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EVALUATION OF SIZE AND SHAPE OF THE SILVER NANOPARTICLES PREPARED BY CHEMICAL SYNTHESIS FOR THERAPEUTIC APPLICATIONS.

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Abstract

The silver nanoparticles are known such as diffusers and efficient light absorbers, because of their strong interactions with visible light through the phenomenon of surface Plasmon resonance (SPR). Local frequency LSPR strongly depends on the size, shape and dielectric medium. The synthesis of silver nanoparticles of different sizes was carried out, using different molar concentrations of silver nitrate at different temperatures in two different solvents (ethanol and methanol). the synthesized nanoparticles were characterized by UV-Visible spectroscopy. The results show the presence of an absorption peak at around 440 nm. A theoretical study based on the use of the simulator COMSOL Multiphysics was developed. It was demonstrated, that the nanoparticles have a spheroids shape and their sizes are of the order of 12 nm. The theoretical results were validated by experimental results.

Keywords: *Silver nanoparticles, localized surface plasmon resonance, LSPR, modeling.*

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1. INTRODUCTION

The silver nanoparticles are particularly attractive because of their single optical properties [1-3]. For example they exhibit a strong absorption band in the area UV-visible and an intense diffusion of the incidental light with scales length much smaller than the wavelength. It is the phenomenon of surface Plasmon resonance (SPR) [4-7] which occurs when the incidental light on the nanoparticles is in resonance with the collective oscillations of the electrons of conduction in metal nanostructures.

The metal nanoparticles are used in many applications such as chemical detections for example the detection of Mercury ions in aqueous mediums, biological detections for example the detection of bio markers or proteins sailing in the body fluids representative certain diseases cardiovascular and certain cancers, the imagery by the use of the nanoparticles like agent of contrast for the optical imagery, the delivery of therapeutic agent like drugs or genes and their release by external stimuli like the light and the thermal photo treatment targeted various diseases like cancer [8-14]. The plasmonic nanoparticles can be manufactured with a high degree of accuracy and in various forms [15] this with an aim of exploiting to the maximum their optical properties which extend from visible until the infrared, and which are influenced by the size and the form of the nanoparticles as well as dielectric medium surrounding them [16-18].This work concerns the synthesis of silver nanoparticles of controlled size. These nanoparticles are obtained by reduction of silver salt ($AgNO_3$) by the benzoic acid, in the presence of PVP .The size as well as the form of the nanoparticles are indirectly given according to the index of refraction of the solution of silver nanoparticles which we exploited in the study of three elaborate ideal models with software COMSOL Multiphysics based on the Finite Element Method (FEM) , in order to determine the nanoparticle which can qualitatively reproduce the behavior observed in experiments.

2. EXPERIMENTAL STUDY:

2.1 Materials:

The silver nitrate (Ag NO3,99.92% of purity) is used as precursor, the polyvinylpyrrolidone (PVP, the average molecular weight are of 40.000) is used like stabilizing, the benzoic acid is used like reducing agent, methanol and the ethanol is used as solvents.

2.2 Protocol of synthesis:

Silver nanoparticles were produced by a chemical process of reduction. A silver nitrate solution (0,0025 M of AgNO3) was prepared by diluting 0,42 g in 10 ml of ethanol with simultaneous mixture of a benzoic acid solution (0,5 G in 10 ml of ethanol) and the solution of PVP (1g in 10 ml of ethanol) to room temperature under vigorous magnetic agitation during 20 min. the mixture of reaction was heated at various temperatures (40 °, 50 °, 60 °, 70 °). Then, we varied the concentration of AgNO3 by taking the concentrations 0,0015M, 0.0030M, 0.0035M and by keeping same the other parameters.

The same protocol for the synthesis of the silver nanoparticles is remade with methanol.

2.3 UV-VISIBLE ABSORPTION SPECTROSCOPY

The study of the optical properties by spectroscopy of absorption constitutes one of the essential stages for the characterization of the silver nanoparticles synthesized.

It reveals the formation of silver nanoparticles thanks to the detection of a strong absorption of light by the nanoparticles in the area of the visible light.

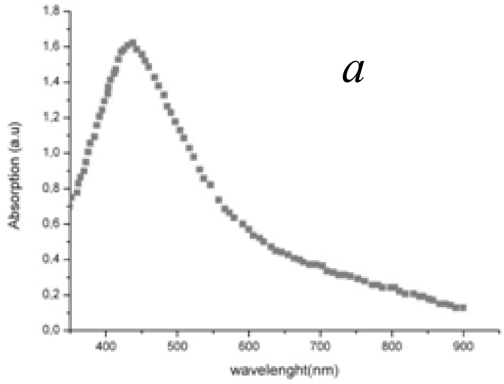
The UV-visible spectra are recorded with a UV-visible spectrophotometer Ultrospec 2100 PRO, in a range wavelength extending from 200 to 900 nm.

