

Article

Exploring the Possibilities of Biological Fabrication of Gold Nanostructures Using Orange Peel Extract

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Abstract: Development of nanotechnology requires a constant innovation and improvement in many materials. The exploration of natural resources is a promising eco-friendly alternative for physical and chemical methods. In the present work, colloidal gold nanostructures were prepared using orange peel extract as a stabilizing and reducing agent. The initial pH value of the solution and the concentration of the gold precursor had an effect on the formation and morphology of nanoparticles. The method developed is environmentally friendly and allows control of nanoparticles. By controlling the pH and, especially, the gold concentration, we are able to synthesize crystalline gold nanowires using orange peel extract in the absence of a surfactant or polymer to direct nanoparticle growth, and without external seeding. UV-VIS spectroscopy, transmission electron microscopy (TEM), and X-ray diffraction (XRD) were used to characterize the nanoparticles obtained by biosynthesis.

Keywords: biosynthesis; nanoparticles; gold; nanowires; orange peel extract

1. Introduction

Nanostructured materials have received considerable attention due to their unique physical and chemical properties and their potential application [1–3]. The synthesis of nanoparticles with a controlled shape and size is one of the most promising research areas. The excellent properties of some materials strongly depend on crystallographic and morphological characteristics [4]. It is well-known that triangular nanoparticles of gold exhibit two characteristic absorption bands referred to as the transverse (out of plane) and longitudinal (in plane) surface plasmon resonance bands. The ability to tune the optical properties of the gold nanotriangles can be very useful in applications such as cancer cell hyperthermia [5] and architectural optical coatings [6]. One-dimensional nanostructures have also unusual anisotropic properties. For example, if metal nanoparticles are smaller than approximately tens of nanometers, electrons should be confined along the diameter of long metallic nanowires. Metallic nanowires are useful to connect different components in nanodevices. Metal nanorods and nanowires are able to absorb and scatter light along the long and the short axis because they have two plasmon bands [7]. These structures have been used as components in flexible electronics [8] and biological or gas sensing applications [9].

Synthesis of metal nanoparticles via chemical and physical methods has been employed in nanotechnology due to their affordability and ease of modulation in functional behavior of nanostructures [10–12]. However, toxic effects of various chemicals and organic solvents used in physical and chemical methods have promoted an increasing interest in biomass as a biosynthetic machinery for the production of metal nanoparticles [13–16]. Biosynthesis of gold nanoparticles has been reported using bacteria [17], yeasts [18], actinomycetes [19], fungi [20], and plants [21]. Although biological methods are regarded as safe, cost-effective, sustainable, and clean processes, they also have some drawbacks in culturing microbes and using biomasses, which are time-consuming and difficult in providing better control over size distribution, shape, and crystallinity [22]. These are the problems that have plagued the biological synthesis approaches.

The use of plants in the recovery of noble metals from ore mines and runoffs is known as phytomining. Compared to the conventional chemical methods, phytomining is a cost-effective, environmentally compatible method [23]. The use of plants and its by-products as sustainable and renewable resources in the synthesis of nanoparticles is more advantageous over prokaryotic microbes, which need expensive methodologies for maintaining microbial cultures and downstream processing [21,24].

Another dimension was added to the “green chemistry” approach for pure metal synthesis with the use of plant broths. Synthesis of noble metal nanoparticles using plant extracts is very cost effective, and therefore can be used as an economic and valuable alternative for the large-scale fabrication of metal nanoparticles. Extracts from plants may act both as reducing and capping agents in nanoparticle synthesis. The bioreduction of metal nanoparticles by combinations of biomolecules found in plant extracts (enzymes, proteins, amino acids, vitamins, polysaccharides, and organic acids, such as citrates) is environmentally benign, despite of its chemical complexity [25,26].

In this work, biosynthesis of gold nanostructures has been investigated using aqueous chloroaurate ions and orange peel extract as a clean technology to recover gold from dilute solutions. Orange peel is a residue obtained after juice extraction in the food industry. Waste orange peel is composed of sugars, cellulose, hemicellulose, pectin and D-limonene [27]. The morphology of the nanoparticles produced

could be controlled by varying the initial pH value and the concentration of gold ions in the reaction medium. Triangular nanoplates and nanorods were obtained at low pH and nanospheres at high pH values. Additionally, gold nanowires were produced by increasing the gold ion concentration.

