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Gold Nanoparticles Formation Mechanism by Photochemical Synthesis

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In this research, the effect of tetrachloroauric acid concentration, irradiation time and silver nitrate concentration on the morphology and radiation absorption of gold nanoparticles obtained by photochemical synthesis was determined. Absorption spectra were measured using Ultraviolet-Visible Spectrophotometry (UV-Vis), while nanoparticles morphology was determined by Transmission Electron Microscopy (TEM). The results demonstrated a decrease in the longitudinal band maximum absorption, associated to a change in the geometry of the nanoparticles, when increasing the concentration of tetrachloroauric acid; the increase in irradiation time produces a blue shift in the longitudinal band position and a reduction of the Full Width at Half Maximum (FWHM); and the concentration of silver nitrate is linearly related to the longitudinal band wavelength. From these results, a possible formation and growth mechanism for gold nanoparticles obtained by photochemical synthesis is proposed, which allows advancing in the surface properties understanding and its application on a wide range of research fields.

1. Introduction

In the last years, nanotechnology has become one of the science branches of major scientific interest due to the magnification of the optical, catalytic, electrical and electromagnetic properties of materials at nanometer scale (Daniel and Astruc, 2004). Thus, the synthesis of metallic nanoparticles has generated a great impact on a wide variety of applications such as: catalysis, optics, biology, genetics, pharmaceutics and biomedicine, the latter aimed at cancer treatment using localized hyperthermia (Shajari et al., 2017) (Sun et al., 2017). In particular, gold nanoparticles are highly used due to their characteristics, such as: high biostability and biocompatibility, which are required for biological applications (Haine and Niidome, 2017); ability to have isotropic or anisotropic character (Liu et al., 2017); and the capacity to absorb a large amount of radiation with oscillation frequencies near to the infrared region of the electromagnetic spectrum (Burrows et al., 2016). This radiation absorption is caused by the phenomenon of Surface Plasmon Resonance (SPR), which consists of the collective oscillation of the electrons at the nanoparticle surface, whose oscillation frequency (or wavelength) is in resonance with frequencies corresponding to the visible and near infrared electromagnetic spectrum (Chakraborty et al., 2015). This resonance phenomenon depends mainly on the shape, size and composition of the nanoparticle (Liu et al., 2017). One of the most effective methods to obtain gold nanoparticles is the photochemical synthesis, which performs simultaneously the nucleation and growth processes using ultraviolet (UV) radiation to reduce gold atoms to their metallic state (Lakhani et al., 2015) (Kim et al., 2002). However, the photochemical synthesis is very sensitive to different variables involved in the process such as: pH, temperature and irradiation time, as well as tetrachloroauric acid, surfactant and nitrate of silver concentration, among others (Zhu et al., 2017). Thus, the large number of variables involved in the photochemical synthesis make the nanoparticles formation and growth mechanism complex, and it has not been fully elucidated (Burrows et al., 2017). For this reason, in this research the effects of tetrachloroauric acid concentration, irradiation time and silver nitrate concentration on nanoparticles morphology and absorption spectrum are evaluated, and a possible formation and growth mechanism for gold nanoparticles obtained by photochemical synthesis is proposed.

