Localized Plasmon in Silver Nanoparticles Synthesized by Microwave Radiation

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Abstract: This work presented the silver (Ag) nanoparticles (NPs) synthesis, by the technique assisted by radiation in the microwave spectrum, each sample was prepared as an aqueous solution based on AgNO_3 at 1 mmol. This mixture was homogenized in polyethylene glycol keeping a proportion of 1:10. A new variable that we called stabilization time was introduced. Every sample was submitted to microwave radiation varying the stabilization time. The exposure time of 60 s and the power of the radiation in 1200 w were maintained. The morphology was characterized using SEM (scanning electron microscopy), where we find sizes of a spheres clusters around 70-170 nm, suggesting the particle size between 20, 30 and 40 nm. The optical characterization of the silver NPs was based on the UV-VIS spectrophotometry. An LPR (localized plasmonic resonance) of wavelength in 320 nm for 3 samples was found, 318 nm for other 2 samples and in 324 nm for the last sample. A Plasmon shift was located due to the variation of the stabilization time. Besides that, we have changed the FWHM (full width at half max) the Plasmon as we modified, indicating a size variation and distribution of the same, according to the data found by electronic micrograph. The intensity of the LPR has moved with the change of the stabilization time, suggesting a higher resonance of the free electrons near the border of the NPs. The pH of every sample was measured with optical methods that are non-invasive, finding that the pH of two samples went off of the measuring range that the instrument has. For those we had to use an invasive method, the values obtained for the pH were in the basic range with values between 6 and 8.

Key words: Microwave, plasmon, stabilization, resonance.

Nomenclature

Nps:	Nanoparticles
ϵ' :	Dielectric constant
ϵ'' :	Dielectric loss
M:	Molarity
Mw:	Microwaves
S.t :	Stabilization time
Awl:	Absorbed wavelength
R.t:	Radiation time

1. Introduction

The metallic nanoparticles synthesis has acquired a wide interest in the investigative field, due to a huge variety of applications going from therapeutics to bio-molecular detection [1]. Mixing noble metals and polymers, mechanic, thermic, electrical and other

specific properties of the materials seem enhanced [2]. Looking at the metals, one of them has taken importance. The silver shows a particular effectivity of destroying and paralyzing Gram positive-negative bacteria [3]. The surface plasmonic resonance is almost the most important effects produced by Ag Nps. It's an induced dipole by the free electron collective excitation with resonant frequency located in the electromagnetic visible region. According to the functional Plasmon characteristic, a large variety of optical properties from the material electric field can be determined. The interaction between light and matter may be amplified to get bigger superficial phenomena [2, 4]. A nano-metric material has dimensions under 100 nm with varied shapes like spheres, cubes, pyramids, rods, etc. This morphology, sizes and electric field intensities determine the Nps properties, each one with a characteristic plasmonic

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resonance [5-8]. Various methods have been implemented to synthesize NPs Ag. The synthesis assisted by polymers in aqueous as the Arabic gum and polyvinylpyrrolidone is located among those [8]. In this order, one of the most used methods is the chemical reduction. The presence of reducing agents handles with regulating the growth of the NPs. Likewise, other methods based on electrochemical, thermal decomposition, inverted micelles, laser ablation, sonochemistry among others are effective to synthesize Ag Nps [7]. Yet, a method that has taken great acceptance in the scientific community is the synthesis assisted by microwave, which represents a more efficient and cheaper way to synthesize NPs Ag with low environmental impact. In this process, the energy produced by the electromagnetic field does oscillate molecules due to dipole thus providing a rapid heating of the solution, (see Fig. 1). This happens due to interaction theoretical making there is a warming selective generating a shift accelerated in the temperature. This change produces rupture of the links present in the molecule, by the action of the electromagnetic field, thus producing even heat through molecular friction. The power dissipation of the energy radiated in the microwave spectrum per unit volume of the sample (P) is given by Eq. (1).