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 (Barcelona, Spain).

2.2. Synthesis of Gold Nanoparticles

The experimental method consists of mixing aqueous solution of metallic precursor with orange peel extract (9:1) and stirring the mixture. The orange peel extract was previously prepared by boiling the dried orange peel in deionized water. Then, the extract was obtained by filtration using 0.2 μm nylon membrane filters from Whatman (Dassel, Germany). The initial pH of orange peel extract was 5.0. Chloroauric acid (HAuCl_4) was used as precursor. Gold nanoparticles were synthesized at room temperature. The influence of solution pH (2, 4, 7, and 9) was investigated in 100 mg/L (0.5 mM Au^{3+}) of metal precursor aqueous solutions. The pH was adjusted by addition of NaOH solution and HCl in Au solutions. The effect of precursor concentration to obtain gold nanowires was tested by using 100 mg/L (0.5 mM Au^{3+}), 250 mg/L (1.25 mM Au^{3+}) and 500 mg/L Au^{3+} (2.5 mM Au^{3+}).

2.3. UV-VIS Absorbance Spectroscopy Studies

The UV-VIS spectra of samples at different pH values were analyzed using a Libra S11 single beam spectrophotometer (Cambridge, UK) operated at a resolution of 5 nm with quartz cells. Blanks of each sample set were prepared with deionized water.

2.4. TEM Measurements

The shape of the nanoparticles was observed by transmission electron microscopy (TEM). Samples of the biosynthesized gold nanoparticles 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-2100 instrument (Tokyo, Japan) operated at an accelerating voltage of 200 kV.

2.5. X-ray Diffraction Analysis

The measurements were carried out by powder X-ray diffraction (XRD) on a Philips X'pert-MPD equipment (El Dorado County, CA, USA) with a Cu anode operating at a wavelength of 1.5406 Å as the radiance source. Samples were placed on off-axis quartz plates (18 mm diameter \times 0.5 mm DP cavity). The scanning range was from 10° to 60° 2 θ with an angular interval of 0.05° and 4 s counting time. The crystalline phases were identified using standard cards from the International Centre for Diffraction Data (ICDD, Newtown Square, PA, USA) Powder Diffraction File database.

3. Results

The present work was focused on the development of a biosynthetic method to control the production of gold nanostructures using green chemistry. For that, authors propose an efficient exploitation of wastes from food industry production. The color of gold solutions changed from pale yellow to dark blue or pink in 30 min (Figure 1). This change would be an indication of gold reduction by orange peel extract and the formation of nanoparticles. Orange peel extract contains organic acids, amino acids, and proteins, as well as the important presence of saccharides, which provides reduction power for the nanostructures' preparation. In order to complete the study, an attempt to develop a biosynthetic method for the production of gold nanowires using green chemistry was carried out.

