Tracking method for the microwave-assisted synthesis of silver nanoparticles

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An eco-friendly method for the microwave-assisted synthesis of silver nanoparticles in the presence of tannic acid acting both as stabilizer and reducing agent has been examined. To follow up the realtime reaction changes, the microwave-assisted synthesis was carried out directly inside the quartz cell of the UV – VIS spectrophotometer used for analysis. The forming mechanism of the silver nanoparticles was studied by correlation between the recorded UV – VIS spectra and results obtained by DLS and TEM analysis.

1. Introduction

Nanoparticles synthesis and nanotechnology in general, has attracted the attention of many researchers over the past 10 years or so. The attraction of nanoparticles lies in the hundred of attractive characteristics which can be achieved by reducing suitable materials from the bulk to the nanometer size (1-100 nm), these characteristics ranging from increased surface/volume ratio to novel quantum confinement effects. Examples of property enhancements include magnetic, optical, biosensing, thermoelectric, semiconducting, catalytic, energy storage and thermal properties. Industries that are interested in novel nanoparticles include data storage, plasmonic, photonic, microelectronic, energy, pharmaceutical, biomedical and cosmetics. An interesting aspect of nanoparticles is the wide range of materials classes in which nanoparticles are useful including semiconductor, dielectric, metallic, ceramic, composite and polymer nanoparticles. The drawback of nanoparticles synthesis is the high thermodynamic instability due to high surface energy of the dispersed phase that, when the kinetic conditions are favorable, can lead to an irreversible coagulation or aggregation of the nanoparticles. Furthermore, the nanoparticles can react with some components from their own environment. It is well known that the stability of a particle in solution is dependent upon the total potential energy function and pH.

A large number of methods for nanoparticles synthesis are reported; reactions in liquid, solid or gas phase have been examined in order to get the desired properties of the final product knowing that the chemical nature, shape and size of the nanoparticles have an important impact on their ionic potential, electronic affinity and ionic transport properties.

Presently, the most used techniques for the synthesis are: pyrolysis, evaporation at high temperature, plasma synthesis, colloidal methods and molecular self-assembly [1].

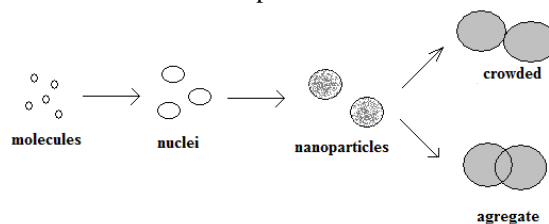The following figure schematically represents the general mechanism of nanoparticles formation:

Fig. 1. Formation mechanism of nanoparticles

When chemical synthesis is involved, very low concentration of reagents are used. Particularly, the synthesis of metal nanoparticles is achieved via a reduction reaction during which the metallic ions from solution are reduced to atoms forming clusters that are transformed further into nanoparticles by aggregation [2]. The reducing reagents mostly involved are sodium citrate, formaldehyde, alcohol; the use of natural products, e.g. glucose, geraniol, vitamins, polysaccharides, amino acids, plant extracts, to obtain nanoparticles is of particular interest, in view of obtaining more eco-friendly final products.

In this paper, we use tannic acid for the synthesis of silver nanoparticles. Tannic acid, a specific form of tannin, is a polyphenol. The molecule of tannic acid consists of 5 to 10 molecules of gallic acid and glucose – Fig. 2. In nature, tannic acid can be found in high quantities in different fruit and plants (tea, nettle, wood, berries, Chinese galls, oak wood). Due to its anti-bacterial, anti-enzymatic and astringent properties, tannic acid has numerous food and pharmacological applications; it is an additive in medicinal products and is used as a flavouring agent and as an anti-oxidant in various foods and beverages.
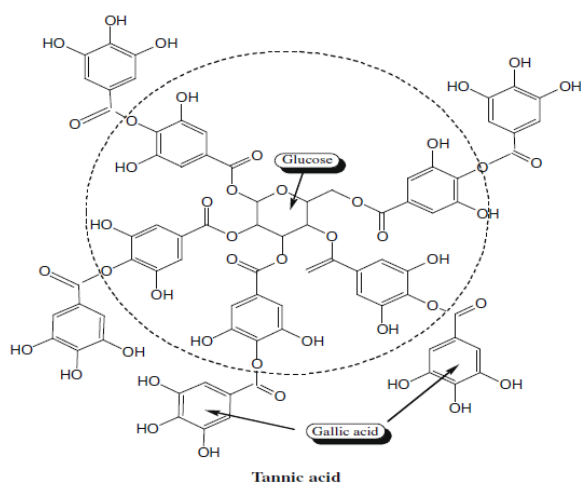

Fig. 2. Chemical structure of tannic acid, a deca-galloyl glucose consisting of a central glucose molecule esterified at all five hydroxyl-terminated moieties with two gallic acid molecules. The dotted circle highlights pentagalloylglucose and the core structure of tannic acid [12].

