

Synthesis of silver nanoparticles using agar–agar water solution and femtosecond pulse laser irradiation



Ricardo Almeida de Matos^{a,*}, Thiago da Silva Cordeiro^b, Ricardo Elgul Samad^b,
Letícia Bonfante Sicchieri^b, Nilson Dias Vieira Júnior^b, Lilia Coronato Courrol^{a,b}

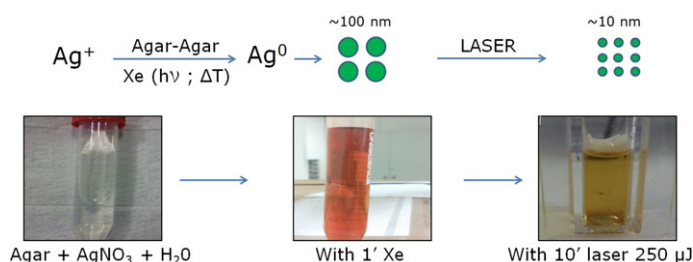
^a Universidade Federal de São Paulo, UNIFESP, São Paulo, Brazil

^b Instituto de Pesquisas Energéticas e Nucleares, IPEN-CNEN/SP, São Paulo, Brazil

HIGHLIGHTS

- ▶ Green synthesis of spherical silver nanoparticles using agar–agar.
- ▶ Reduction of silver nanoparticles diameter by femtosecond pulse laser irradiation.
- ▶ Silver nanoparticles of different sizes.
- ▶ No additives, such as solvents, surfactants or reducing agents were used in the procedure.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 19 October 2012

Received in revised form

22 December 2012

Accepted 22 January 2013

Available online xxx

Keywords:

Silver nanoparticles

Green synthesis

Laser ablation

Femtoseconds

Photolysis

ABSTRACT

We report a method to synthesize silver nanoparticles using an agar–agar solution illuminated by light from a xenon lamp, followed by irradiation by ultrashort laser pulses. Spherical nanoparticles of ~ 100 nm were created by the xenon lamp illumination, and after the ultrashort pulses irradiation their sizes were reduced to under 10 nm. Bideionized water was used as solvent and surfactants or reducing agents were substituted by agar–agar and light, characterizing the process as a “green” synthesis, a completely inoffensive procedure for the environment. The xenon light was used to reduce silver ions (Ag^+) into metallic silver (Ag^0), and the laser irradiation was important to decrease the nanoparticles diameter. The average particles size, size distribution, morphology, and structure were determined by dynamic light scattering (DLS), transmission electron microscopy (TEM), energy-dispersive X-ray spectroscopy (EDX) and UV/visible absorption spectrophotometry.

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

Metallic nanoparticles have attracted much attention because of their special properties and potential applications, which result mostly from its large surface area and the surface plasmon resonance (SPR) effect (collective oscillation of surface electrons).

* Corresponding author at: Instituto de Ciências Ambientais, Químicas e Farmacêuticas (ICAQF), Departamento de Ciências Exatas e da Terra (DCET), Universidade Federal de São Paulo (UNIFESP) - campus Diadema, Rua Prof. Artur Riedel, 275 CEP 09972-270 - Diadema, SP, Brazil. Tel.: +55 11975528962.

E-mail address: ricardoam7@gmail.com (R.A.d. Matos).

Silver nanoparticles [1,2] present a strong bactericidal effect and are known to be powerful antibiotics [3,4], besides being used in anticancer [5] and antiviral [6–9] therapies.

Many alternatives methods have been employed to synthesize silver nanoparticles, but the most common used is the chemical reduction, which requires a precursor (silver nitrate), stabilizers and reducing agents [10]. Several non toxic reducing agents such as potassium bitartrate [10], ascorbic acid [11], sodium citrate [12], or toxic ones as hydrazine [13] and polyethylene glycol [14] (toxic in monomer form), can be used. Smaller nanoparticles are formed with a strong reducing agent [15]. The development of “green” techniques is of the highest importance, mainly to avoid the use of toxic