$$P = cE^2 f \epsilon'' = cE^2 f \epsilon' \tan \delta \quad (1)$$

Eq. (1) The power dissipation of the energy radiated.

where, δ is constant, E is the electric field in the

material, f is the frequency of the radiation, ϵ' and ϵ'' are the dielectric constant and dielectric loss respectively, ϵ' represents the relative permittivity, which is a measure of reaction of a molecule when it is polarized by an electric field and so $\tan \delta = \epsilon''/\epsilon'$ is energy dissipation factor or tangent of loss. Eq (1) indicates that ϵ'' is the parameter physical that shows the ability of the material of heat is in the field of the microwave [9]. The solvents used for the synthesis of the microwave spectrum must have a dipole moment high and with a high permeability, able to absorb large amounts of energy, as the poly is ethylene glycol [10].

Likewise, the scope in which the Ag NPs have been developed is vast and covers many areas. The research areas are optics, electronics, and physics, catalytic, chemical, biological, pharmaceutical and medical. Due to properties of the NPs, they can be designed for localized and effective distribution of drugs through the bloodstream, as well as to adhere to the cells [11, 12]. In this way, it has been possible to use the NPs for the detection of cancerous tumors. By the high sensitivity, an amplified signal characteristic of the adhesion between cells is generated. With genetic malformations, the NPs Ag thus provides a facility in the detection of cancer using methods not invasive [13]. For this reason, the implementation of plasmonic structures in biosensors takes advantage of the optical response of the NPs which generated a characteristic Plasmon resonance from materials such as drugs, vitamins, hormones, or DNA [14].

Fig. 1 Effect of electromagnetic waves on water molecules.

2. Experimental Setup

The Ag NPs were synthesized by radiation in the spectrum of the microwave in an aqueous solution of silver nitrate (AgNO_3) 0.1 M and PEG (polyethylene glycol) as the solvent because of its high point of boiling (250 °C). The sample preparation procedure is outlined in Fig. 2. This solution base was mixed with polyethylene glycol, which allows transmitting a large amount of energy caloric to show its radiation.

For the synthesis, the variation of S.t. (stabilization time) was a fundamental condition for the formation of nanoparticles, which corresponds to the time interval between preparation and radiation in the spectrum of the microwave, as well as the parameter to take into account the homogeneity of the sample. Dynamic interactions between the compounds of the solution are generated during the process of stabilization. These partially dissociate the molecule of AgNO_3 , but without breaking the link between the Ag and the NO_3 (a type of stretch). This interaction handles with maintaining colloidal solution, since distancing compounds, molecules are lighter and interactions between hydrogen-hydrogen (bridge of

hydrogen) are strong enough to suspend them in the Middle (see Fig. 3).

Used intervals were 1, 5, 8, 60 to 90 min, and these intervals are what they call S.t. Subsequently, samples obtained and stabilized were exposed to the radiation in a microwave oven adapted to a system of circulation and temperature control, with an output of 1,200 W and a frequency of 2.450 GHz (see Fig. 4).

During the process of radiation, each sample presented various colors. Starting with intense yellow, through red and ending in opaque yellow. After contacting with the oxygen in the atmosphere a more grayish tone was acquired, achieving stabilization in this last pitch. For removing NPs Ag, a wash in two stages was conducted; the first consisted of centrifuging the solution colloid for precipitating them NPs Ag present, and thus to remove PEG by ethanol. The second stage consisted of washing ethanol with des-ionized water, which finally dissolved the NPs Ag. During this process, we can infer that these were coated with two layers of different elements. The first composed of water and the second by PEG since this was the medium in which the aqueous solution was scattered. Exposure to radiation in the microwave

Fig. 2 Outline of the formation process of the solution prior to radiation by MW.

Fig. 3 Formation process prior to radiation situation.

Fig. 4 Typical installation for the realization of synthesis of Nano microwave-assisted metal structures.