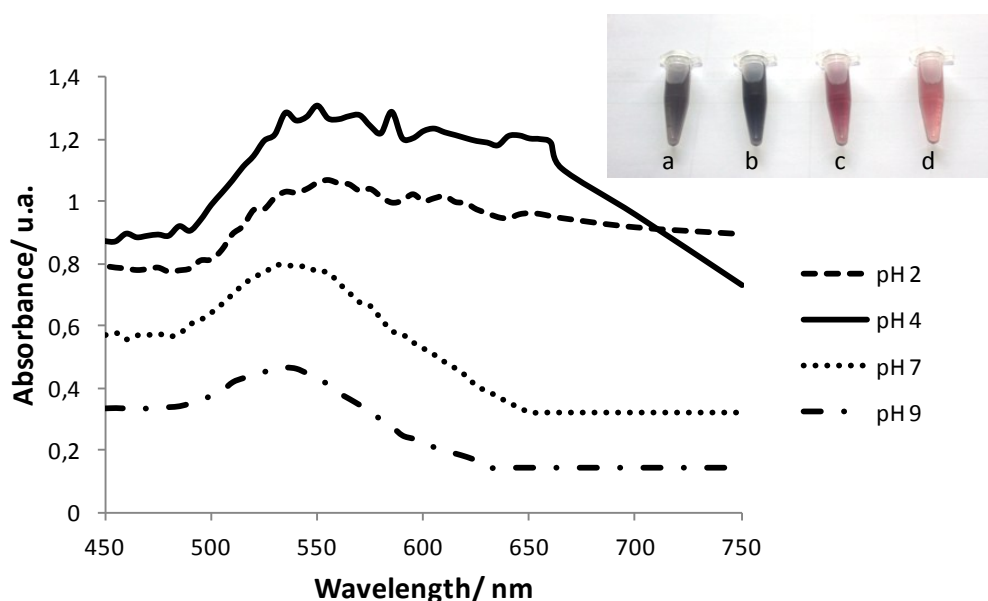


Figure 1. UV-VIS spectra of gold nanoparticles using 100 mg/L HAuCl_4 prepared at different initial pH values: pH 2, 4, 7, and 9. The inset shows the solutions corresponding to these spectra: (a) pH 2; (b) pH 4; (c) pH 7; and (d) pH 9.

3.1. Biosynthesis of Gold Nanoparticles: Influence of pH

3.1.1. UV-VIS Spectral Study

It is well known that the differences in UV-VIS absorption spectra and color of solution could be dependent on different surrounding mediums and size, shape, and crystallinity of the metal nanoparticles. The color of chloroaurate solutions changed to pink or blue depending on the pH tested, indicating a change in metal oxidation and the formation of gold nanoparticles. As shown in the inset in Figure 1, the color of the colloidal gold solutions is a function of pH.

In all cases, a surface plasmon resonance (SPR) band absorption peak appears centered at approximately 540 nm, which is characteristic of gold nanoparticles. At a longer wavelength, a second band related to aggregates of spherical nanoparticles [28] or anisotropic nanostructures [29] is present in solutions at pH 2 and 4.

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. The longitudinal SPR band is a strong function of the edge length of the triangles [5]. Gold nanorods and nanowires exhibit both a band corresponding to the short axis and another one corresponding to the long axis at a longer wavelength. At pH 2, the absorbance curve is practically flat in the range of 500–825 nm and the intensity is lower than at pH 4. In addition, this spectrum corresponds to the blue sample. In this case, the two peaks of the SPR bands cannot be clearly observed due to the overlap of the longitudinal absorption of the nanorods with different aspect ratios at relevant wavelengths [30].

At pH 7 and 9, the spectra exhibit a unique resonance wavelength at approximately 540 nm associated to the formation of the nanospheres since all their electronic oscillations are equivalent. The band at pH 9, however, is broader indicating the polydispersity of size.

3.1.2. Characterization of Gold Nanoparticles

The morphology of the gold nanoparticles was observed by transmission electron microscopy. Figure 2 shows representative TEM images of the nanoparticles synthesized using orange peel extract at different pH values. TEM observations revealed that gold nanoparticles formed at acidic medium were mainly triangular, polygonal and rod-shaped nanoparticles (Figure 2a,b). The edge length of the rods can reach 120 nm at pH 2. When the pH was increased to 4, the size of the nanoparticles decreased and the length of the triangles' edge and the rods was ~40 nm.

