INFLUENCE OF SODIUM CITRATE CONCENTRATION ON THE SYNTHESIS OF GOLD NANOPARTICLES, USING THE TURKEVICH METHOD

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ABSTRACT: The present work aimed to synthesize gold nanoparticles (AuNPs) using the Turkevich method, considered one of the simplest and easiest chemical synthesis techniques; this synthesis consists of reacting chloroauric acid ($HAuCl_4$) using different concentrations of sodium citrate ($Na_3C_6H_5O_7$) at a temperature around 90ºC, to obtain a variety of sizes of AuNPs and presenting low formation of aggregates during the synthesis process, which leads to obtaining a stable colloidal suspension, which was meticulous, characterized by UV-vis, SEM, and XRD. UV-vis exhibits a maximum absorption of 522 nm due to the surface plasmon resonance (SPR) absorption band of AuNPs. The SEM images of the AuNPs show an average particle size of approximately 32nm and 120 nm with good homogeneity and monodisperse, spherical shapes, becoming polydispersed and less spherical as their size increases. The AuNPs XRD showed four main characteristic peaks of gold corresponding to the planes (111), (200), (220), and (311); the polydispersity index (PDI) of 0.210.
KEYWORDS: Nanomaterials, synthesize and AuNPs

1 I INTRODUCTION

The original work of synthesis of AuNPs dates back to 1951 when colloidal gold was formed by reacting chloroauric acid ($HAuCl_4$) and trisodium citrate ($Na_3C_6H_5O_7$); detailed work by Turkevich [1], becoming one of the milestones of the synthesis of AuNPs. Since then, this synthesis has been modified and improved

for various applications [2] due to its attractive physical properties that include surface plasmon resonance (SPR), a property that depends on its size and shape [3], since then gold nanoparticles (AuNPs) have been made using different techniques and routes. Over the past decade, the synthesis of this nanomaterial has attracted enormous attention due to its exceptional chemical stability, simplicity of synthesis, and attractive optical properties [4], making them applicable in various fields of technology, including nanoelectronics [5], catalysis [6] and nanobiotechnology [7]. Later, Frens demonstrated that the size of AuNPs in Turkevich synthesis, could be controlled by varying the sodium citrate concentration [8]; this adjustment influences nanoparticle growth through rapid nucleation followed by diffusion-controlled growth at elevated temperatures [9]. Therefore, in this work, AuNPs were synthesized using the well-known Turkevich-Frens method, taking into account the concentration ratio of sodium citrate, since it fulfills the function as a reducing agent and at the same time as a stabilizer of the nanostructures [10, 11]; apart from drastically influencing their growth. Several factors were taken into account such: as temperature, the relationship between the concentration of chloroauric acid and sodium citrate, the order of addition of the precursors, the synthesis time, and the stirring conditions, which significantly influenced the morphology and size of the resulting AuNPs [12]; obtaining a colloidal solution of AuNPs in which the particles formed are stable and monodisperse, without an additional stabilizing agent.

2 | MATERIALS AND METHODS

2.1 Materials

Sodium citrate ($Na_3C_6H_5O_7$) was obtained from Synth (Brazil), and chloroauric acid ($HAuCl_4$) from Sigma–Aldrich (Brazil). All reagents were of analytical grade, and all solutions were prepared using purified water from a Millipore Milli-Q system.

2.2 Synthesis of AuNPs

The synthesis of AuNPs was carried out by applying the Turkevich-Frens method, using different concentrations of sodium citrate, to obtain a wide variety of controlled nanoparticle sizes [8]; four solutions were prepared with purified water, each with 20 ml of $HAuCl_4$ at a concentration of 0.2 mM in a beaker with a capacity of 50 ml, stirring them magnetically for 10 minutes, once these solutions were finished four other solutions were prepared with purified water in molar proportions of sodium citrate, which were: (3.40 mM, 5.1 mM, 6.8 mM, and 8.5 mM) in four different beakers, taking each of these solutions to magnetic agitation for 10 minutes. Each of the concentrations of $HAuCl_4$ is heated to 97ºC in a magnetic stirrer at 450 rpm. To prevent contamination and evaporation of the solvent during synthesis a petri dish was used to cap the beaker; after each of the $HAuCl_4$

solutions reached the boiling point 1 ml of the sodium citrate concentrations respectively was quickly added, maintaining the same temperature and stirring, until a ruby-red solution is obtained in each. Finally, they are left to cool to room temperature; once they are cold, they are hermetically covered keeping them at 4ºC doing this same process for each of the concentrations see the process in Figure 1.