Fig. 5 Representation of the molecular structure of the reagents used in synthesis.

spectrum allowed that AgNO_3 molecule disassociated giving rise to molecular Ag. The residual water molecules mixed into HNO_3 (nitric acid) in low concentrations with PEG (see Fig. 5). The NPs Ag were prepared using an aqueous solution of nitrate of silver homogenized with PEG, the mixture was subjected to radiation in the microwave spectrum.

3. Experimental Results

3.1 Synthesis Results

The study to the optical response of the NPs Ag

used the technical absorption spectroscopy with a Thermo Fischer Scientific team and model Evolution 300 UV-VIS, frequency of 50/60 Hz 150 VA power. It was found that synthesized samples had a maximum absorption at different values of wavelength. Plasmon localized on the NPs of Ag was not located on the same wavelength. But, three of the signs coincided with the same Plasmon. Besides, two others had a Plasmon resonance on the same wavelength and one of the five samples did not coincide with any of the two previous groups. In spite of this, gaps in the

wavelength of absorption are small but at the same time absorption intensities differ and increase sharply for each sample of NPs synthesized Ag (see Fig. 6).

This type of difference in wavelength of absorption allowed qualifying the nanoparticles synthesized according to the Plasmon retrieved in order to be able to find similar relations regarding sizes of NPs and distribution of these in each absorption band and to have sharper clarity regarding these three groups (see Fig. 7).

In this order of ideas, the nanoparticles subject to the plasmon located in 320 nm presented different size distributions. We found that the NPs Ag synthesized

in a time of 3 min stabilization showed a distribution of sizes much larger. Opposite to the NPs Ag which was synthesized with a stabilization time of 5 min, a smaller size distribution yields. Also these two types of distributions, were located in a size intermediate between them mentioned before, related with a time of stabilization of 90 min (see Fig. 8).

$$\Gamma = a + \frac{b}{r} \quad (2)$$

Eq. (2) Bandwidth of the plasmon.

where, Γ represents the bandwidth of the plasmon measured in eV, both a and b are measured in eV and nm respectively, r is measured in nm particle size.

Fig. 6 Variation in the intensity of absorption and wavelength for synthesized samples of NPs Ag.

Fig. 7 The intensity of absorption for plasmon 318, 320 and 324 nm of NPs Ag with different times of stabilization in the synthesis.

Relationship (Eq. (1)) indicates a growing inverse of the bandwidth of the plasmon with particle size, as well as a variation of sizes was found according to the increase in the bandwidth of the plasmon for particles with 320 nm plasmons. Also this behavior for particles with plasmons in 318 nm is repeated, and a distribution of sizes of NPs Ag much was larger. The sizes related to samples with 8 min of stabilization are defined for NPs Ag subjected to a period of

stabilization in the synthesis of 60 min. This is due to the variation in the bandwidth of plasmon for each sample (see Fig. 9). But for this case that sample types have a plasmon resonance in 318 nm and the difference in size is due to the variation of the bandwidth of the plasmon as indicated in Eq. (2). To relate the different peaks obtained through absorption spectroscopy the data were used (see Table 1), which compares the largest core of each of the peaks

Fig. 8 Distribution of bandwidth for various shows NPs AG with a common plasmon 320 nm and different S.t located between 3, 5, and 90 min.

Fig. 9 Distribution of bandwidth for some Nps samples with a common plasmon in 318 nm and different S.t located between 8 and 60 min.

Table 1 Wavelengths of absorption for different contributions to the UV-Visible spectrum of synthesized samples.

Sample	Radiation time [s]	Power [W]	Stabilization time [min]	Distributions	Wavelength of absorption [nm]
Ag 1.1	60	1,200	90	1	243.14
				2	269.23
				3	320.28
				4	325.39
Ag1.2	60	1,200	60	1	229.82
				2	259.27
				3	318.74
				4	319.81
Ag 1.3	60	1,200	8	1	241.87
				2	281.52
				3	319.54
				4	345.85
Ag 1.4	60	1,200	5	1	244.36
				2	319.04
				3	319.05
				4	350.34
Ag 1.5	60	1,200	1	1	250.34
				2	283.09
				3	323.28
				4	365.21

contributing to the greatest unit of the plasmon. And it is related to the time of stabilization each sample had. There is evidence that after a certain time the sample does not suffer considerable changes in stability and homogeneity.