2. Methodology

The photochemical reactor is composed of a quartz tube of dimensions: 80 cm long, 12 mm inner diameter and 4 mm thickness, and a cylindrical UV lamp of dimensions: 91 cm long and 25 mm diameter, with 256 nm wavelength and 15 W intensity. The reagents used for photochemical synthesis are analytical grade. The solutions are prepared with milli-Q deionized water of 18.2 MΩ resistivity. All the laboratory instruments used in the photochemical synthesis are made of glass or ceramics to avoid the reduction of gold caused by the contact with metals. The glass material was previously immersed in aqua regia for 2 hours, rinsed with distilled water and oven dried at 80 °C for 2 hours to guarantee the quality and reproducibility of the results (Shajari et al., 2017). The solution prepared for photochemical synthesis consists of: 10 mL tetrachloroauric acid; 20 mL of hexadecyltrimethylammonium bromide (CTAB) 120 mM concentration; 2 mL of silver nitrate; 650 µL of acetone; 450 µL of cyclohexane; and 170 µL of ascorbic acid 90 mM concentration. This solution is placed inside the quartz tube to be irradiated with UV light. The suspension obtained is centrifuged 3 times at 10,000 RPM for 15 minutes, collecting the nanoparticles in the precipitate and dispersing in deionized water. The analyzed values for tetrachloroauric acid concentration are: 3.0; 4.5; 6.0 and 7.5 mM. The irradiation is performed during 60 minutes, collecting an aliquot every 5 minutes for later analysis. Finally, silver nitrate concentration takes values of: 0; 1.4; 2.3; 3.2; 4.1 and 5.0 mM. The experiments were performed in triplicate to ensure the reproducibility of the results. The characterization of gold nanoparticles suspensions corresponds to the absorption spectrum obtained by a Rayleigh VIS 723-G Spectrophotometer with wavelength scanning between 330 and 1,000 nm, in quartz cuvettes with 1 cm optical path using deionized water as reference sample. Microscopy images are obtained using an Electronic Transmitting Microscope Tecnai G2-20 – SuperTwin FEI, located at the Centro de Microscopia of the Universidade Federal de Minas Gerais (UFMG). The samples are prepared by placing 10 µL of each nanoparticles suspension on a copper-coated carbon grid.

3. Results and discussion

Generally, absorption spectra obtained by UV-Vis Spectrophotometry for gold nanoparticles have two absorption bands (Huang et al., 2009). The first one, called transverse band, corresponds to the electrons oscillation in the nanospheres surface or in nanorods smallest dimension. The second absorption band, called longitudinal band, is associated with the presence of the SPR phenomenon in the largest dimension of gold nanorods, and occurs in the visible - near infrared range of the electromagnetic spectrum. The position of the longitudinal band is proportional to the aspect ratio (length/width) of the nanorods, while the relative intensity is measured as the maximum absorption of the longitudinal band divided by the maximum absorption of the transverse band, and is an indicator of the photochemical synthesis yield towards nanorods formation respect to nanospheres formation (Chen et al., 2013). Accordingly, in Figures 1A and 1B it is observed that the increase in the tetrachloroauric acid concentration produces a decrease in both the relative intensity and the position of the longitudinal band of the nanoparticles formed. It is possible that this behavior corresponds to the variation in the ratio between tetrachloroaurate ions and CTAB molecules. The increase in tetrachloroauric acid concentration in the solution causes that CTAB micelles present a smaller amount of molecules, which limits their growth. Thus, as the gold atoms are added to the nanoparticles, the micelles have a higher resistance to anisotropic growth and tend to maintain their spherical geometry or produce nanorods with a low aspect ratio, as seen in Figures 1C- 1F.

Figure 2A shows the time variation of gold nanorods absorption spectra, where it is observed that the transverse band wavelength is 516 nm and remains constant in time, while the longitudinal band wavelength presents a blue shift from 683 to 640 nm as the photochemical synthesis time increases. Since the longitudinal band wavelength depends on the gold nanorods aspect ratio, it is possible that the observed behavior is caused by the accelerated anisotropic growth of a small fraction of the nuclei formed, leading to obtain a small amount of high aspect ratio nanorods (Wen et al., 2016). However, overtime the nuclei present a more controlled growth rate because the available gold atoms concentration decreases, which leads to the formation of nanorods of relatively smaller aspect ratio. In this way, the ratio between the low and high aspect ratio nanorods increases as the photochemical synthesis progresses, promoting a decrease in the longitudinal band wavelength. In addition, the low relative intensity observed in Figure 2B during the first minutes corresponds to a small ratio between nanorods and nanospheres formed, while the increase over time in relative intensity indicates that initially formed nanospheres tend to grow anisotropically to form gold nanorods (Liu et al., 2017). On the other hand, the Full Width at Half Maximum (FWHM) is a measure of the gold nanoparticles size dispersion (Chakraborty et al., 2015). In the first few minutes of the photochemical synthesis, a large FWHM value appears due to high nanoparticles size dispersion, since most of them are nanospheres while a small fraction corresponds to high aspect ratio nanorods. However, as the nanospheres grow anisotropically to form nanorods, the size dispersion becomes smaller, as represented by the decreasing behavior observed in Figure 2C.