Tannic acid's weak acidity (pK_a = 6-8) is due to the numerous phenol groups in the structure. When dissolved in alkaline solutions containing $AgNO_3$ a part of the gallic acid - the backbone of tannic acid molecule - reduces the $AgNO_3$ to Ag^0 and forms silver nanoparticles [3].

The use of microwave energy to produce silver nanoparticles in a colloidal system appears to be particularly attractive due to simplicity, fast heating of aqueous samples and versatility, especially when there is no need of high temperatures and pressures. The use of microwave energy for synthesis is reported to result in more effective heating, faster energy transfer, selective heating, reduced thermal gradients, reduced equipment size, faster response to process heating control, faster set-up [4]. During absorption, the energy of microwaves is transformed into kinetic energy, thus enabling the selective heating of the microwave-absorbent molecules [5].

The aim of this study was to follow up the formation and behaviour of silver nanoparticles during their synthesis by recording UV - VIS spectra as the reaction proceeded. The reduction of Ag^+ to Ag^0 as well as the

stabilization of the obtained nanoparticles was performed using tannic acid.

2. Experimental

2.1. Reagents

Experiments were performed using alkaline solutions of tannic acid and $AgNO_3$; anhydrous K_2CO_3 was used for pH control of the solution. The reagents were of analytical purity and they were used without further purification: tannic acid ($C_{76}H_{52}O_{46}$) M_w = 1701.2 g/mol (Merck), $AgNO_3$ (Chimopar), anhydrous K_2CO_3 (Chimopar), bi-distilled water. Aqueous solutions of tannic acid 0.1 mmol and $AgNO_3$ 6 mmol were prepared; appropriate amounts of K_2CO_3 were added to the tannic acid solutions to maintain its pH = 7.

2.2. Microwave reactor set-up

Experiments were carried out in a reactor consisting of: MWG, 2.45 GHz microwave solid state generator with output power adjustable from 0 to 25 W (SAIREM GMS25SM) with on-screen indication of forward power (FP) and reflected power (RP) and microwave energy output through coaxial cable. A two stub coaxial tuner type AI NN 200, TSCT, was used for impedance matching of the system. The microwave energy was introduced in to the quartz reactor (spectrophotometer's own quartz cell, SFM) through an adjustable coaxial antenna, ACA, that can move up and down the reactor. A jacketed metal holder surrounds the quartz reactor with the double role of shielding the reactor and prevent microwave leakage out (and interference with the SFM's electronics) and also, of keeping the reaction media at the desired temperature. A small hole allowing the passage of the VIS-UV beam through the quartz cell was cut in the wall of the metal holder. A miniature magnetic stirring bar was used for reaction mixture homogeneity. An optic fibre thermometer, OFT, type OPSENS, Picosens was used for the in-situ measurement of the temperature inside the reactor– Fig. 3.

2.3. Analysis

The UV-VIS spectra were recorded using a UV-VIS spectrophotometer (SFM) model Jasco V550; literature values of the maximum UV-VIS absorption give λ = 410-430 nm for 2-20 nm silver nanoparticles.

Particle size was measured using high resolution transmission electron microscopy (HRTEM) associated with microanalyses techniques (EELS electron energy loss spectroscopy, EDAX), which enabled real optical images of the nanoparticles and allowed their characterization through the assessment of the chemical bond type. The apparatus used was a TECNAI F30 G2 transmission electron microscope with linear resolution of 1 Å and dots resolution of 1.4 Å. Dynamic light scattering (DLS)