A detailed analysis was made for each of the retrieved spectra, resulting in the breakdown of this. In various spectra characteristic of less intensity corresponding to a particle size, these were related to spectra obtained by the decomposition, parameter for this relationship was the maximum for each peak absorption wavelength, since it is known that this has a strong relationship with the size of the nanoparticle, in addition that it is known that synthesized samples have several particle sizes (see Fig. 10).

3.2 TEM Characterization

As you can see in Fig. 10, the top row of images which are more stabilized samples have a relationship between them, as well as images of the bottom row, with this it can be inferred that at a certain point the sample base is fully stabilized. For this reason, it may take some time, yet is not evidence of a really

important change, as it happens, in the samples that had 5 and 8 minutes of stabilization.

In the second sample, already become not evident the areas with high density of colloids, with this have a tool to ensure that the stabilization time greatly affects the growth and morphology of the particles to synthesize. We see as evidenced the occurrence of each of the contributions to the main spectrum, as there are different particle sizes in each sample, it is supposed that each has a wavelength of maximum absorption different, but related.

The dispersion of NPs Ag can demonstrate from the dispersion of clusters in aqueous solution, indicating the high effectiveness of the absorption of radiation by the NPs Ag as plasmons of each of the spectra previously discussed. In addition to this, to carry out a detailed to micrographs image analysis, the sizes of nanoparticles follow a dispersion pattern illustrated by the curves shown above (see Fig. 11).

As I was mentioned earlier (see Table 1) each synthesized sample has a characteristic peak, formed from different peaks associated with different sizes of nanoparticle. Also it can be revealed in the comparison

Fig. 10 Size distribution obtained through the image analysis conducted on TEM micrographs of synthesized samples.

of micrographs TEM (see Fig. 10).

During the image analysis of the difference of sizes, and to separate the peaks in the spectrum, we see that mild, with only a maximum bends are reached. This form of peak suggests that the particles are spherical, which was found previously by micrographs.

In any case, the analysis of the characteristic of each spectrum peaks is a strong tool that gives information about the size distribution, morphology and relationship between the numbers of particles in each size. Each sample by its characteristic peaks may

be related in this way, it is said that peaks between each of the samples are related. As you can see in this case, all the samples have a peak close to 320 nm, which for all varies in intensity for samples Ag 1.4 and Ag 1.5. Where it reaches an intensity is related to the density of particles that respond to that length of wave. In addition the peak also verifies the character almost-spherical particles (see Fig. 12). In addition to the above characterizations, pH values at each of the specimens synthesized were measured by optical methods of non-invasive using a 600 nm laser, which found a diversity of values related to points that presented high saturation in the value of the same, indicating a high concentration of sample NPs Ag as well as its high acidity to pH (see Table 2).

Although there is not a relationship that jumps to the view easily between the pH of the NPs Ag and its size, it is possible to see a relationship between the plasmon resonance and the stabilization of each sample time. There is evidence of a clear division into three large groups in this case according to the absorption spectrum discussed previously. Similarly the influence of the stabilization time on features in size and morphological of the NPs Ag is highlighted in the spectrum (see Fig. 7), which splits a range of sizes in a band of 5 to 7 nm in the spectrum of time, indicating a possible control of the size of NPs Ag by making use of specific time of stabilization so that parameter would make it possible to reformulate the characteristics of size as variable dynamic to the moment of performing the synthesis.