Firstly we characterized our colloidal solutions according to the temperature for a concentration of AgNO3 of 0.0025 moles by holding the other constant parameters in two different solvents. The results obtained are gathered in the following table.

Table 1. Absorption maxima (λmax) of silver nanoparticles prepared from AgNO3 solution (0.0025 M) at different temperatures in different solvents.

AgNO3	λmax (nm)					
	30°	40°	50°	60°	65°	70°
In ethanol	446,1	439,8	444,1	445,1	_	439,6
In methanol	440,5	440,7	440,6	445,8	451,4	_

In the figure1, we present the absorption spectra for a concentration of AgNO3 of 0.0025 moles.



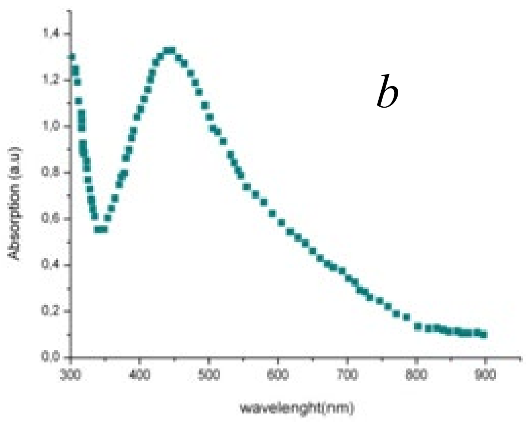
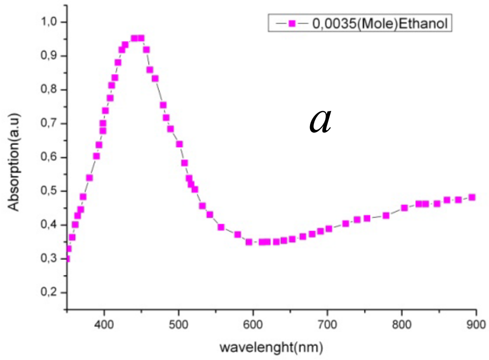


Fig1. UV-Vis absorption spectra of silver colloidal particles synthesized from AgNO3 solution (0.0025M) at 30°C in different solvents (a) Ethanol, (b) Methanol.

Then we varied the concentration of AgNO3 from 0.0015 to 0.0035 moles in two solvents, the samples are taken at constant temperature 30°.The results obtained are gathered on table 2.

Table2. Absorption maxima (λ_{max}) of the silver colloidal particles prepared from different concentrations of silver nitrate at room temperature 30° in different systems

AgNO3	λmax (nm)			
	0,0015 M	0,0025M	0,0030M	0,0035M
In ethanol	439,8	436,4	441,5	438
In methanol	435,6	440,5	446,2	442,4



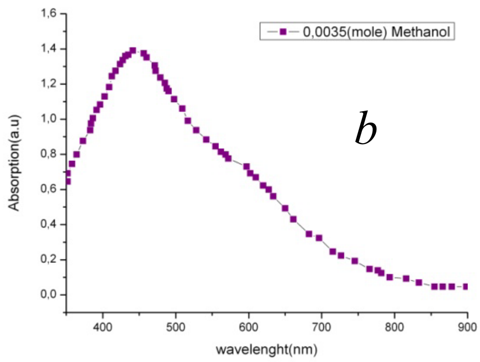


Fig2 .UV-vis absorption spectra of silver colloidal particles synthesized from $AgNO_3$ solution (0.0035M) at room temperature 30° in different solvents: (a) ethanol,(b)methanol.

Figure 2 presents an example of peak of absorption for the concentration 0.0035 mole.

We notice that the results obtained for ethanol are better contrary to the peaks of absorption obtained with methanol or we notice a spreading out of the spectrum, probably with a phenomenon of agglomeration of the silver nanoparticles

3. THEORETICAL STUDY:

3.1 *Ideal model:*

In order to predict the optical behavior of the nanoparticles worked out by chemical synthesis according to our preceding protocol, as well as the size and the form of the nanoparticles, we developed a theoretical approach while basing ourselves on the resolution of the Maxwell's equations; by the finite element method, and while making use of simulator COMSOL Multiphysics.