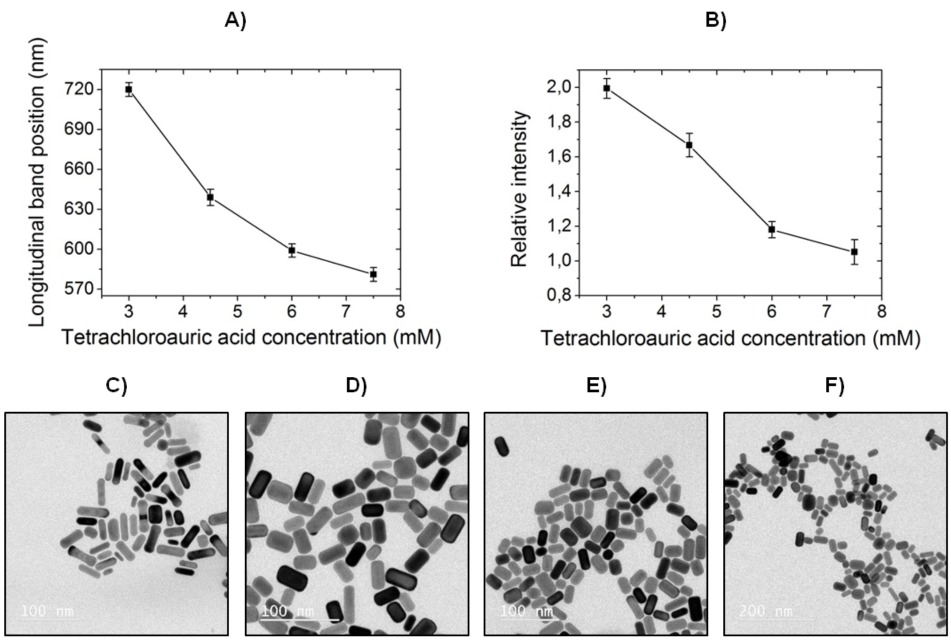

Figure 1. Tetrachloroauric acid concentration effect. A) Longitudinal band position. B) Relative Intensity. TEM micrographs of gold nanoparticles obtained with tetrachloroauric acid concentration equal to C) 3.0 mM, D) 4.5 mM, E) 6.0 mM and F) 7.5 mM.