As you can see in Fig. 6, although the four peaks are very similar, there are some differences such as the width, intensity, and acuity of each. All samples have similar particle sizes, and these variations are caused by non-homogeneity in samples different particle sizes. Taking as a simple example by analyzing the corresponding to the sample image of Ag 1.4, there are a large number of corpuscles, there are 3 protruding, by its enormous size in comparison to the others. This kind of heterogeneities is what is responsible

Fig. 11 Size distributions obtained through the image analysis conducted on TEM micrographs of synthesized samples.

Fig. 12 Distribution of sizes obtained through the analysis of image made on micrographs TEM of the samples synthesized.

Table 2 The scale of the variation of pH in terms of absorbance for NPs Ag.

Stabilization time (min)	Absorbance (a.u)	pH	Intensity plasmon
90	0.12308	6.99	261288
60	0.139283	6.95	250111
8	0.012417063	7.01	563867
5	0.021972152	7.84	633127
3	1.90105	6.14	166290

Fig. 13 Spectra obtained, compared to their respective TEM micrograph.

for the characteristics of the peaks vary, which can lead to an analytical error to think that obtained from particle size may be an average of sizes, more than that 2 different particle sizes.

This type of dynamic formulation can be sustained from the relationship between the value of plasmon resonance in each sample and the size of it, in which the same distribution groups lie, within which the variation is highlighted on NPs Ag size, allowing guess that by controlling the time of stabilization of the sample that has been synthesized will be possible to set the value of plasmon resonance and on this control of NPs Ag which is given in this spectrum band, so that the plasmon located also is controlling the time of stabilization (see Fig. 14).

This would allow a second mechanism relating to

the domain of the plasmon position; *i.e.*, not only it can be controlled by means of the variation of the function dielectric of the half and changing the coefficient of reflection of the same if not controlling their parameters prior to synthesis, and for this case it can be named the time of stabilization. This idea about parameters is related in the dipole approximation of Mie theory (see Fig. 15).

$$C_{ext} = \frac{24\pi^2 r^3 \epsilon^{3/2}}{\lambda} \frac{\epsilon_m''}{(\epsilon_m' + 2\epsilon)^2 + (\epsilon'')^2} \quad (3)$$

Eq. (3) Mie theory approximation.

The dielectric function is the permittivity of the medium. It is wavelength concerning the plasmon, r the particle size and the NPs-related extinction coefficient.

Fig. 14 Variation simultaneously from the time of stabilization of NPs Ag with the value of the resonance of the plasmon located.

Fig. 15 Variation simultaneously the size of NPs Ag with the value of the localized plasmon resonance.

4. Conclusions

Ag NPs were synthesized by means of radiation in the microwave spectrum, making use of an aqueous solution of silver nitrate (AgNO_3) 0.1 M and (PEG) as a solvent. Before radiation, the time of stabilization of the mix was taken into account, taking this parameter

as a variable characteristic of each synthesis. It was found that according to the quantity implemented of such variable, Ag^+OH and N^+OH is managed to form clusters, which influenced in the training of the NPs of Ag. This time of stabilization of the sample allowed splitting samples synthesized into three basic groups according to the plasmon resonance in common. This

was accomplished through the study of the optical response of the NPs in the UV-Visible spectrum, allowing you to define absorption bands at wavelengths of 318, 320, and 324 nm. Also, the variation in the bandwidth of the plasmon allowed to guess the particle size finding as well as the NPs theory predicted a growing inverse of the size with the growth of the bandwidth of the plasmon. Finding that for the stabilization of 90 and 60 min time the NPs had a much larger size distribution compared with the present size of the NPs synthesized with a stabilization time 3 min, which had much smaller sizes. However, a distribution of sizes between them was found as previously explained. Size of particle related with times of stabilization covered in them for 5 min, which allows Intuit a form alternative of control the resonance of the plasmon. Without having modified the function dielectric you could have controlled of the plasmon position without changing the medium. On the other hand, measures of pH of each show are carried out subsequent to the synthesis making use of methods optical not invasive finding that for time of 90, 60 and 30 min of stabilization them samples presented high acidity in against position to them samples related with 8 min and 5 min which presented a basic behavior.

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