowires, J. Nano Res. 11 (2009) 885–894.
[20] K. Okitsu, Y. Mizukoshi, T.A. Yamamoto, et al., Sonochemical synthesis of gold nanoparticles on chitosan, Mater. Lett. 61 (2007) 3429–3431.
[21] M.E. Meyre, M. Treguer-Delapierre, C. Faure, Radiation-induced synthesis of gold nanoparticles within lamellar phases. Formation of aligned colloidal gold by radiolysis, Langmuir 24 (2008) 4421–4425.
[22] M. Nakamoto, Y. Kashiwagi, M. Yamamoto, Synthesis and size regulation of gold nanoparticles by controlled thermolysis of ammonium gold(I) thiolate in the absence or presence of amines, Inorg. Chim. Acta 358 (2005) 4229–4236.
[23] D. Mandal, M.E. Bolander, D. Mukhopadhyay, G. Sarkar, P. Mukherjee, The use of microorganisms for the formation of metal nanoparticles and their application, Appl. Microbiol. Biotechnol. 69 (2006) 485–492.
[24] K.N. Thakkar, S.S. Mhatre, R.Y. Parikh, Biological synthesis of metallic nanoparticles, Nanomedicine: Nanotechnol. Biol. Med. 6 (2010) 257–262.
[25] K. Kalishwaralal, V. Deepak, S.R.K. Pandian, M. Kottaisamy, S. BarathManiKanth, B. Kartikeyan, S. Gurunathan, Biosynthesis of silver and gold nanoparticles using *Brevibacterium casei*, Colloids Surf. B: Biointerfaces 77 (2010) 257–262.
[26] A.R. Binupriya, M. Sathishkumar, K. Vijayaraghavan, S.-I. Yun, Bioreduction of trivalent aurum to nano-crystalline gold particles by active and inactive cells and cell-free extract of *Aspergillus oryzae* var. *viridis*, J. Hazard. Mater. 177 (2010) 539–545.

[27] S.P. Dubey, M. Lahtinen, M. Sillanpää, Tansy fruit mediated greener synthesis of silver and gold nanoparticles, Process Biochem. 45 (2010) 1065–1071.
[28] D. Raghunandan, M.D. Bedre, S. Basavaraja, B. Sawle, S.Y. Manjunath, A. Venkataraman, Rapid biosynthesis of irregular shaped gold nanoparticles from macerated aqueous extracellular dried clove buds (*Syzygium aromaticum*) solution, Colloids Surf. B: Biointerfaces 79 (2010) 235–240.
[29] T.J. Beveridge, R.G.E. Murray, Site of metal deposition in the cell-wall of *Bacillus subtilis*, J. Bacteriol. 141 (1980) 876–887.
[30] K. Deplanche, L.E. Macaskie, Biorecovery of gold by *Escherichia coli* and *Desulfovibrio desulfuricans*, Biotechnol. Bioeng. 99 (2008) 1055–1064.
[31] M.I. Husseiny, M.A. El-Aziz, Y. Badr, M.A. Mahmoud, Biosynthesis of gold nanoparticles using *Pseudomonas aeruginosa*, Spectrochim. Acta Part A: Mol. Biomol. Spectrosc. 67 (2007) 1003–1006.
[32] B.D. Sawle, B. Salimath, R. Deshpande, M.D. Bedre, B.K. Prabhakar, A. Venkataraman, Biosynthesis and stabilization of Au and Au–Ag alloy nanoparticles by fungus, *Fusarium semitectum*, Sci. Technol. Adv. Mater. 9 (2008) 35012–35017.
[33] J.L. Huang, Q.B. Li, D.H. Sun, Y.H. Lu, Y.B. Su, X. Yang, H.X. Wang, Y.P. Wang, W.Y. Shao, N. He, J.Q. Hong, C.X. Chen, Biosynthesis of silver and gold nanoparticles by novel sundried *Cinnamomum camphora* leaf, Nanotechnology 18 (2007) 1–11.
[34] S.P. Chandran, M. Chaudhary, R. Pasricha, A. Ahmad, M. Sastry, Synthesis of gold nanotriangles and silver nanoparticles using *Aloe vera* plant extract, Biotechnol. Prog. 22 (2006) 577–583.
[35] S. He, Y. Zhang, Z. Guo, N. Gu, Biological synthesis of gold nanowires using extract of *Rhodopseudomonas capsulate*, Biotechnol. Prog. 24 (2008) 476–480.
[36] H. Niu, B. Volesky, Characteristic of anionic metal species biosorption with waste crab shells, Hydrometallurgy 71 (2003) 209–215.
[37] Y.N. Mata, M.L. Blázquez, A. Ballester, F. González, J.A. Muñoz, Gold biosorption and bioreduction with brown alga *Fucus vesiculosus*, J. Hazard. Mater. 166 (2009) 612–618.
[38] N. Kuyucak, B. Volesky, Accumulation of gold by algal biosorbent, Biorecovery 1 (1989) 189–204.
[39] A.M. Schwarzberg, C.D. Grant, T. van Buuren, J.Z. Zhang, Reduction of $HAuCl_4$ by Na_2S revisited: the case for Au nanoparticle aggregates and against Au_2S/Au core/shell particles, J. Phys. Chem. C 111 (2007) 8892–8901.
[40] M. Grzelczak, J. Pérez-Juste, P. Mulvaney, L.M. Liz-Marzán, Shape control in gold nanoparticle synthesis, Chem. Soc. Rev. 37 (2008) 1783–1791.
[41] Q. Li, T. Bürgi, H. Chen, Preparation of gold nanorods of high quality and high aspect ratio, J. Wuhan Univ. Technol.—Mater. Sci. Ed. 25 (2010) 104–107.
[42] A. Ahmad, S. Senapati, M.I. Khan, R. Kumar, M. Sastry, Extracellular biosynthesis of monodisperse gold nanoparticles by a novel extremophilic actinomycete, *Thermomonopora* sp., Langmuir 19 (2003) 3550–3553.