Effect of pH and chloroauric acid concentration on the geometry of gold nanoparticles obtained by photochemical synthesis

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Abstract. Due to their excellent surface properties, gold nanoparticles have been used in a wide range of applications from optics and catalysis to biology and cancer treatment by thermal therapy. Gold nanoparticles can absorb a large amount of radiation according to their geometry, such as nanospheres and nanorods. The importance of gold nanoparticles geometry is based on the electromagnetic spectrum wavelength where exists a greater absorption of radiation, which belongs to the visible region for nanospheres and ranges between visible and near infrared regions for nanorods, conferring greater biomedical applicability to the latter. When using photochemical synthesis method, which consists of reducing gold atoms to their metallic state with UV radiation, the geometry of gold nanoparticles depends on different variables such as: 1) pH, 2) concentration of chloroauric acid, 3) the surfactant, 4) concentration of silver nitrate, 5) temperature and 6) irradiation time. Therefore, in this study the geometry of the gold nanoparticles obtained by photochemical synthesis was determined as a function of solution pH and chloroauric acid concentration, using Spectrophotometry in the Ultraviolet Visible region (UV-vis) as characterization technique. From the analysis of the UV-vis spectra, it was determined that at an acidic pH the particles have two absorption bands corresponding to nanorods geometry, while at a basic pH only nanospheres are found and at a neutral pH the lower relative intensity of the second band indicates the simultaneous existence of the two geometries. The increase in the concentration of chloroauric acid produces a decrease in the amount of synthesized nanorods, seen as a decrease of the relative intensity of the second absorption band. Therefore, obtaining gold nanoparticles with nanorods geometry favours fields such as biomedicine, because they are capable of absorbing infrared radiation and can be used as photosensitive agents in localized thermal therapy against cancer.

1. Introduction
Nanoscale particles have been studied for years due to their physicochemical properties, which are different to those of their macroscopic equivalents [1]. This is due to the confinement of the electrons in the surface of a particle to a nanometric space, which leads to the appearance of the phenomenon known as Surface Plasmon Resonance (SPR) [2]. This phenomenon consists of the collective oscillation of the electrons at the nanoparticle surface, whose oscillation frequency is in resonance with frequencies corresponding to the electromagnetic spectrum [3].

Surface Plasmon Resonance depends mainly on the composition, size and shape of the nanoparticles, besides the medium in which they are dispersed [4]. Thus, gold is one of the most
interesting metals for the synthesis of nanoparticles due to characteristics such as: 1) biostability, 2) biocompatibility, 3) absorption of large amounts of radiation at near-infrared frequencies due to the SPR and 4) the ability to form isotropic structures, such as nanospheres, or anisotropic structures such as nanorods [5-7].

Generally, the geometry of the gold particles corresponds to nanospheres because it is the most stable structure and relatively easy to synthesize. In these cases, the resonance phenomenon occurs at frequencies belonging to the visible region of the electromagnetic spectrum, which correspond to wavelengths around 520nm [8]. However, the wavelength at which the resonance occurs can range between the visible and the infrared regions for gold nanorods, making it possible to use this type of particles in a greater variety of applications ranging from optics and catalysis up to biology and cancer treatment by thermal therapy [9].

The geometry can be clearly identified from the absorption spectrum in the Visible Ultraviolet region (UV-vis), which is strongly associated with the SPR as shown in Figure 1 [10]. When the geometry of the nanoparticles is spherical, the spectrum contains a single high intensity band with maximum absorption in the range of 500 to 530nm wavelength. On the other hand, when the geometry corresponds to nanorods the spectrum contains two absorption bands: the first one with low intensity located in the wavelength range between 500 and 530nm, as it happens with the spheres, and the second one of high intensity localized between 600 and 1000nm, according to the length of nanorods [11].

Figure 1. Absorption spectrum in the visible ultraviolet region of: (a) gold nanospheres, (b) gold nanorods.

One of the most recent methods used to obtain gold nanoparticles is photochemical synthesis, during which the gold atoms are reduced to their metallic state using ultraviolet (UV) radiation. One of the major advantages of this method is the time of synthesis, which oscillates between 30 and 90 minutes, increasing the possibilities of producing nanoparticles on a larger scale [12].

However, the geometry of the nanoparticles obtained by photochemical synthesis depends on different variables such as: 1) pH, 2) concentration of chloroauric acid, 3) surfactant, 4) concentration of silver nitrate, 5) temperature, 6) the irradiation time and 7) the presence of acetone and cyclohexane [12]. Therefore, in this study the geometry of the gold nanoparticles obtained by photochemical synthesis was determined as a function of solution pH and chloroauric acid concentration, using spectrophotometry in the Visible Ultraviolet (UV-vis) region as characterization technique.
2. Experimental

The reagents used during the photochemical synthesis are: 1) chloroauric acid 2) silver nitrate, 3) hexadecyltrimethylammonium bromide (CTAB), 4) ascorbic acid, 5) acetone, 6) cyclohexane, 7) hydrochloric acid and 8) ammonium hydroxide. All reagents are acquired with analytical grade, except for chloroauric acid which is produced in the laboratory of Nanomaterials–ICEx, UFMG. All solutions are prepared with milli-Q deionized water of 18.2 MΩ resistivity.