stabilizer/reducing agents [16]. Laser photolysis [17] is an alternative to chemical processes for the production of nanoparticles, and the exposure of silver nanoparticles to femtosecond laser radiation largely reduces the average size of nanoparticles [18–20]. Yao-Yu Cao et al., [21] have succeeded in fabricating silver structures smaller than 200 nm by means of a multiphoton-induced reduction technique combined with the inhibition of unwanted metallic particle growth using surfactants. Nakamura et al., [22] fabricated Ag nanoparticles using a highly intense optical field produced by focused femtosecond laser pulses in a silver nitrate solution. They proposed that solvated electrons and hydrogen radicals, which are strong reducing agents, are produced from water molecules under ultrashort laser irradiation. However, Nakamura et al. [21] observed that the use of polyvinylpyrrolidone (PVP) as reducing agent suppressed crystal growth and agglomeration during this process. They concluded that addition of PVP reduces the particle size and makes the size distribution narrower.

So, in this work, a technique for synthesizing silver nanoparticles is reported, in which, instead of toxic chemical polymers (as PVP), only the natural polymer agar-agar and Xe light are used. Agar-agar can be defined as a hydrophilic colloid [23] extracted from certain seaweeds of the *Rhodophyceae* class. It is a mixture of polysaccharides whose basic monomer is galactose.

The purpose of this study was to synthesize silver nanoparticles by photolysis induced by ultrashort laser pulses, using agar-agar as stabilizing medium. The influences of the xenon lamp irradiation time and laser irradiation parameters were studied. The relevant mechanisms contributing for the silver nanoparticles production are discussed.

2. Materials and methods

All the reagents used in this study had analytical grade. Silver nitrate (AgNO_3), and commercial agar-agar polysaccharide standard agar-agar (A-7002) were purchased from Sigma-Aldrich.

A concentration variation study of the silver nitrate and agar-agar aqueous solution was carried out, and the best results were found when 30 mg of AgNO_3 were mixed with 250 mg of agar-agar in 100 ml of bideionized water. This process was accompanied by vigorous stirring for 5 min, and the resulting solution was illuminated by a xenon lamp (Cermax 400 Watts, not focused and placed at 10 cm from the sample reservoir) for 30 s. The UV photons from the Xe lamp broad emission (ranging from 185 nm to 2000 nm) convert the silver nitrate to metallic silver, which aggregates into nanoparticles. Simultaneously to this reduction, the solution heating induced by the IR spectrum of the lamp, enhances the aggregation process toward the formation of larger silver clusters. This process was repeated for 1 and 2 min of illumination.

The solution exposed to xenon for 1 min was irradiated with ultrashort pulses from an amplified Ti: Sapphire laser system (Femtopower Compact Pro). The pulses were centered at 785 nm, with duration of 40 femtoseconds (FWHM), and a repetition rate of 1 kHz. The laser beam was focused by a 25 mm converging lens inside a 1 cm acrylic cuvette containing the solution (Fig. 1). The intensity at the focus was estimated to be $\sim 10^{14} \text{ W cm}^{-2}$. Seven different irradiations were done on samples previously exposed to xenon for 1 min. In the first three, the pulse energy was kept constant at 250 μJ , and the irradiation times were 1, 5 and 10 min. The four remaining solutions were irradiated for 3 min each, and the pulse energies were 100, 150, 200 and 250 μJ .

UV-vis absorption spectra were measured by a Varian Cary 17D spectrophotometer, using 1 cm quartz cells.

The synthesized silver nanoparticles were characterized by a dynamic light scattering (DLS) using a Zeta Plus analyzer (Brookhaven).

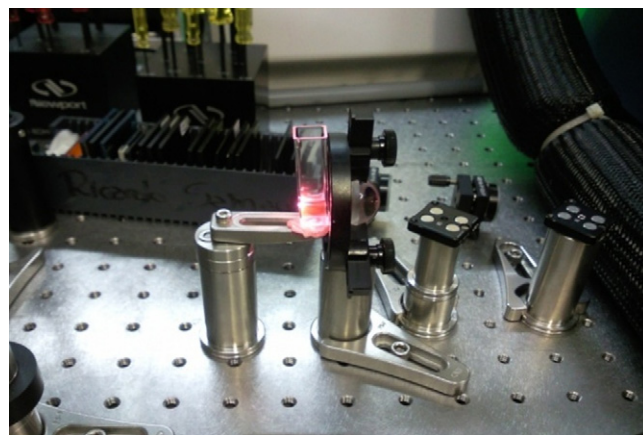


Fig. 1. Laser irradiation setup.