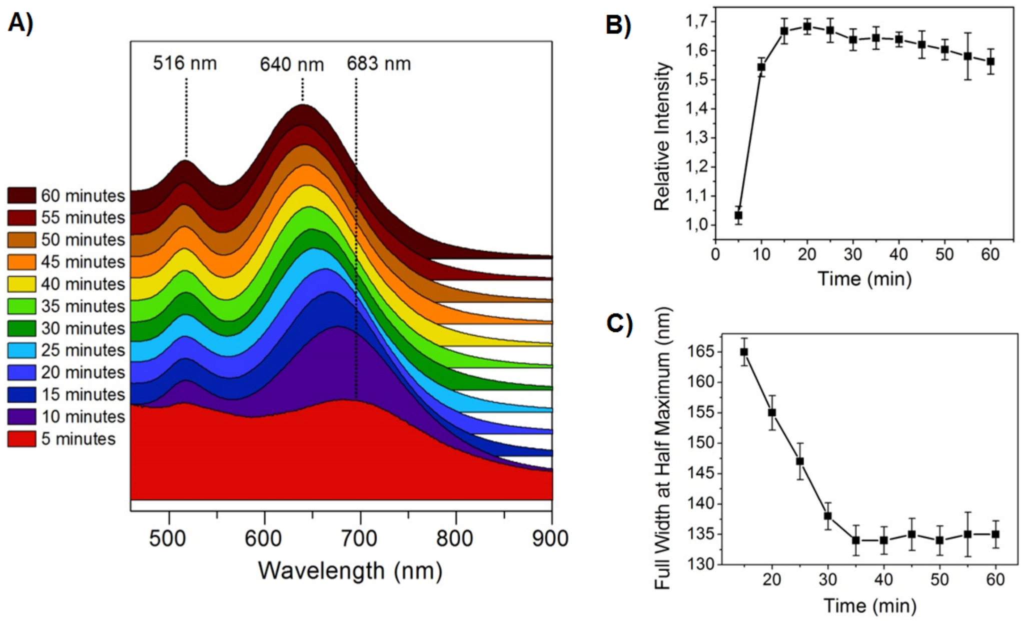

Figure 2. Time effect on gold nanoparticles photochemical synthesis. A) Absorption spectra. B) Relative Intensity. C) Full Width at Half Maximum.

As shown in Figure 3A, the suspension prepared without silver nitrate (0 mM concentration) produces an absorption spectrum with a single band located at 520 nm, which is characteristic for gold nanospheres. On the other hand, in the presence of different silver nitrate concentrations, the absorption spectra show two absorption bands, characteristic for gold nanorods. In addition, Figure 3B shows the longitudinal band wavelength (λ_{max}) where the maximum absorbance is produced and its lineal dependence on the silver nitrate concentration (C_{silver}) according to Eq(1), with determination coefficient R^2 equivalent to 0.9943:

$$\lambda_{max}(nm) = 22.11 * C_{silver}(mM) + 613.44 \tag{1}$$

From this mathematical model, it is possible to control the longitudinal band wavelength by adjusting the silver nitrate concentration, within the concentrations range analyzed in the present research. This behavior can be associated to the results obtained by Zhu et al. (2017), who determined the silver atoms ability to deposit preferentially on the {1 0 0} and {1 1 0} facets of the growing nanoparticle, which prevents the gold crystallization on these facets and favors the growth on {1 1 1} facets. For this reason, the increase in silver nitrate concentration favors the gold nanorods anisotropic growth to reach a higher aspect ratio. Due to aspect ratio increase, the electrons involved in the SPR oscillate a greater distance on the nanoparticle surface, which leads to the increase of the longitudinal band wavelength (Wang et al., 2015).