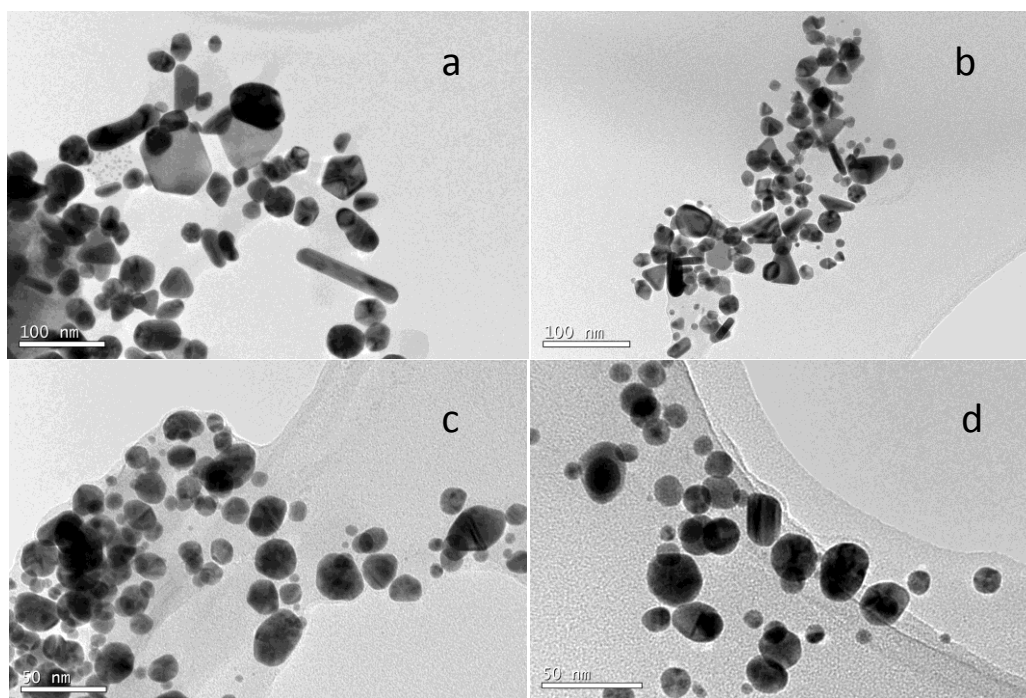


Figure 2. TEM images of gold nanoparticles using 100 mg/L HAuCl_4 prepared at different initial pH values: (a) pH 2; (b) pH 4; (c) pH 7; and (d) pH 9.

An increase of initial solution pH favored the formation of nanospheres. At pH 7 and 9, spherical nanoparticles were formed (Figure 2c,d). The analysis showed that the average diameter of the nanospheres obtained at pH 7 was about 20 nm. At pH 9, there were nanoparticles with a diameter of 25 nm and smaller nanoparticles of 10 nm of diameter.

EDS microanalysis and XRD of the gold nanoparticles showed that the sample was essentially metallic gold (Figure 3). Elemental gold peaks were found in the EDS study to confirm the nature of the metallic nanoparticles (Figure 3a). The structural properties of gold nanoparticles were confirmed using XRD technique. XRD pattern showed that diffraction peaks corresponded to the diffraction planes (111), (200), (220), (311) and (220) of face-centered cubic gold (Figure 3b).

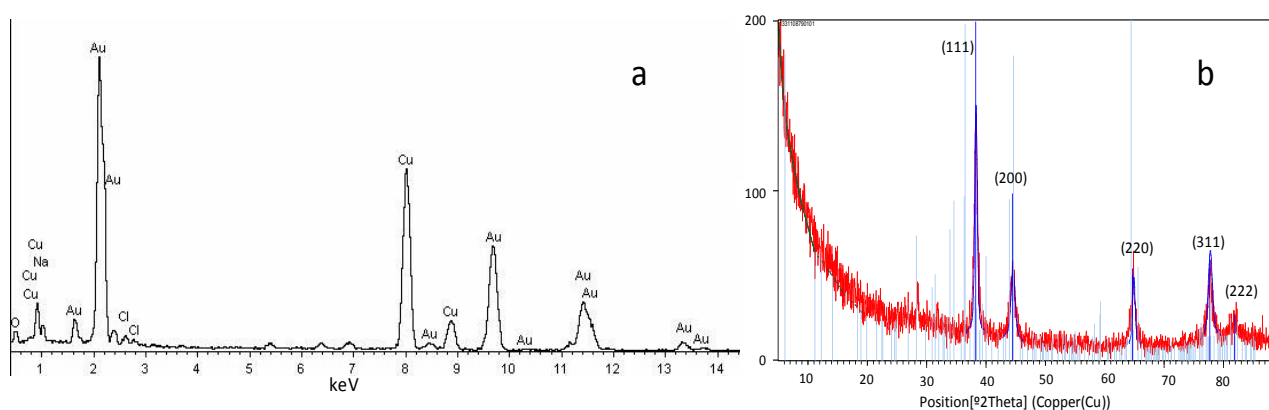


Figure 3. (a) EDS spectrum and (b) XRD pattern of gold nanoparticles.

3.2. Biosynthesis of Gold Nanowires: Influence of Gold Ion Concentration

It is already known that hydroxide ions play a key role in the production of nanowires. In spite that the capping agent was available, competition between the biomolecules of the biomass and hydroxide ions for gold ions favored the aggregation of nanoparticles due to the lower ability of biomolecules to stabilize the nuclei formed. In turn, nanoparticle aggregation led to the formation of nanowires. This process could be favored not only in the presence of hydroxide ions but also with increasing gold ion concentration. Hence, gold nanowires production was investigated by increasing the concentration of HAuCl_4 at high pH value (pH 10).