2.3 Methods

The AuNPs were characterized using various techniques. UV-vis absorption spectroscopy was performed with a Perkin Elmer Lambda 1050 spectrophotometer in the wavelength range of 420–690 nm, using a quartz cuvette and diluting the sample with deionized water. Images scanning electron microscopy (SEM) were obtained using an FEI Phenom microscope operating at an electron acceleration voltage of 10 keV, with a resolution of 3 nm and a magnification of 300.000 x; the particle size and size distribution of each sample were obtained by image analysis using the program (Image J). X-ray diffraction (XRD) analyses were performed using a Shimadzu XRD 7000 X-ray diffractometer with (Cu-Kα radiation λ = 1.5418Å), 40 KeV voltage, and 30 mA current in the range of 20º - 80º.

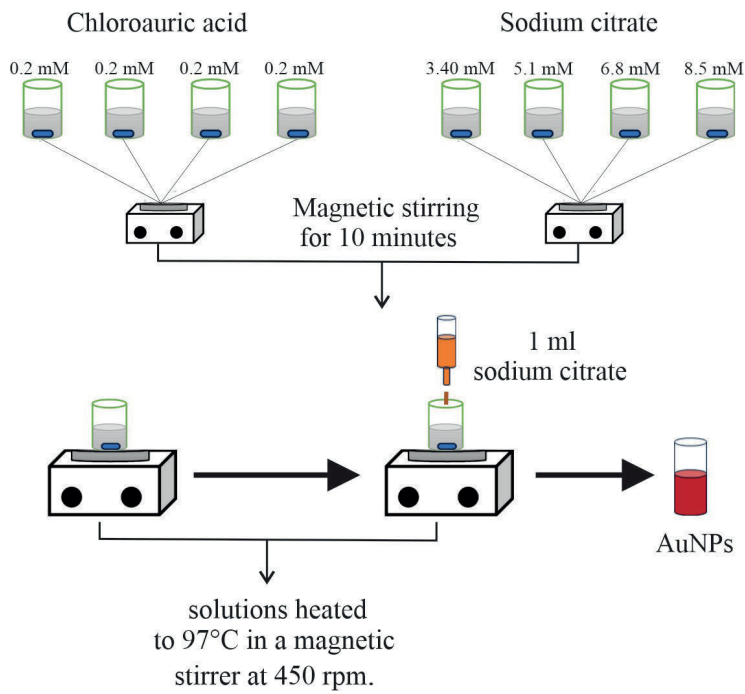


Figure 1: AuNPs synthesis.

3 | RESULTS AND DISCUSSION

3.1 UV-Vis Spectroscopy

The AuNPs exhibit a surface plasmon resonance that results in a strong absorbance band in the visible region (500 - 600 nm), measured by UV-vis spectroscopy. The spectrum obtained is observed in Figure 2; AuNPs exhibit a maximum absorption at 522 nm.

The surface plasmon phenomenon is the oscillations of free electrons on the surface of solid materials supported by metal nanoparticles. When the frequency of the incident light; coincides with the natural frequency of the surface electrons, the surface plasmon phenomenon occurs [13].

Band intensity and wavelength depend on the properties of AuNPs, including structure, shape, and size. Typically, the surface plasmon band for spherical (32 to 120) nm AuNPs has peaks around 522 nm in UV-vis. As the wavelength changes to higher values, the diameter of the nanoparticles increases [14].

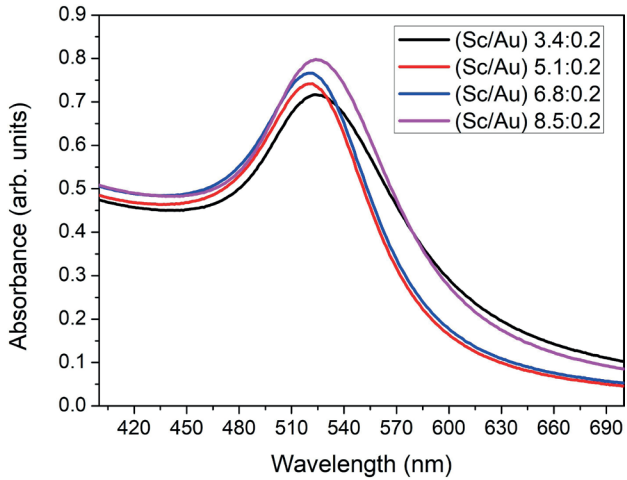


Figure 2: UV-vis absorption spectrum of AuNPs.

3.2 Effect of molar ratio

The advantage of the Turkevich method is the ability to control the size of AuNPs by changing the molar ratio of sodium citrate. In this work, AuNPs were synthesized, with sizes between 32 nm and 120 nm, increasing the molar ratio from 3.40 to 8.5, as shown in Table 1. Nanoparticles with increasingly larger diameters and less spherical shapes were formed, as the molar ratio of sodium citrate, increased addition presents a slight amplitude of the absorption order, which indicates that the nanoparticles become increasingly polydisperse, with polydispersity indices ranging from 0.210 to 0.441. However, the size and distribution of AuNPs are affected due to the increase in ionic forces and electrostatic repulsions between

AuNPs, which reduces colloidal stability in small proportions.

