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Synthesis and characterization of gold nanoparticles in solution using chitosan as reducing agent

Síntesis y caracterización de nanopartículas de oro en solución utilizando quitosán como agente reductor

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ABSTRACT

Currently the metallic nanoparticles, in particular of noble metals like gold are gaining importance due to their potential applications in various fields, as their physicochemical properties and their low toxicity the materials become of great importance. In this paper the synthesis of gold nanoparticles was carried out in solution using a reducing agent as is the biomolecule chitosan as reducing agent and were also characterized by a spectrophotometric technique as ultraviolet visible to verify the efficiency of the synthesis process, the spectrum showed that the synthesized nanoparticles have an absorption band at 525 nm. characteristic of gold particles to nanometric size.

Keywords:

Nanotechnology, Reducing agent, Gold Nanoparticles, Chitosan.

RESUMEN

En la actualidad las nanopartículas metálicas, en especial, las de metales nobles como el oro, han cobrado importancia debido a sus potenciales aplicaciones en diversas ramas, ya que sus propiedades fisicoquímicas y su bajo grado de toxicidad las convierten en materiales de gran importancia. En este trabajo, se realizó la síntesis de nanopartículas de oro en solución, utilizando como agente reductor la biomolécula quitosán. Además, las nanopartículas fueron caracterizadas por una técnica espectrofotométrica ultravioleta visible, para verificar la eficacia del proceso de síntesis. El espectro mostró que las nanopartículas sintetizadas presentan una banda de absorción centrada en 530 nm, característica propia de partículas de oro de tamaño nanométrico.

Palabras clave:

Nanotecnología, Agente Reductor, Nanopartículas de Oro, Quitosán.

Introduction

At the production engineering conference held in 1974, Professor Norio Taniguchi was the first person to coin a name and concept for the new science known as nanotechnology, defining it as a branch of technology where objects and devices are manufactured with sizes of the order of 1 nm [1].

What identifies the different fields of action of this discipline, derives from the nanometric dimensions of objects, these are called nanomaterials, because at nanometric scales the behavior of these particles is special and the dimensions are below 100 nm [2].

Nanoparticles are within the group of nanomaterials, these are nanoscopic particles with dimensions between 1 and 100nm, their most known form is the spherical, also, there are other nano structures grown in 2D in the form of thin films, and nanowires or bars in 1D [3].

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There are several types of nanoparticles, among them there are those that come from coal which generally have a shape of sphere or tubular, the brightest properties are good electrical conductivity, high elasticity and excellent hardness. In addition, there are those that present metallic base, and semiconductor also called quantum dots, these were discovered in 1980 in colloidal solutions, the term "quantum dot" was coined by the American physicist Mark A Reed who defined that they have properties that are intermediate between conventional semiconductors and discrete molecules. The properties of these nanomaterials are unique and generally depend on size [4].

Quantum dots compete with organic molecules for applications in biological labeling, solid state lighting and optoelectronic devices of processable solution, in addition they have other applications such as those based on optical properties, which allows them to be used as colorimetric sensors. In general, nanoparticles of diverse metals such as silver, gold and titanium, among others, are known. Dendrimers are also nanoparticles, finally there are composites, whose characteristic is that they can be combined with other structures to improve their properties [5].

In this work, metallic gold nanoparticles were synthesized. In order for these nanoparticles to grow, it is vitally important to know in depth the most efficient techniques used in the laboratory. In the literature, these nanoparticles are also called nanoclusters, colloids, nanocrystals and quantum dots [6] - [8].

Metal nanoparticles have been widely studied, as they have specific physicochemical properties for each metal, which differ from the properties of the volumetric solid metals they are composed of. The physical properties of the transition metals depend on the electronic transitions that occur in the orbitals d present, which gives each material unique optical and magnetic properties [9] - [11].

In addition, the properties also depend on the morphological and geometric characteristics of the particles, for example, the smaller their size the more applications they have [12], [13].

Metals such as silver, gold, and palladium have been used to manufacture metallic nanoparticles, due to the particularity that they have absorption spectra unique to each metal, a condition that allows us to observe the colors of the spectra characteristic for each of them.

Several synthesis processes are known, the most used are the physical and chemical, within the physical the most important are laser ablation, sonochemical synthesis, microwave irradiation and thermolysis [14], [15].

Chemical methods are based on the generation of nanoparticles, from the assembly atom by atom until the formation of the nanomaterial, in the literature are referenced a large number of chemical methods, but the most used are those of reduction of metallic salts, and to a lesser extent is the radiolytic and photochemical reduction [16].

To perform the chemical reduction, it is necessary to start from a precursor salt and a reducing agent, the most used reducers are sodium borohydride and dimethylformamide, sodium citrate, glycerol and ethylene glycol, among others, all of them have the function of reducing the metal to the natural state, perhaps the disadvantage of these reducers is that most are toxic [17], [18].