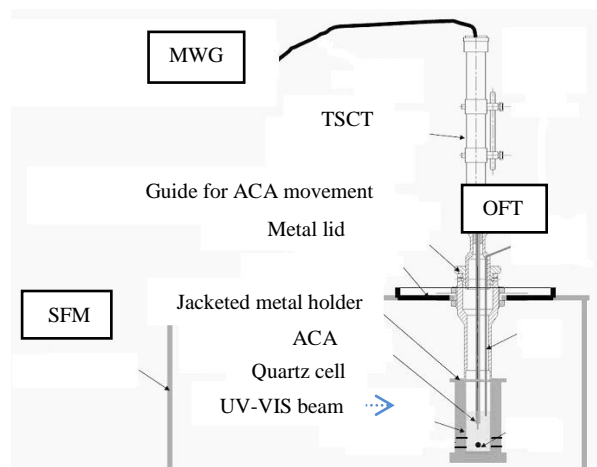analysis was performed on a Zetasizer Nano ZS type device from Malvern Instruments.

Fig. 3. Experimental set-up for silver nanoparticles microwave-assisted synthesis and continuous in situ tracking of UV – VIS spectrum

3. Results and discussion

3.1. Nanoparticles stabilization

In general, it is known that the stability of a dispersion depends upon the balance of the repulsive and attractive forces that exist between particles as they approach one another. If all the particles have a mutual repulsion then the dispersion will remain stable. However, if the particles have little or no repulsive force then some instability mechanism will eventually take place e.g. flocculation, aggregation etc. In certain circumstances, the particles in disperson may adhere to one another and form aggregates of successively increasing size that may settle out under the influence of gravity. However, in the case of nanoparticles dispersed in a solvent, both the Van der Waals attraction forces and the Brownian motion play an important role, while the influence of gravity becomes negligible.

There are two fundamental mechanisms that affect dispersion stability, Fig. 4 [6]:

- *Steric repulsion* - this involves polymers, surfactants or ligands absorbed on to the particle surface forming a protective layer and preventing the particle surfaces coming into close contact. The protective agent must have a high affinity for the particle surface and to be easily dispersed in the solvent. If enough polymer adsorbs, the thickness of the coating is sufficient to keep particles separated by steric repulsions between the polymer layers, and at those separations the van der Waals forces are too weak to cause the particles to adhere.

- *Electrostatic or charge stabilization mechanism*, as described by the DVLO theory, is the effect caused by the interaction between two particles in suspension due to a combination between the Van der Waals forces attraction potential and the electrical repulsion potential. The electrostatic stabilization is a method of kinetic stabilization.

Each mechanism has its benefits for a particular system. Steric stabilization is a thermodynamic method, suitable for multi-phase systems, requiring just the addition of a suitable polymer. However it can be difficult to subsequently flocculate the system; if this is required, the polymer can be expensive and in some cases the used polymer is undesirable e.g. when a ceramic slip is cast and sintered, the polymer has to be 'burnt out'. This causes shrinkage and can lead to defects [7].
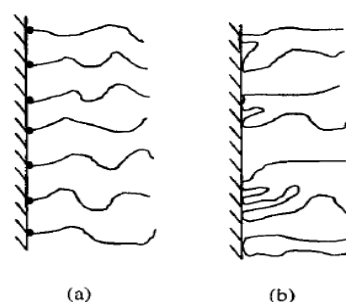

Fig. 4. Interactions between the stabilizing agent and the solid surface: a) anchored compound (steric stabilization); b) adsorbed compound (electrostatic stabilization)

To understand the role of the tannic acid and its nucleation ability for Ag nanoparticles, it is necessary to briefly explain and describe the transformations of this compound. Tannic acid contains 25 hydroxyl groups in its molecule, but only 10 pairs of 1,2-dihidroxiphenil are able to take part in the redox reaction to form quinines - Fig. 5 [8] and donate electrons, because of the chelating action of adjacent hydroxyl groups and constraints on carbon valency.
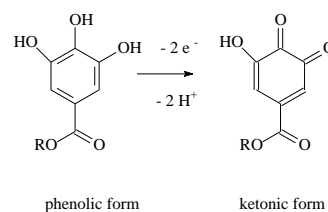

Fig.5. Redox reaction of tannic acid from phenol to ketonic form.

Since the acid tannic molecule is able to donate 20 electrons, the optimal stoichiometric molar ratio tannic acid/$AgNO_3$ for the chemical synthesis of silver nanoparticles is calculated at 0.05.