Chloroauric acid (mM)	Sodium citrate (mM)	Diameter of the AuNPs (nm)	Polydispersity index
0.2	3.4	32	0.210
0.2	5.1	60	0.278
0.2	6.8	80	0.334
0.2	8.5	120	0.441

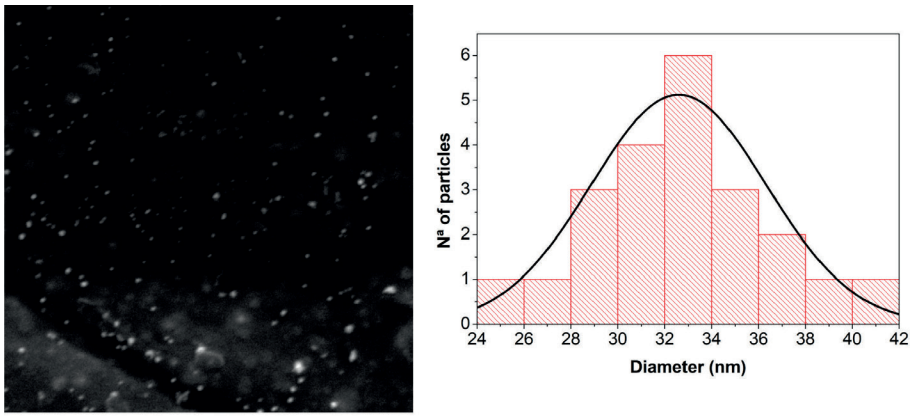
Table 1: Data comparing the size of AuNPs and their polydispersion concerning different concentrations of sodium citrate.

3.3 Other factors of the Turkevich method

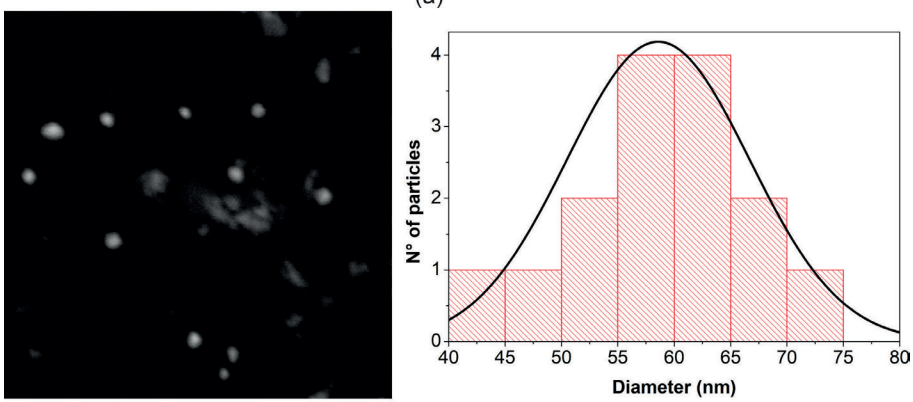
Another critical factor reported in the Turkevich method was the order of addition of the reagents [15]. In the standard synthesis protocol, sodium citrate is introduced into a boiling chloroauric acid solution, resulting in small nanoparticles with a uniform distribution [16]. On the contrary, if the order of addition is reversed and the citrate solution is brought to the boiling point, it would allow the citrate to transform into different nanostructured species before reacting with chloroauric acid due to the thermal oxidation of citrate. Last but not least, the effect of temperature on the chloroauric acid solution is an important factor since the increase of heat in the solution leads to the formation of nanoparticles with diameters of approximately 3 nm in the synthesis by the Turkevich method [17].