One considers the electromagnetic-nanoparticle interaction wave described by the equation of wave of Maxwell [19]:

$$\nabla \times \left(\frac{1}{\mu_r}\nabla \times E\right) - k_0^2\left(\varepsilon_r - j\frac{\sigma}{\omega\varepsilon_0}\right)E = 0 \quad (1)$$

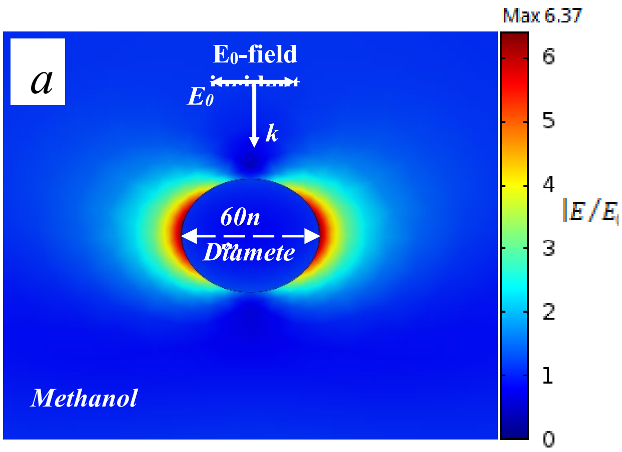
The absorption Coefficient Q_{abs} is obtained by integrating the thermal losses (U_{av}) compared to the volume of the nanoparticle:

$$Q_{abs} = \frac{1}{\pi r^2}\frac{2}{\sqrt{\varepsilon_0/\mu_0}E_{inc}^2}\int (U_{av})\, dV \quad (2)$$

Where E_{inc} is the amplitude of incidental electric field, r is the radius of the nanoparticle; ε_0 and μ_0 are respectively the permittivity and the permeability of the vacuum.

3.2 Results of modeling:

In first, we supposed that the nanoparticles worked out by chemical reduction have a form of nanospheres or nanorods or nanospheroids .The nanoparticles are surrounded by layers perfectly absorbing then excited by an electromagnetic wave wavelength of 400 nm - 800 nm parallel to polarize the major axis for the case of the spheroid and the stick. The experimental parameters used are: the permittivity of the silver nanoparticles which is extracted from the experimental data of Palik [20] and the index of refraction of the surrounding medium 1,34 and 1,37 which are respectively extracted from the colloidal solution with the solvent ethanol and methanol.



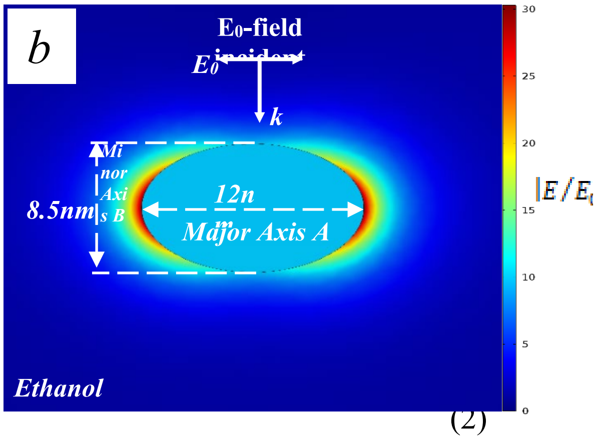


Fig 3: Contours of the electric field around: a) spherical and b) spheroid silver nanoparticles.

In the case of methanol we found for a wavelength similar to the experimental results, while basing ourselves on the theory of Mie, of the spherical nanoparticles, whose diameter is of 60 Nm; according to the spectra of the experimental results that it's rather an agglomeration of nanoparticles with certainly of irregular contours.

On the other hand for ethanol the results of the spheroids present exaltations of the fields to the wavelength obtained in experiments, and spectra similar between the two theoretical and experimental results from where any confirmation that the nanoparticles in a solvent ethanol have dimensions of 12 nm diameter and 1,4 nm of aspect ratio for a spheroid form. Nevertheless in a medium solvent methanol it is difficult to predict the form and the size of the nanoparticles because of the phenomenon of agglomeration.

4. CONCLUSION:

We proceeded to the study of the optical properties of the silver nanoparticles which are strongly influenced by the size, the form, the index of refraction of the surrounding medium but also by the physical and chemical experimental conditions. The UV-visible absorption spectroscopy of the solutions of silver nanoparticles prepared for various molar concentrations of $AgNO_3$ with various temperatures in various systems shows for the majority of them only one peak of absorption. However the temperature probably acts on the widening of the absorption spectra of the nanoparticles resulting from methanol medium due to a phenomenon of agglomeration. The results of simulation by software COMSOL Multiphysics show an agreement of the silver nanoparticles synthesized in solvent ethanol with the spheroid model of 12 nm diameter. On the other hand, it is difficult to predict the form and the size of the nanoparticles in a medium solvent methanol because of the phenomenon of segmentation.

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