In these methodologies, extracts of fruits, fungi, and biomolecules are used, among others, for the synthesis of AuNPs (gold nanoparticles), the need arose to use in this work a biomolecule such as chitosan, a polymeric carbohydrate obtained by a decarboxylation reaction of chitin whose substance is extracted from the shell of molluscs, which performs the growth process without generating toxic residues [19].

Whenever a nanoparticle synthesis process is performed, it is important to characterize the new material in order to know the morphology, size and success of the synthesis process. In this work, the nanoparticle characterization was performed by means of UV-visible spectroscopy, a technique used in the area of nanomaterials, since this technique seeks to find the absorption band known as plasmon resonance (SPR). The absorption of light in small metallic particles is associated with a coherent and collective excitation of the “free” electrons in the conduction band, producing a phase oscillation known as surface plasmon resonance (SPR). Looking at it from a microscopic point of view, what happens is that the alternating electromagnetic field of the incident light interacts with the nanoparticles, inducing a polarization in the surface of the same one, due to the displacement of the free electrons with respect to the network of cations. The energy of this resonance of the surface plasmon depends both on the density of free electrons and the dielectric medium that surrounds the particle, located in the range of visible light for noble metals (SPR).

For gold nanoparticles the plasmon resonance band can be found in a range from 520 nm to 540 nm within the electromagnetic spectrum [20], [21].

Materials and methods

Materials and equipment

Micropipette from 10 to 200 µL, Analytical balance, Ohaus brand, accuracy 0.0001 g. Heating plate with magnetic agitation, Thermo scientific, UV-Vis 240 PC Spectrophotometer, Shimadzu.

Reagents

Glacial acetic acid, Carlo Erba, Trihydrated tetrachloroauric acid, Sigma-Aldrich, Distilled water, Chitosan, Sigma-Aldrich

Preparation of the metallic salt solution

A 0.1 mM aqueous solution of trihydrated tetrachloroauric acid (HAuCl4·3H2O) was prepared for the synthesis of gold nanoparticles.

Synthesis of gold nanoparticles

Initially 100 mL of chitosan solution in 1% acetic acid were prepared, which were heated to boiling point on a heating plate, then 100 µL of HAuCl4-3H2O solution was added to this solution, left to heat at 100 °C for 15 minutes, in constant agitation until a red colour was produced.

Characterization of gold nanoparticles

2 mL. of the nanoparticles in solution were taken and placed in a quartz cell, which was introduced in the UV-Vis spectrophotometer, followed by scanning throughout the visible ultraviolet region to obtain at the end the absorption spectrum of the AuNPs.

Results and discussion

Synthesis of gold nanoparticles by reduction with chitosan

Figure 1 shows the aqueous solution of trihydrated tetrachloroauric acid before the synthesis process where it can be seen that it has a typical yellow coloring of gold salts.

Figure 2 shows the colloidal solution of gold nanoparticles (AuNPs) after the synthesis process. According to what has been shown, it can be said that gold as a noble metal in the aqueous state presents different tonalities of color, quality that depends on the particle size, purity and optical properties that it possesses.

Figure 1. Aqueous solution of trihydrated tetrachloroauric acid

According to the difference in colouring of the two aqueous solutions, a condition that allows a difference to be established between the chemical states of gold, since, in the yellow solution, gold is forming a salt with a cation (Au^{+3}), and in the other red solution, the metal is in its natural state (Au^{0}), the difference in colours is due to the fact that the metal has undergone a chemical reduction process.

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Figure 2. Synthesis of AuNPs at different concentrations of chitosan

Figure 3 shows the reaction scheme of the process that represents the synthesis of AuNPs from the reducing agent and the precursor salt to finally obtain gold at nanometric size. The first step of the process is the hydrolysis of the chitosan in acidic medium until the formation of glucosamine, then an open chain equilibrium of the glucosamine occurs with a break of the bond by the anomeric carbon and the final stage of the process is the oxidation of the aldehyde group to carboxylic acid and later reduction of Au+3 to Au0 the reaction obeys to a mechanism of a redox reaction.