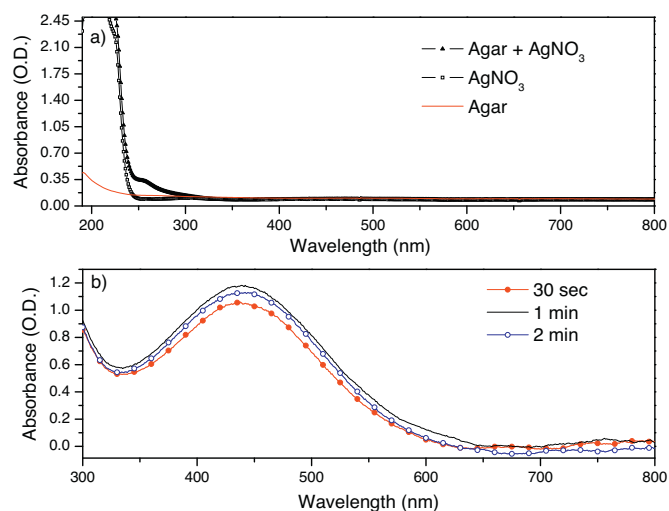


Fig. 2. (a) Absorption spectra of agar water solution, AgNO_3 water solution and agar mixed with AgNO_3 water solution; (b) influence of Xenon lamp illumination time on the absorption spectra of agar mixed with AgNO_3 water solution, measured for 30 s, 1 and 2 min illumination.

The elemental analysis was performed in the Energy Dispersive X-ray Spectroscopy using an EDX-900 Shimadzu.

The samples were observed in a transmission electron microscope (TEM, JEOL JEM- 200C) in the Materials Science and Technology Center of IPEN-CNEN/SP. For the measurements a drop of the silver nanoparticles solution, dispersed in bideionized water, was placed onto a carbon-coated copper grid. The excess liquid was removed using a paper wick and the deposit was dried in air prior to imaging.

3. Results and discussion

The absorption spectra of the agar-agar, AgNO_3 and agar-agar with AgNO_3 solutions are shown in Fig. 2a, and all solutions exhibit absorption bands only in the ultraviolet range. Fig. 2b displays the absorption spectra of agar with AgNO_3 solutions after illumination by the xenon lamp for 30 s, 1 and 2 min, and it can be observed that an 440 nm centered band appeared in all solutions, with higher absorbance intensity for the 1 min illuminated solution. These absorption band correspond to the surface plasmon resonances (SPR), which are collective oscillations of surface free electrons [1] in the potential well defined by the metallic nanoparticle size [24,25].

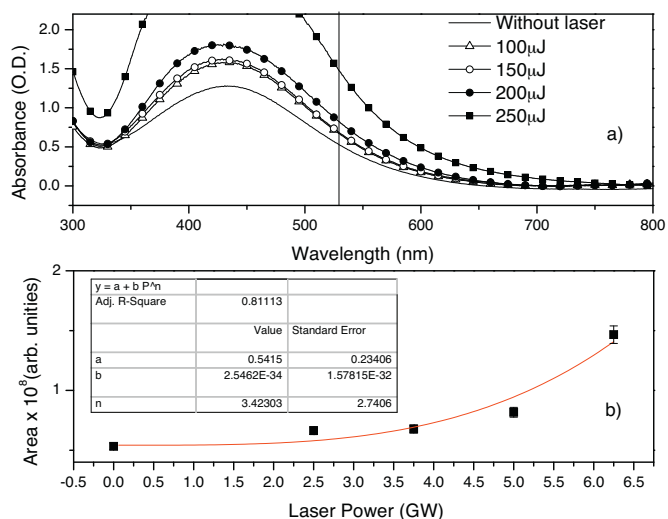


Fig. 3. Influence of laser power. (a) The absorption spectra of the AgNP solutions measured before and after laser irradiation with 100, 150, 200 and 250 μJ pulse energies for three minutes irradiation. (b) Absorbance (around 530 nm) in a function of laser power.