TEM images of the samples evidenced that gold concentration has an enormous influence in the shape and size of the gold nanoparticles synthesized using orange peel extract. As it is shown in Figure 4a, spherical nanoparticles were obtained at 100 mg/L. There were some particles with an average size of 42 nm and other very tiny nanoparticles of 5 nm. When the initial concentration of gold precursor was 250 mg/L, triangular and polygonal nanoparticles were obtained and their edges can reach up to 110 nm, and were surrounded by spherical nanoparticles with 20 nm of diameter (Figure 4b). When the gold precursor concentration was increased to 500 mg/L, nanowires with an average diameter of 30 nm were formed (Figure 4c). Figure 4d shows the fine nanostructure of one section of the gold nanowires depicted in Figure 4c.

At the lowest initial gold concentration, the amount of capping agent was enough to stabilize the first particles formed in solution.

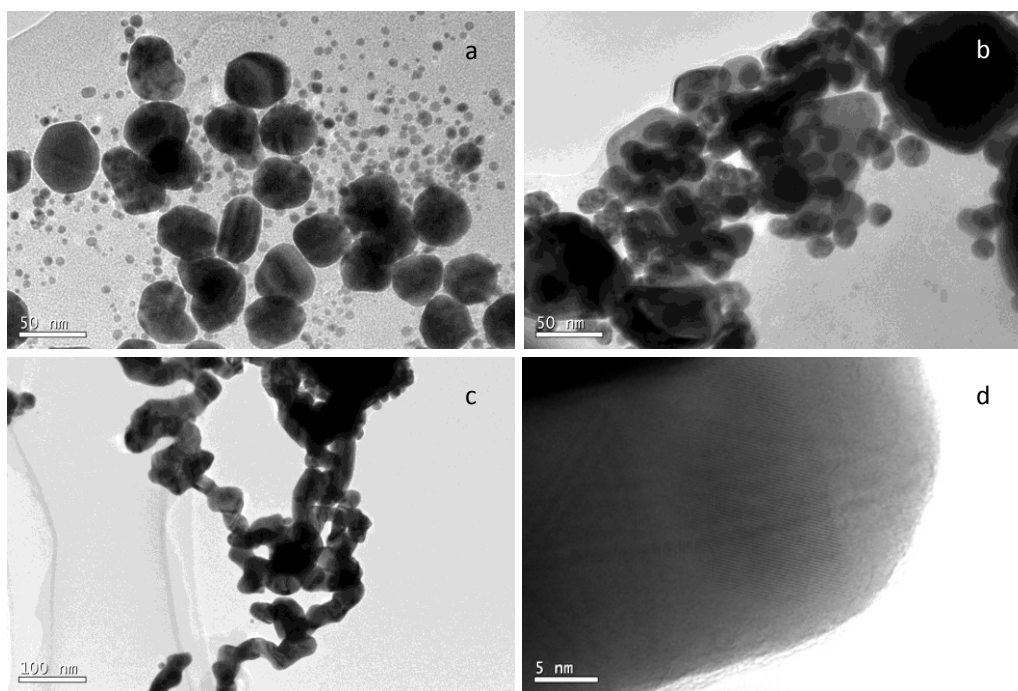


Figure 4. Effect of gold ions concentration. TEM images of gold nanoparticles obtained at pH 10 using different HAuCl_4 concentrations: (a) 100; (b) 250; and (c) 500 mg/L; (d) detail of nanostructure of the gold nanowires.

Increasing concentration, gold nanoparticles size increased since they were not thermodynamically stable and stuck together. At the highest concentration, gold nanowires were produced. The formation of these nanowires can be related to the Ostwald ripening effect. In Ostwald ripening, smaller particles dissolve preferentially with subsequent crystallization onto larger particles, which involves nucleation and growth processes of larger particles from smaller ones.

4. Discussion

The green synthesis of silver and platinum nanoparticles using orange peel extract have been previously reported [31]. It is found that the pH value influences the morphologies of the nanostructures. The results indicated that the properties of silver and platinum nanoparticles depend strongly on their morphologies and sizes. In general, silver nanospheres with lower diameter possess the higher antimicrobial activity. However, silver nanowires are useful to connect different components in nanodevices. Small and spherical platinum nanoparticles exhibited better catalytic properties.