3.2. Silver nanoparticles synthesis

Silver nanoparticles synthesis was carried out in alkaline solutions in the presence of tannic acid as reducing and stabilizing agent; the reaction was performed directly in the spectrophotometer's quartz cell at controlled temperatures. The thermostated jacketed metal

holder controls the reactor temperature. Heating of the reaction mixture was achieved either electrically or with microwaves.

The effect of three parameters, molar ratio tannic acid/AgNO₃, reaction time and reaction temperature have been closely investigated in this study.

In a typical example, to obtain the desired concentration of silver, appropriate volumes of solutions of AgNO₃ 6 mmol and tannic acid 0.1 mmol were added together in to the quartz cell for total reaction volume of 3 ml – Table 1.

Table 1 Experimental conditions, total volume 3 ml.

Exp. no.	Molar ratio (MR) tannic acid/AgNO₃	Concentration of silver (mmol/L)
P1	0.050	0.3
P2	0.050	0.2
P3	0.050	0.1
P4	0.025	0.2
P5	0.075	0.2
P6	0.100	0.2

The heating was done at four temperature levels, i.e. 40 ^{0}C, 50 ^{0}C, 60 ^{0}C and 70 ^{0}C and the UV-VIS spectra were registered at 1, 3, 5, 10 and 15 minutes. The results of synthesis were interpreted by comparison with the UV-VIS spectra of tannic acid solutions at the corresponding concentration.

3.2.1. The effect of reaction temperature

Fig. 6 shows a typical time course of microwave-assisted synthesis of silver nanoparticles at 40 ^{0}C, 50 ^{0}C, 60 ^{0}C and 70 ^{0}C. The reaction rate increases with temperature however, the reaction rates are relatively low and the reduction of Ag^+ to Ag^0 was not completed within 15 min. With regards to the nanoparticle dimensions - correlated with the wavelength value for a maximum absorption – it has been noticed that at low conversion the differences are more important, i.e. higher dimensions at lower temperatures, these differences becoming of lesser value towards the end of the process. Such behaviour can be explained if the steric stabilization of forms nanoparticules occurs and if their dimensions are controlled through a diffusion process [11]
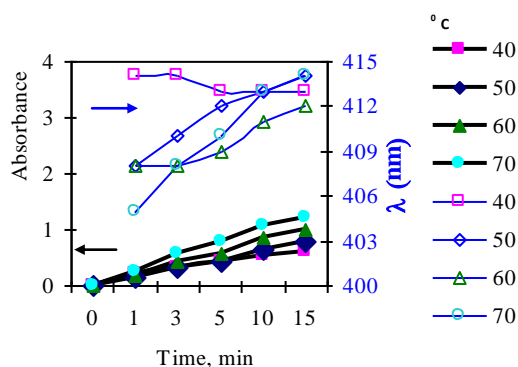
Fig. 6. Microwave- assisted synthesis of silver nanoparticles: Temperature effect [AgNO₃] = 0.1 mmol/L; MR=0.05

3.2.2. The effect of molar ratio tannic acid/AgNO₃

Firstly, the effect of molar ratio between the tannic acid and AgNO₃ on the synthesis of silver nanoparticles was studied for the conventionally heated reaction mixture – Fig. 7. These data indicate that at molar ratios below 0.05, the reaction rate of the synthesis decreases considerably and the particle diameter increases. At a molar ratio of 0.075, the reaction rate is much higher and the diameter of the formed particles is somewhat smaller. Further increase of the molar ratio to 0.1 results in a very fast reaction rate and saturation in a very short time. This behaviour can be also explained by the activity of tannic acid as a steric stabilization agent. If the density of the tannic acid layer deposited at the surface of the nanoparticules increases (ex. MR = 01 vs. MR = 0.075) the reaction rate toward the end of the process decreases. The results obtained show a decrease of the average diameter of the formed nanoparticules with the increase of the MR.