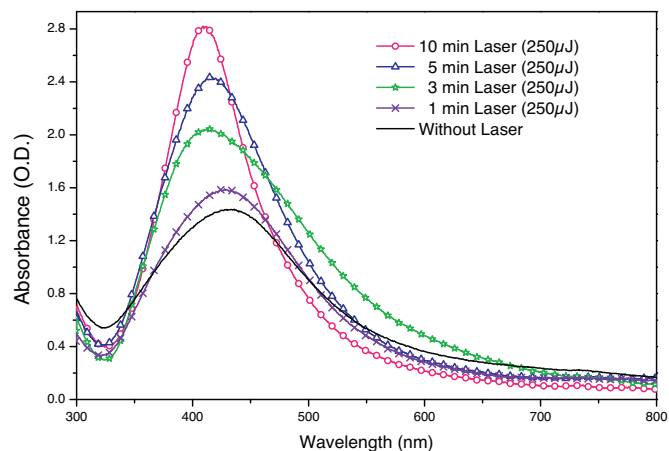


Fig. 4. Influence of laser irradiation time on the absorption spectra of AgNP (laser irradiation with 250 μJ pulse energy, for 1, 3, 5 and 10 min).

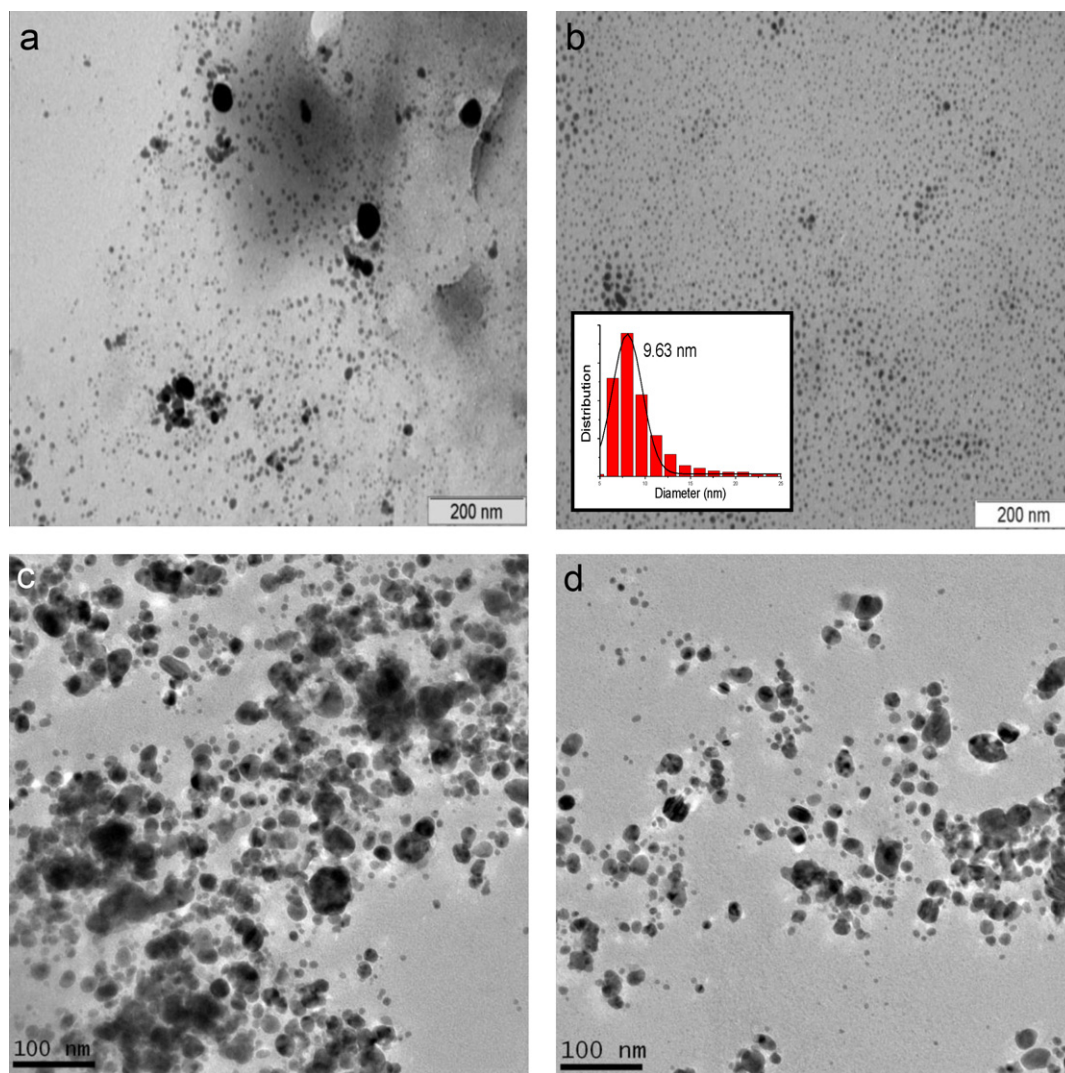


Fig. 5. Micrographies (TEM) of silver nanoparticles solutions irradiated with (a) 1 min Xe light. (b) 1 min Xe light and laser 250 μJ for 10 min. (c) 1 minute Xe light and laser 100 μJ for 3 min, (d) 1 min Xe light and laser 200 μJ for 3 min.

As observed in the Fig. 2a, an aqueous solution of AgNO_3 and agar-agar does not promote ionic silver reduction (if an aqueous AgNO_3 solution is illuminated by a Xe lamp, the Ag^+ is not reduced). However, when this first solution is illuminated by the Xe lamp radiation, the ionic silver is reduced and form nanoparticles (Fig. 2b). In this case a UV photoinduced reaction, that occurs only in the presence of agar-agar, is promoted, leading to the production of neutral silver atoms. The reduction potential of silver ($\text{Ag}^+ + 1e^- \rightarrow \text{Ag}^0$) is 0.8 V, and to reduce silver is necessary to provides electrons by a reduction agent that has a reduction potential smaller than 0.8 V. The agar-agar polymer can provide electrons, but since it's reducing potential is higher than silver's, nanoparticles are not formed in the aqueous agar-agar solution. The Xe lamp light interacts with the agar-agar polymer, increasing its energy and temperature, causing changes that facilitate the redox reaction with the ionic silver and the formation of silver nanoparticles. The reduction of Ag^+ is a photoinduced reaction.

Simultaneously, the illumination heats the solution. The presence of several silver atoms, formed upon the reduction of several Ag^+ ions, enhances the aggregation process toward larger silver clusters. The agar-agar suppresses the nanoparticles growth and agglomeration, limiting the particles size and narrowing its distribution. An ice-water bath could be used to avoid the aggregation process, but the initial aggregation by heat process is necessary to create the initial clusters and polycrystals.

The absorption spectra of the solutions illuminated by the xenon lamp for 1 min, followed by laser irradiation with 100, 150, 200 and 250 μJ pulses for 3 min are shown in Fig. 3a. An evident increase in the absorbance is observed, following the laser energy increment, showing that laser irradiation promotes the production of silver nanoparticles. The absorbance at 530 nm is plotted as a function of the laser power in Fig. 3b. The data is fitted by an $I \propto P^n$ law, where n is the order of the process. The exponent obtained by this curve fitting shown in Fig. 3b has the value 3.4, revealing a mixture of three and four photons processes (the laser emits at 785 nm or 1.58 eV, so three photons correspond to 4.71 eV or 263 nm, and four photons to 6.28 eV or 197 nm).