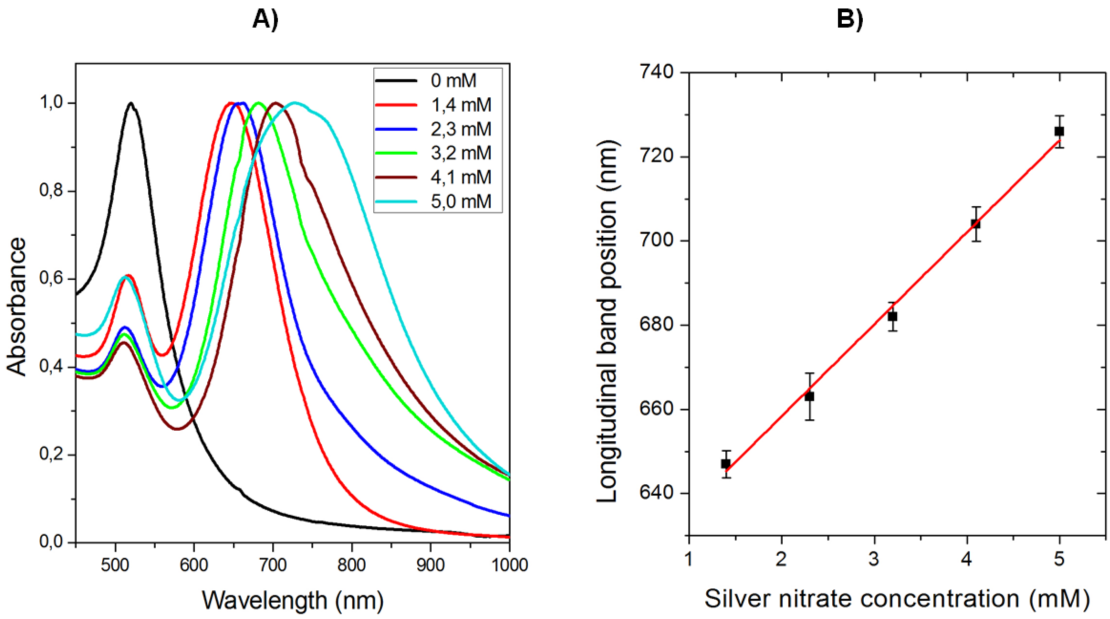

Figure 3. Silver nitrate concentration effect on gold nanoparticles photochemical synthesis. A) Absorption spectra. B) Longitudinal band position.

Based on the results obtained in the present research, a possible formation and growth mechanism for gold nanoparticles obtained by photochemical synthesis is proposed, composed of two stages: the first one consists in gold ions reduction to their metallic state to form the nanoparticles, while the second one contemplates the gold nanorods growth. The CTAB is a cationic surfactant capable of interact with tetrachloroauric acid by electrostatic attraction to form a micelle around these anions at the first stage (Figure 4A). The micelle formed by the CTAB has a bilayer structure that allows it to interact simultaneously with tetrachloroauric acid and water molecules, obtaining a very stable system (Daniel and Astruc, 2004). Nanoparticles formation takes place when gold atoms are in their metallic state (Au^0), so tetrachloroauric acid change its oxidation state from Au^{+3} to Au^{+1} by receiving two electrons released during the ascorbic acid oxidation (Figure 4B). Since the formed ion is not stable, it gets reduced to metallic state by receiving one electron from the free radical formed after the acetone decomposition in the presence of ultraviolet light (Daniel and Astruc, 2004). At the second stage, gold atoms in metallic state form spherical nanoparticles nuclei (Figure 4D). These nuclei grow anisotropically by adding gold atoms preferentially on {1 1 1} facets due to the presence of the silver atoms (Figure 4E) (Zhu et al., 2017). However, nanoparticles growth is limited by silver nitrate concentration and micelles size (Burrows et al., 2017), causing a break in the nanoparticles growth and stabilizing them, reaching the gold nanorods final state (Figure 4F).