3.4 Scanning electron microscopy

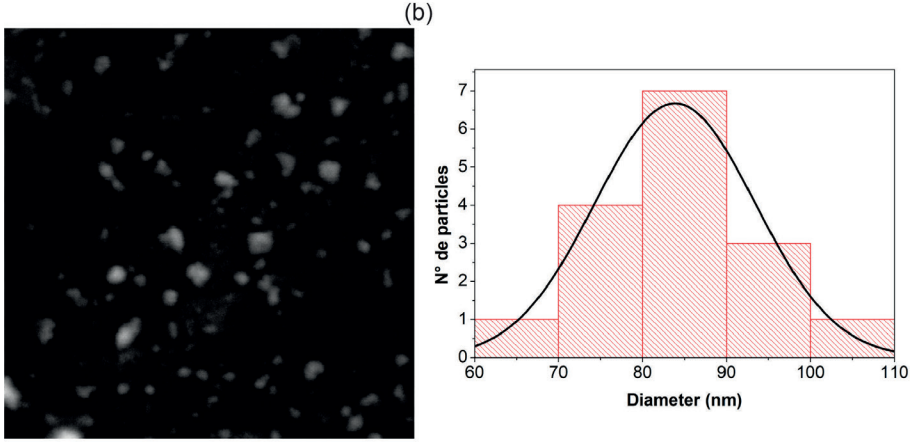
In this work, scanning electron microscopy is used to confirm the formation of AuNPs and study the morphology obtained, as shown in Figure 3. As can be seen, the images obtained show a uniform distribution of spherical AuNPs as the molar ratio of sodium citrate increases, the surface indicates some degree of nanoparticle aggregation, generating several random sizes with irregular shapes. The size of the nanoparticles was measured by applying the program (Image J) to each SEM image, resulting in nanoparticles from 32nm to 120 nm.


Nº of particles
Diameter (nm)

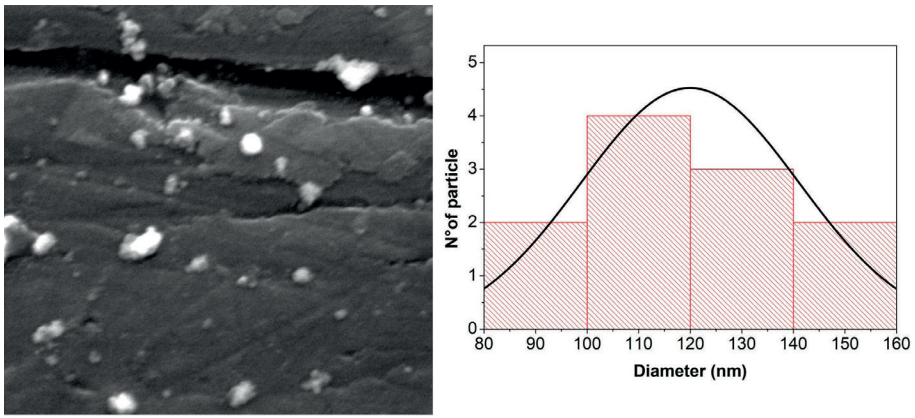
(a)


N° of particles
Diameter (nm)

(b)


N° de particles
Diameter (nm)

(c)



(d)

Figure 3: SEM images of AuNPs nanoparticles with diameters of a) 32 nm, b) 60 nm, c) 80 nm, and d) 120

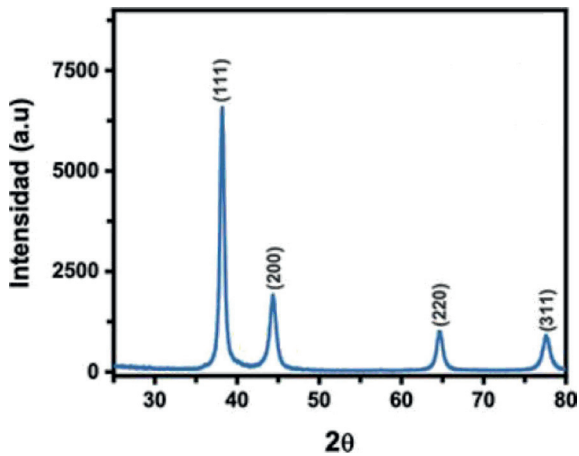


Figure 4: SEM images of AuNPs nanoparticles with diameters of a) 32 nm, b) 60 nm, c) 80 nm, and d) 120

3.5 X-ray diffraction analysis

The crystallinity of the synthesized AuNPs was investigated using the X-ray diffraction (XRD) technique; the pattern exhibited four distinct peaks at 38.2, 44.4, 64.7, and 77.7. All peaks corresponded to standard Bragg reflections (111), (200), (220), and (311) sets of lattice planes corresponding to the synthesis of AuNPs, as shown in Figure 4

4 I CONCLUSIONS

The AuNPs were synthesized using the Turkevich method; the process reacts chloroauric acid ($HAuCl_4$) with different molar concentrations of sodium citrate ($Na_3C_6H_5O_7$) at 97ºC with a magnetic stirring of 450 rpm. The result was a red suspension, indicating the

formation of AuNPs. The nanomaterials were characterized by UV-Vis, SEM, and XRD; UV-VIS spectroscopy shows maximum absorption at 522 nm, the characteristic peak of AuNPs. The SEM images show Spherical AuNPs, presenting a uniform distribution with a certain degree of random aggregation with various sizes, obtained by applying the program (Image J), whose average diameter is around 32 to 120 nm. The diffractograms of the AuNPs showed four characteristic peaks associated with the crystallographic planes (111), (200), (220), and (311).

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