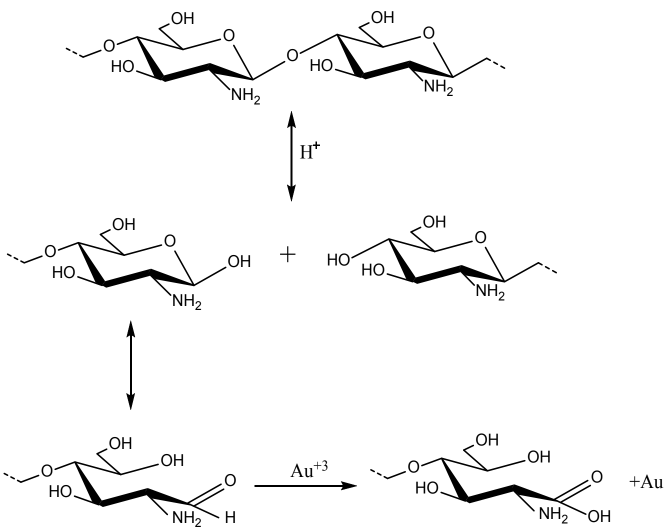

Figure 3. Scheme of the synthesis reaction of AuNPs

According to the coloration obtained for the colloidal solution of gold nanoparticles, which corresponds to a faint red, it can be inferred that AuNPs were obtained since this color is characteristic for nanometric-sized gold solutions. Therefore, it can be said that the synthesis process used was successful and also that the chemical reduction reaction was carried out and finally starting from the hypothesis that gold nanoparticles were obtained at nanometric size result that is confirmed with spectroscopic characterization.

Synthesis conditions and stability of AuNPs

Figure 3 shows that the concentration of the reducing agent plays a very important role in the physical conditions and properties of the nanoparticles, since it can be observed that as the concentration of chitosan increases, the coloration of the colloidal gold solution intensifies, thus indicating that the concentration of the reducing agent directly affects the size of the AuNPs, since as the number of chitosan molecules increases, the coloration intensifies, which suggests that the AuNPs have good stability and are not aggregated.

Characterisation of gold nanoparticles

Whenever a synthesis process is carried out, it is necessary to know either the structure or composition of the final product, using various techniques ranging from elucidation of the structure to know the degree of purity and concentration of the analyte under study.

To solve the problem if gold nanoparticles were obtained in this process, the final product was analyzed by visible ultraviolet a technique that seeks to observe in this case the resonance band of the surface plasmon (SPR) which is characteristic for each metal.

Figure 4 shows the spectrum of UV-Visible absorption of the suspension of synthesized gold nanoparticles in which a symmetrical and wide band close to 530 nm is evidenced. This indicates the presence of spherical Au nanoparticles with less size dispersion and according to the absorbance zone this corresponds to gold particles in nanometric measures, therefore it is corroborated that the synthesis process was adequate and successful.

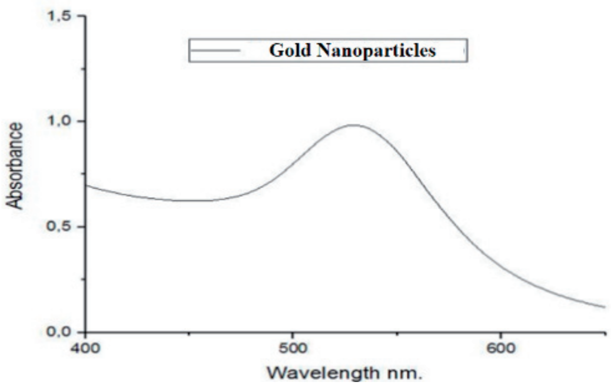

Figure 4. UV-Visible Absorption Spectrum of AuNPs

In order to demonstrate the symmetry and the width of the bandwidth a statistical treatment of the data was carried out more specifically a fitting. Next, the study of the band using least squares is shown in figure 5.

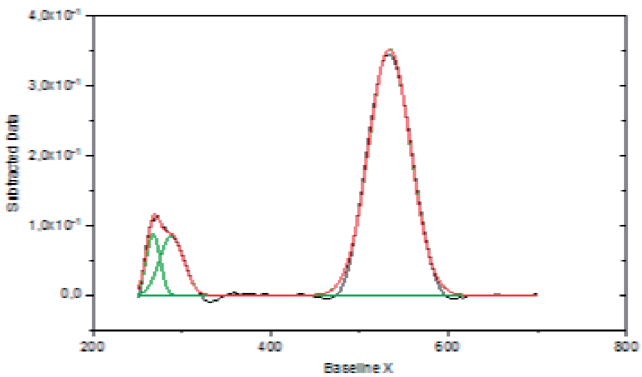

Figure 5. AuNPs absorption band by least squares

The data obtained from the study by least squares are presented in table 1.

Table I. Statistical study data with least squares

Spike	Type of spike	FWHM	Maximum absorbance
1	Gaussiano	55,18	530,55nm

As can be seen in table 1 the type of peak obtained shows that it follows the pattern of a Gauss campaign, it also shows that the FWHM is 55.18 value that is high and represents the width of the band, a result that allows inferring that gold nanoparticles a priori are small in terms of size and are scattered.

Conclusions

The gold nanoparticles obtained by reduction show a band of surface plasmons around 530 nm. which is highly symmetrical and narrow, indicating that the synthesis process was successful.

Chitosan is a biomolecule that allows the reduction of gold to its natural state, therefore, it is a good reducing agent, it is also important to note that its concentration is determinant in the formation of the physicochemical characteristics of nanoparticles.

Visible ultraviolet spectroscopy is a simple and versatile technique in the characterization of nanomaterials since it offers fast and effective results in the identification of bands of surface plasmons characteristic of each metal.

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