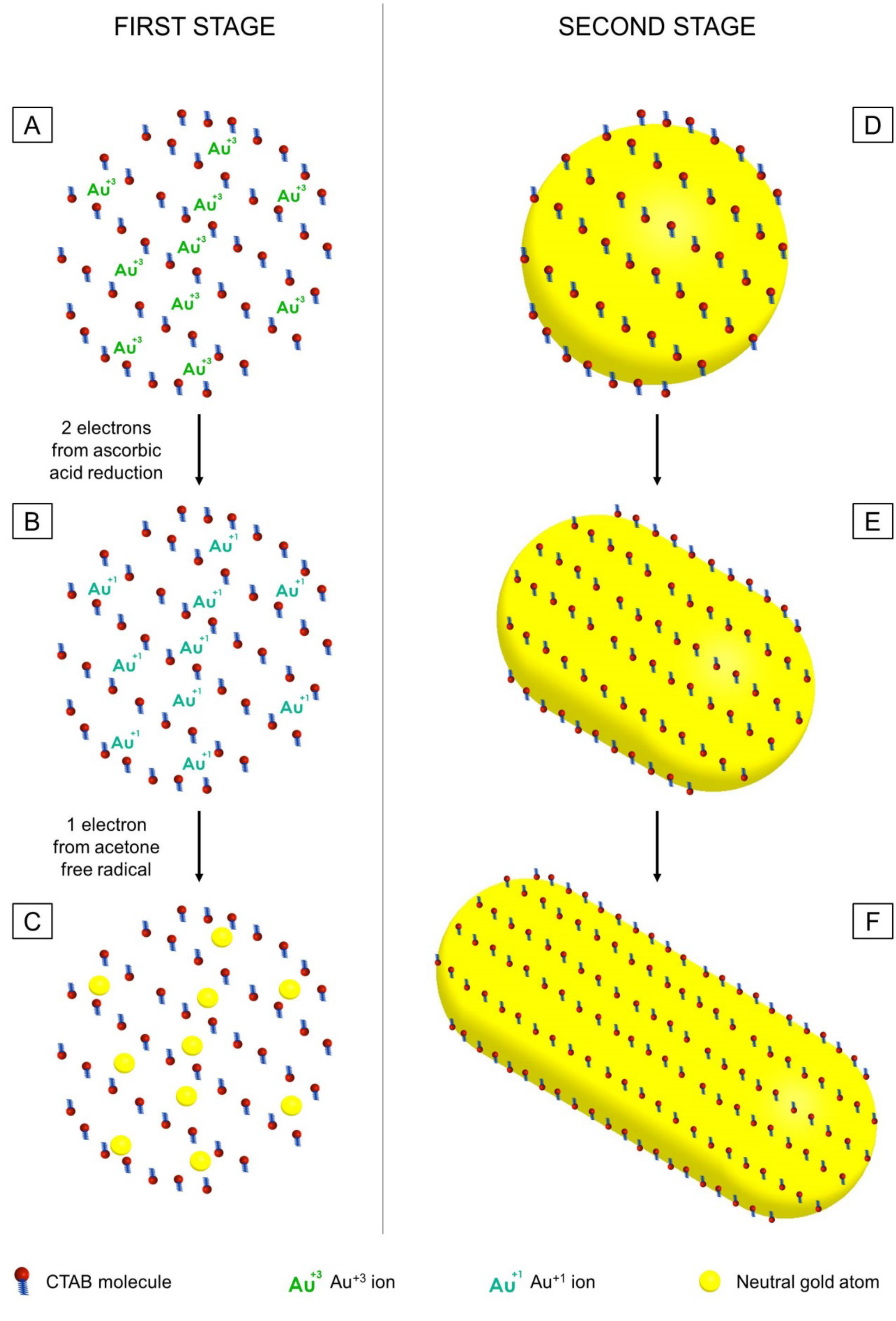

Figure 4. Formation and growth mechanism for gold nanoparticles obtained by photochemical synthesis.

4. Conclusions

Photochemical synthesis is a highly efficient process to obtain gold nanoparticles with different morphologies and electromagnetic properties, which depend on the variables analyzed in this study. The increase in tetrachloroauric acid concentration leads to formation of spherical nanoparticles with a lower absorption capacity of electromagnetic radiation. As the time of gold nanoparticles synthesis increases, a displacement of longitudinal band in the absorption spectrum occurs, and this allows locating the radiation absorption maximum at wavelengths in the visible region of electromagnetic spectrum. The anisotropic behavior of gold nanoparticles growth is due to the different concentrations of silver nitrate used in the photochemical synthesis. The formulation of a possible formation and growth mechanism of gold nanoparticles can lead to control with greater precision its photochemical synthesis process, modifying the optical, catalytic, electrical and electromagnetic properties to optimize their application in a wide variety of research fields such as: catalysis, optics, genetics, pharmaceutics and biomedicine, the latter aimed to studies for a possible cancer treatment by applying localized hyperthermia.

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