Fig. 4 presents the absorption spectra of the solutions irradiated with 250 μJ femtosecond pulses and different exposure times (1, 3, 5 and 10 min). As can be seen, longer irradiation times result in higher absorbance intensities. The plasmon peak position and width depend on the extent of colloid aggregation [26]. The blue shift of the SPR band and width reduction that occur after laser irradiation indicate a decrease in the size of the nanoparticles and a more homogeneous silver nanoparticles (AgNNP) size distribution. This decrease narrows the potential well that trap free electrons,

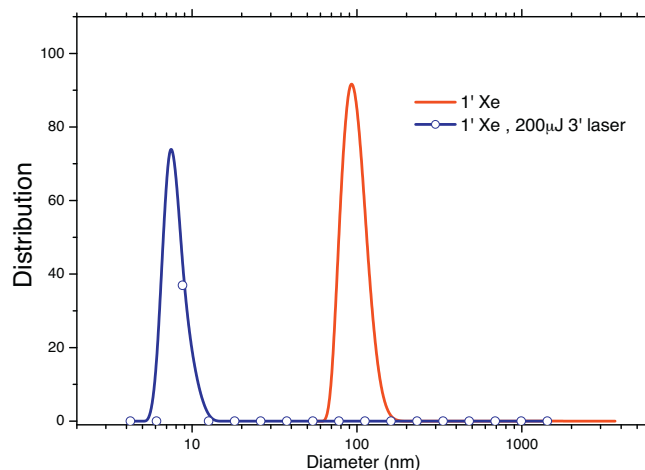


Fig. 6. Particle size distribution before (continuous red line) and after (blue lines with open circles) irradiation by 200 μJ laser pulses for 3 min obtained from dynamic light scattering (DLS). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article).

reducing the allowed oscillating modes, increasing their density in the colloidal silver particles, which results in the SPR blue shift [27].

The silver nanoparticles production with laser irradiation without previous xenon irradiation is very inefficient. The ultrashort pulse duration minimizes heat transfer to the target and the high intensities attainable produce large ionizations that lead to material modifications. This means that ultrashort pulses reduce Ag^+ ions, but the aggregation process toward larger silver clusters does not occur. When used to reduce the silver ions, laser pulses also break the agar-agar structure that encapsulates silver nanoparticles.

A TEM micrograph of the particles obtained after illumination by xenon lamp for 1 minute is show in Fig. 5a. This figure shows that xenon illumination is sufficient to induce the formation of silver nanoparticles. Fig. 5b–d shows micrographies obtained after laser irradiation (250 μJ for 10 min, 100 and 250 μJ for 3 min, respectively), evidencing the presence of spherical particles and confirming the reduction in size by the laser irradiation. The optimal condition is that shown in Fig. 5b (1 min Xe light followed by 250 μJ laser pulses for 10 min), producing particles with an average diameter of 9.63 nm and more than 85% of particles in the range of 6–10 nm.

The particle size distributions were measured by DSL, and the results are shown in Fig. 6. The average size of the particles after

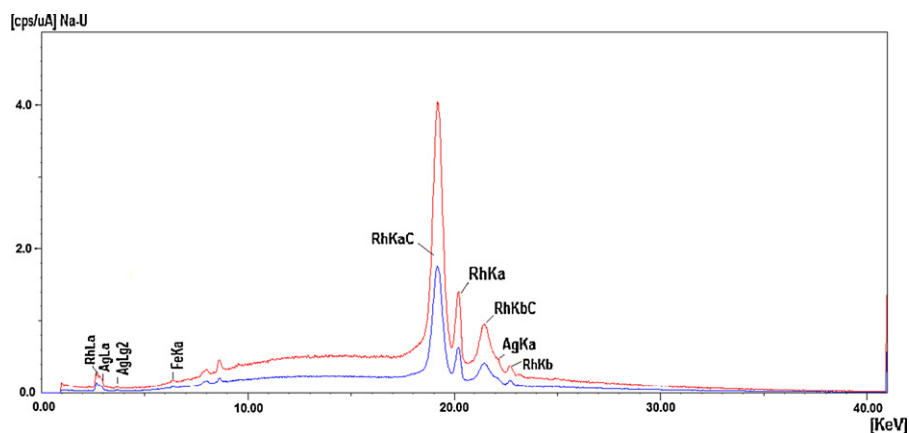


Fig. 7. Energy-dispersive spectroscopy spectrum of silver nanoparticles prepared using 1 min Xe light without (blue) and with (red) 200 μJ laser pulses irradiation for 3 min. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article).