The data of the molar ratio effect on the microwave-assisted conversion of Ag^+ to Ag^0 are presented in Fig. 8. For a better understanding of the microwave heating effect, this set of experiments was carried out at 50 ^{0}C (70 ^{0}C in conventional synthesis); the microwave-assisted synthesis at 50 ^{0}C gives similar results with the conventional synthesis at 70 ^{0}C. The conversion increases with MR, meaning that, due to an effect associated with the microwave treatment, the protective layer surrounding the formed nanoparticle can be easier accesible to the silver atoms formed within the reaction liquid. This layer acts as a 'moderator' agent for the growth of the nanoparticles, the maximum absorbtion taking place between 406 nm and 410 nm, slightly narrower than in conventional synthesis. The average particle dimension has an important increase at MR = 0.025 probably due to an insufficient formation of protective layer by the tannic acid.
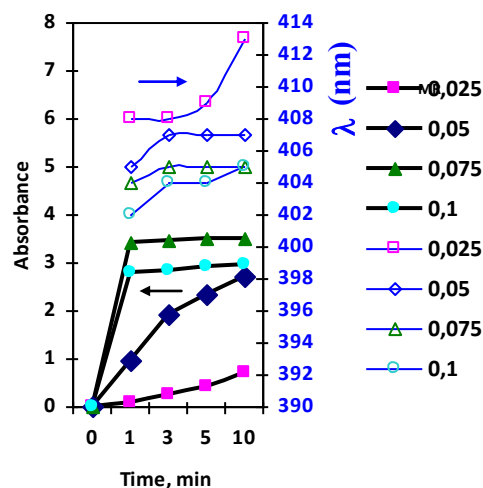
Fig. 7. Conventional synthesis of silver nanoparticles: Molar ratio tannic acid/AgNO₃ effect. [AgNO₃] = 2 mmol/L, pH 7-7.5, T = 70 ⁰C

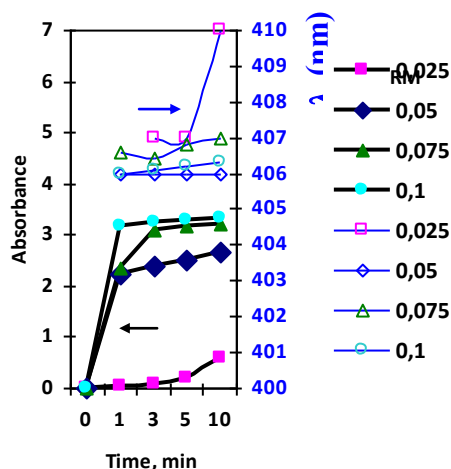*Fig. 8. Microwave-assisted synthesis of silver nanoparticles: Molar ratio tannic acid/ AgNO₃ effect. [AgNO₃] = 2 mmol/L, pH 7-7.5, T = 50 ⁰C*

3.2.3. The effect of silver initial concentration

The influence of the initial concentration of silver on the conventional and microwave-assisted synthesis of silver nanoparticles has been investigated. In conventional heating, Fig. 9, the increase in initial concentration of silver has a favourable impact on both the reaction rate and the final diameter of nanoparticule (smaller diameter). At low concentration of Ag, particle diameter tends to further increase while at higher concentrations, the particle diameter reaches a steady size; for an initial concentration of 0.3 mmol/L the growth process of nanoparticles ends rapidly. This behaviour is in agreement with Cao [11] who shows that the critical radius of the nanoparticle (r*) is indirectly proportional with the variation of Gibbs free energy in 1 unit of solid phase (ΔGᵥ) and ΔGᵥ increases with the precursor's concentration:

$$r^* = -2\frac{\gamma}{\Delta G_v}$$

$$\Delta G_v = -\frac{k \times T}{\Omega}\ln(\frac{C}{C_0})$$

where:
γ = surface energy per unit area
 k = Bolzman constant
Ω = atomic volume
C = concentration of silver atoms in solution
C_0 = solubility of silver atoms

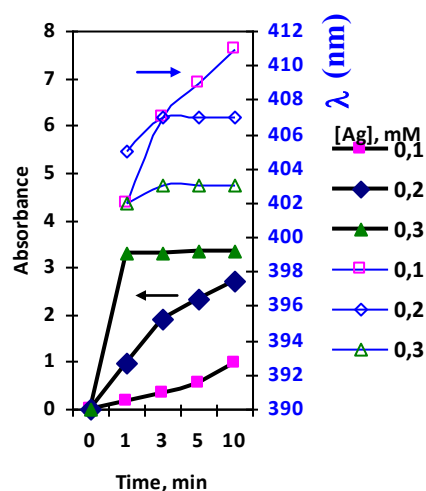*Fig.9. Conventional synthesis of silver nanoparticles: Silver initial concentration MR = 0.05, pH = 7-7.5, T = 70 ⁰C*

The microwave heating has proven to be effective only at very small initial concentrations of silver when the reaction rate is low.