The biosynthesis of nanoparticles with a controlled shape and size is one of the most promising research areas. Gold nanoparticles are interesting due to their applications in optoelectronic, electronic, and magnetic devices, and because of their use as catalysts and sensors. One- and two-dimensional nanostructures for noble metals are especially attractive.

The initial pH value of the aqueous HAuCl_4 solutions for different sets of samples was studied in the synthesis of gold nanoparticles using orange peel extract. At high pH values, spherical and monodispersed gold nanoparticles were obtained. These nanoparticles could be used in non-toxic carriers for drug and gene delivery applications. With these systems, the gold core imparts stability to the assembly, while the monolayer allows tuning of surface properties such as charge and

hydrophobicity. An additional attractive feature of these nanoparticles is their interaction with thiols, providing an effective and selective means of controlled intracellular release [32].

The synthesis of gold nanotriangles under acidic conditions could be produced by slow reduction and crystallization. This 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 orange peel. Moreover, the difference in the growth rates of the various crystallographic planes could lead to the changes in the morphology of the nanoparticles. It can also be observed the hexagonal shapes, truncated triangles or icosahedral shapes. These structures with unique and highly anisotropic planer shapes might find application in photonics, optoelectronics, and optical sensing. Applications in cancer cell hyperthermia, but also the effect of different organic solvent vapors like methanol, benzene and acetone on the conductivity of tamarind leaf extract reduced gold nanotriangles, among others, have been investigated [33].

Gold nanorods and nanowires have usually been synthesized by electrochemical reduction with cetyltrimethylammonium bromide (CTAB) and by seed-mediated growth method using a surfactant template. The synthesis of gold nanowires using biological resources has hardly ever been reported. Recently, networked nanowires were synthesized with an extract of *Rhodopseudomonas capsulata* modulating the concentration of HAuCl_4 [34] and gold nanowires were also obtained using sugar beet pulp by changing the pH and the gold concentration [30]. Reduction with orange peel extract is a method to produce nanowires in the absence of surfactant or polymer to control nanoparticles growth and without externally added seed crystallites. As mentioned previously, gold is a face centered cubic metal and its surface energies associated with different crystallographic planes are usually different. The free energies decrease in the order $\gamma\{111\} > \gamma\{100\} > \gamma\{110\}$, because of the package and the distinct surface atoms density. Surfactants and capping agents can usually cap planes with $\{100\}$ growth, which might lead to anisotropic growth of gold nanoparticles through $\{111\}$ planes [35]. The effect of the hydroxyl ions in the shape and size of the gold nanoparticles using biomass has been previously reported by our group and the results showed that nanowires are produced in alkaline solutions [30]. The explanation for this probably involves Ostwald ripening and the capping action of the biomolecules. The biomolecules of the orange peel extract were insufficient to stabilize completely gold nuclei. The first gold nanoparticles formed were thermodynamically unstable due to their small size and the insufficient amount of capping agent. The uncovered face of gold nanoparticles could orientate against each other through dipole-dipole interaction of biomolecules and the intermolecular hydrogen bounding interaction of biomolecules and hydroxide ions could act as possible driving forces for the formation of 1D assembly. In addition, the surface energy of larger particles is lower than that of smaller ones [36]. The nanoparticles grew and joined together because of their Brownian motion in the solution, forming wire-like structures. The end of these nanorods may be bounded by $\{111\}$ facets whose interaction with OH^- and with biomolecules is very weak and, thus, reactive to the new atoms formed [37]. The weak complexing agent allows the deposition of newly reduced gold atoms and they sinter together and form larger agglomerates of gold (nanowires).

5. Conclusions

Reduction of tetrachloroaurate with orange peel extract is a simple, conducted at room temperature, efficient, and a clean method to synthesize gold nanostructures from dilute hydrometallurgical solutions. Advantages over other biological methods include the reuse of industry wastes, easy handling and scalability. In addition, one- and two-dimensional nanostructures for noble metals are especially attractive.

The key points for nanowires production are: competition between hydroxide ion and biomolecules for gold ions, shortage of biomolecules to cap the nanoparticles and preferential adsorption of AuCl_4^- on the gold nanoparticles surface.

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Author Contributions

L. Castro mainly performed the present study and wrote the paper. M.L. Blázquez, F. González, J.A. Muñoz and A. Ballester provided advice and recommendations on the research and polishing of the paper.

Conflicts of Interest

The authors declare no conflict of interest.

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