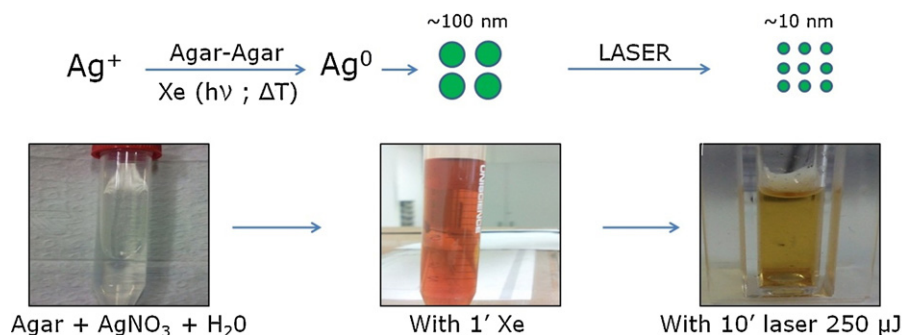


Fig. 8. Silver nanoparticles production.

1 min irradiation by Xe lamp was approximately 100 nm, which was decreased to less than 10 nm after laser irradiation with 200 μ J pulses for 3 min.

The elemental analysis of the silver nanoparticles was performed using EDX. Fig. 7 shows the EDX spectrum of the spherical nanoparticles prepared by 1 min Xe light (blue) and 200 μ J laser pulses for 3 min (red). The peaks around 2.98 keV, 3.68 keV and 22 keV correspond to the binding energies of AgLa, AgLg2 and AgKa, respectively, while the peak situated at 6.38 belong to FeKa present in the agar–agar solution. The other peaks observed in the spectra belong to the standard used in the experiment. Throughout the scanning range of binding energies, no obvious impurity peak was detected. The result indicates that the synthesized product is composed of high purity Ag nanoparticles. Similar EDX spectra were obtained for each sample analyzed.

Based on the presented results, we propose that the production of metallic nanoparticles in the mixture of AgNO₃ and agar–agar water solution occurs according to the following steps (Fig. 8):

(1) The Xe lamp illumination induces the reduction of ionic silver to metallic form, while heating the solution; (2) the silver atoms condense into clusters; (3) due to thermal diffusion, the clusters aggregate to form polycrystals; (4) the galactose in agar–agar encapsulates the silver nanoparticles, preventing aggregation into bigger clusters, leading to the production of nanoparticles with sizes between 20 and 100 nm. (5) Laser irradiation induces fragmentation via multiphoton processes on Ag clusters [28,29] resulting in the production of nanoparticles with sizes between 5 and 20 nm.

4. Conclusions

The synthesis of silver nanoparticles occurred satisfactorily, proving the efficiency of the methodology (easy, quick and without environmental damage). Silver nanoparticles were created by mixing the non-toxic agar–agar aqueous solution with silver nitrate and an enhancement in the plasmon resonance absorption was observed with illumination by xenon light for 1 min. Femtosecond laser pulse irradiation of agar–agar silver nanoparticles promotes multiphotonic processes that induces fragmentation and the reduction of the nanoparticles to sizes between 5 and 20 nm (the samples were stored at room temperature and were stable for many months).

The novelties presented here are the possibility to use an environmentally friendly encapsulating agent, the agar–agar, the use

of Xenon lamp as reducing agent to increase the number of particles produced, and the ultrashort pulses interaction that allows the use of the laser parameters such as energy, irradiation time and repetition rate to control the particle sizes.

Acknowledgements

The authors would like to thank Nildemar Aparecido M. Ferreira for the electron microscope analysis, Marcos Hortelani for EDX measurements, Prof. Dr. Cristiano Luis Pinto de Oliveira for DLS measurements and CNPq for the financial support.