3.3. Particle size

Measurements of the obtained nanoparticles size were carried out via TEM analysis. Fig. 10 shows the image of particles obtain in experimental condition of P3, i.e. MR = 0.05 and silver concentration 0.01 mmol/L after 15 min reaction time at T = 40 ⁰C. TEM images show nanoparticles with average diameter of 20 nm, polymorphic crystal structure and nearly spherical shape.
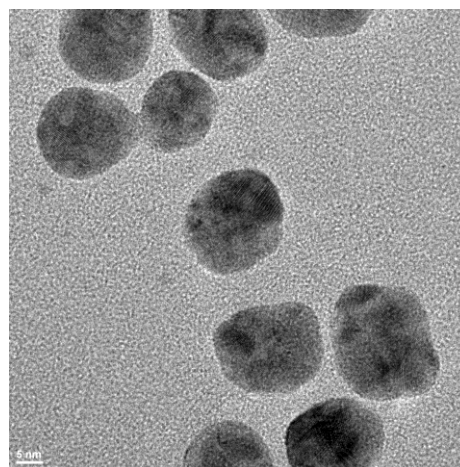

Fig. 10. TEM image of formed silver nanoparticles Microwave synthesis P3, MR = 0.05, silver concentration 0.01 mmol/L after 15 min reaction time at T = 40 ⁰C

The HRTEM analysis together with EDAX and EELS shows the existence of distinct particles of controlled size and shape. Tannic acid proved to be a rapid reduction agent capable of achieving more Ag seeds since the very beginning of the synthesis; this effect was further enhanced by the use of microwave energy which assured a fast and uniform temperature increase of the reaction mixture. A high concentration of Ag seeds from the very beginning of the synthesis prevents the formation of larger nanoparticles and their agglomeration.

The role of tannic acid as a stabilizing agent in the described synthesis is shown by DLS analysis of the sample which shows the average diameter of the silver nanoparticle wrapped in tannic acid – Fig. 11.

When the silver nanoparticles are stabilized by tannic acid the molecule streches away from the nanoparticles. This explains the rather large size distribution measured by DLS. Because DLS measurements are performed on the nanoparticles solution, the diameter of the particle will be measured as two times the thickness of the tannic layer plus the diameter of the actual particle. The result obtained by TEM is still closer to the actual size of particle than that measured by DLS.

The role of the tannic acid is to prevent the agglomeration process of silver nanoparticles by creating a protective layer around the formed nanoparticles.
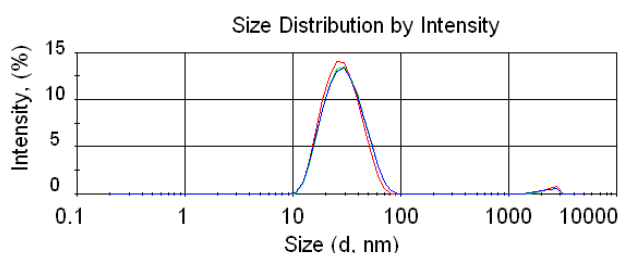

Fig. 11. DLS spectrum of P3 sample, 40 ^{0}C, 15 min, microwave-assisted synthesis

It was established that each molecule of tannic acid is able to act as chelating agents producing a complex atomic reorganization to facilitate the nucleation process. At a molar ratio of 0.05, the tannic acid complex is saturated with 20 silver atoms, which produces a rapid nucleation in a short induction time, hence resulting in the formation of small silver nanoparticles.

The role of tannic acid as an organizer during nucleation is described in the specialized literature by the model Maxwell - Garnett for dielectric mixtures [10].

4. Conclusions

Tannic acid was used as a reducing and stabilizing agent in the synthesis of silver nanoparticles by a simple method, eco-friendly and energetically efficient. The synthesis method assisted by microwaves proved to be much easier and simpler to use than other synthesis methods. Operational parameters are easier to control allowing a high reproducibility of working conditions, thus obtaining a suspension of silver nanoparticles with the same distribution and morphology, two very important parameters for their subsequent applications. By carrying out the nanoparticle synthesis directly in the measuring cell of the spectrophotometer allows for nanoparticles' formation and growth in-situ tracking and optimization. Our further studies will be focused on the use of the obtained suspensions of nanoparticles, mainly in microbiology as additives in the filters used in water treatment, food industry and pharmaceuticals.

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