The photochemical reactor consists of a quartz tube of 800 cm long, 12 mm inner diameter and 4 mm thickness, and a UV lamp of 914 mm long and 25 mm diameter that generates light of 256 nm wavelength and intensity of 15 W/cm². All the laboratory instruments used during the synthesis are of glass, ceramic or plastic to avoid the reduction of the gold due to contact with metals. The glass materials were previously immersed in aqua regia for 2 hours, washed with distilled water and oven dried at 80°C for 2 hours to guarantee the quality and reproducibility of the results obtained [13].

The solution for photochemical synthesis is prepared from: 20 mL of CTAB (120 mM), 10 mL of chloroauric acid solution with specific concentration, 2 mL of silver nitrate (1.4 mM), 650 μL of acetone, 450 μL of cyclohexane and 170 μL of ascorbic acid (90 mM). This solution is placed inside the quartz tube and irradiated with UV light for 1 hour. The suspension obtained is centrifuged 3 times at 10,000 RPM for 15 minutes, collecting the precipitate concentrated in nanoparticles and dispersing in deionized water.

The pH of the irradiated solution takes values of 3, 5, 7 and 9, and is adjusted by adding hydrochloric acid or ammonium hydroxide right before being placed in the quartz tube. For its part, the solution of chloroauric acid takes concentration values 1.5, 3.0, 4.5, 6.0 and 7.5 mM. The characterization of the gold nanoparticle suspensions is made from the absorption spectrum obtained by a Rayleigh VIS 723-G Spectrophotometer with scanning wavelengths between 330 and 1000 nm, step of 1 nm, in quartz cuvettes with optical path of 1 cm and using deionized water as the reference sample.

3. Results and discussion

The absorption spectra of the colloidal suspensions obtained by varying the pH during the photochemical synthesis are shown in Figure 2, which are normalized so the maximum absorbance value of the first band is equal to 1. It is possible to observe that the photochemical synthesis of gold nanoparticles is highly sensitive to the pH of the irradiated solution. Thus, when the pH is 3 or 5 it is possible to distinguish two absorption bands where the second one has a relatively higher intensity than the first one, indicating that the suspended particles correspond mostly to gold nanorods. On the other hand, when the pH is neutral the second band has a slightly higher intensity than the first one, which indicates the simultaneous presence of spherical and rods nanoparticles. Finally, when the pH is 9, only an absorption band is observed whose maximum is located at a wavelength around 515 nm, indicating the exclusive presence of gold nanoparticles with spherical geometry.

The sensitivity of photochemical synthesis to pH is due to the rate at which ascorbic acid releases H⁺ ions and donates the electrons that reduce the gold atoms to their metallic state. When the pH is basic the concentration of H⁺ ions in solution is very low, causing fast dissociation of ascorbic acid and simultaneous reduction of a large amount of gold atoms, which leads to the formation of many nuclei. Because of this, the available concentration of reduced atoms decreases and the accelerated growth of the nuclei takes place to form nanospheres, avoiding the growth of anisotropic structures.

In the case of neutral pH, the rate at which ascorbic acid dissociates is lower, and so is the number of nuclei. This allows the available concentration of reduced atoms to be such that some of the nuclei have enough time to grow into anisotropic structures as nanorods, while the other nuclei produce spherical nanoparticles. On the other hand, when the pH is acid the concentration of H⁺ ions in the solution is higher, causing a slow and progressive dissociation of ascorbic acid and giving time to most of nuclei to grow anisotropically, leading to a lot of gold particles with nanorods geometry.
The absorption spectra of the colloidal suspensions obtained by varying the chloroauric acid concentration are shown in Figure 3, which are also normalized so the maximum absorbance value of the first band is equal to 1. It is possible to observe the decrease in the intensity of the second band of the absorption spectra as the concentration of chloroauric acid increases. For the concentrations of 1.5, 3.0 and 4.5 mM the intensity of the second band is relatively high, which is associated with the presence of gold nanorods. However, the second band has a lower intensity for the concentrations of 6.0 and 7.5 mM, related to the simultaneous presence of nanospheres and nanorods.
One possible explanation for this behaviour is based on the way the gold nanoparticles are generated. Once the gold atoms are reduced to their metallic state, they are located inside micelles formed by the CTAB surfactant, which can behave differently according to the conditions of the solution. When the amount of CTAB is high, the excess of these molecules is added to the micelles, which lengthen and allow to generate gold nanorods. In contrast, when there are no excess molecules of CTAB, the micelles maintain their shape and this leads to nanospheres formation [14]. Thus, an increase in the concentration of chloroauric acid can cause lead to the absence of enough CTAB molecules to lengthen the micelles, which generates that only a small part of the formed particles are nanorods while the majority are nanospheres, which is evidenced from the absorption spectra.

4. Conclusions
The analysis of the absorption spectra in the Visible Ultraviolet region allowed to determine the great influence of the pH and chloroauric acid concentration on the geometry of the nanoparticles obtained by photochemical synthesis. The pH 3 and 5 promoted the majority formation of gold nanorods, neutral pH allowed the simultaneous formation of nanorods and nanospheres, and pH 9 produced the exclusive formation of gold nanospheres. This behaviour is due to the rate at which ascorbic acid dissociates in the presence of the H⁺ ions of the solution. On the other hand, the increase in the concentration of chloroauric acid produces a decrease in the intensity of the second absorption band, associated to the lower presence of gold nanorods in relation to nanospheres, possibly due to the lower proportion of CTAB with respect to the golden ions. In this way, obtaining gold particles with nanorods geometry increases their capacity to be used in different applications such as biomedicine, since these absorb radiation in the infrared region of the electromagnetic spectrum and can be used as photosensitive agents in localized thermal therapy against cancer.

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