References

- [1] A.J. Haes, S.L. Zou, G.C. Schatz, R.P. Van Duyne, *J. Phys. Chem. B* 108 (2004) 109.
- [2] Z.P. Zhang, M.Y. Han, *Chem. Phys. Lett.* 374 (2003) 91.
- [3] N. Duran, P.D. Marcato, R. De Conti, O.L. Alves, F.T.M. Costa, M. Brocchi, *J. Brazil Chem. Soc.* 21 (2010) 949.
- [4] C. Marambio-Jones, E.M.V. Hoek, *J. Nanopart. Res.* 12 (2010) 1531.
- [5] M. Rahban, A. Divsalar, A.A. Saboury, A. Golestani, *J. Phys. Chem. C* 114 (2010) 5798.
- [6] L. Lu, R.W.Y. Sun, R. Chen, C.K. Hui, C.M. Ho, J.M. Luk, G.K.K. Lau, C.M. Che, *Antiviral Ther.* 13 (2008) 253.
- [7] J.K. Gour, A. Srivastava, V. Kumar, S. Bajpai, H. Kumar, M. Mishra, R.K. Singh, *Dig. J. Nanomater. Bios.* 4 (2009) 495.
- [8] V.K. Khanna, *Defence Sci. J.* 58 (2008) 608.
- [9] T. Vo-Dinh, H.N. Wang, J. Scaffidi, *J. Biophoton.* 3 (2010) 89.
- [10] J.E. Lee, J.W. Kim, *Colloid Polym. Sci.* 282 (2004) 295.
- [11] L. Suber, I. Sondi, *J. Colloid Interface Sci.* 288 (2005) 489.
- [12] D.V. Sondi, E. Goia, *J. Colloid Interface Sci.* 260 (2003) 75.
- [13] D.D. Evanoff, G. Chumanov, *J. Phys. Chem. B* 108 (2004) 13948.
- [14] C. Ducamp-Sanguesa, R. Herrera-Urbina, et al., *J. Solid State Chem.* 100 (1992) 272.
- [15] S.N. Lakshmi, T.L. Cato, *J. Biomed. Nanotechnol.* 3 (2007) 301.
- [16] V.K. Sharma, R.A. Yngard, Y. Lin, *Adv. Colloid Interface Sci.* 145 (2009) 83.
- [17] A. Pyatenko, M. Yamaguchi, M. Suzuki, *J. Phys. Chem. B* 109 (2005) 21608.
- [18] G.A. Shafeev, E. Freysz, F. Bozon-Verduraz, *Appl. Phys. A* 78 (2004) 307.
- [19] R.A. de Matos, T.S. d. Cordeiro, R.E. Samad, N.D. Vieira, L.C. Courrol, *Colloids Surf. A* 389 (2011) 134.
- [20] R.A. de Matos, T.S. d. Cordeiro, R.E. Samad, N.D. Vieira Jr, L.C. Courrol, *Appl. Phys. A-Mater. Sci. Proc.* 109 (2012) 737.
- [21] Y.-Y. Cao, N. Takeyasu, T. Tanaka, X.-M. Duan, S. Kawata, *Small* 5 (2009) 1144.
- [22] T. Nakamura, H. Magara, Y. Herbani, S. Sato, *Appl. Phys. A-Mater. Sci. Proc.* 104 (2011) 1021.
- [23] E. Gomez-Ordóñez, P. Ruperez, *Food Hydrocolloid* 25 (2011) 1514.
- [24] A. Politano, G. Chiarello, *Surf. Rev. Lett.* 16 (2009) 171.
- [25] S.L. Zhu, Y.Q. Fu, *Biomed. Microdev.* 11 (2009) 579.
- [26] S.L. Smith, K.M. Nissamudeen, D. Philip, K.G. Gopchandran, *Spectrochim. Acta A* 71 (2008) 186.
- [27] L. Rivas, S. Sanchez-Cortes, J.V. Garcia-Ramos, G. Morcillo, *Langmuir* 17 (2001) 574.
- [28] T. Hirakawa, P.V. Kamat, *J. Am. Chem. Soc.* 127 (2005) 3928.
- [29] H. Fujiwara, K. Sasaki, *J. Appl. Phys.* 86 (1999) 2385.