Using femtosecond lasers to modify sizes of gold nanoparticles

Thiago da Silva Cordeiro[b], Ricardo Almeida de Matos[a], Flávia Rodrigues de Oliveira Silva [b], Nilson Dias Vieira Jr. [b], Lilia Coronato Courrol[a,b] , Ricardo Elgul Samad[b]
[a] Universidade Federal de São Paulo, UNIFESP, São Paulo, Brazil
[b] Instituto de Pesquisas Energéticas e Nucleares, IPEN-CNEN/SP, São Paulo, Brazil

ABSTRACT

Metallic nanoparticles are important on several scientific, medical and industrial areas. The control of nanoparticles characteristics has fundamental importance to increase the efficiency on the processes and applications in which they are employed. The metallic nanoparticles present specific surface plasmon resonances (SPR). These resonances are related with the collective oscillations of the electrons presents on the metallic nanoparticle. The SPR is determined by the potential defined by the nanoparticle size and geometry.

There are several methods of producing gold nanoparticles, including the use of toxic chemical polymers. We already reported the use of natural polymers, as for example, the agar-agar, to produce metallic nanoparticles under xenon lamp irradiation. This technique is characterized as a "green" synthesis because the natural polymers are inoffensive to the environment.

We report a technique to produce metallic nanoparticles and change its geometrical and dimensional characteristics using a femtosecond laser. The 1 ml initial solution was irradiate using a laser beam with 380 mW, 1 kHz and 40 nm of bandwidth centered at 800 nm.

The setup uses an Acousto-optic modulator, Dazzler, to change the pulses spectral profiles by introduction of several orders of phase, resulting in different temporal energy distributions. The use of Dazzler has the objective of change the gold nanoparticles average size by the changing of temporal energy distributions of the laser pulses incident in the sample. After the laser irradiation, the gold nanoparticles average diameter were less than 15 nm.

Keywords: metallic nanoparticles, gold nanoparticles, femtosecond lasers, plasmon resonances, dispersive filter, nanoparticles production, nanoparticles irradiation, nanoparticles fragmantation.

1. INTRODUCTION

Nowadays, the study of metallic nanoparticles proprieties is important to several areas, including medical[1], scientific[2] and industrial applications[3]. This is the main reason that motivates the scientists to study its proprieties.

There is some techniques to produce metallic nanoparticles, but the most of these approaches uses chemical product on the production process that are pollutants to the environment[4]. To avoid environment damage, new green techniques have been developed, using eco-friendly materials and photochemical reduction [5-7].

Metallic nanoparticles exhibit properties dependent of its relation between superficial area and its volume[8-11]. This fact show the need of control the nanoparticles geometrical and dimensional characteristics, because several experiments and applications are dependent of these metallic nanoparticles sizes and shapes.

Ultrashort pulses have been use to control sizes and shapes of metallic nanoparticles in water solutions[12] and the irradiation of these colloidal solutions has the objective of promotes the selective excitation of resonant surface plasmons[8, 13-16], using specific wavelengths[17], and to fragment the conglomerates through the Coulom explosion[18-21], creating smaller fragment disposes on clusters, in a mechanic ablation mechanism. Femtosecond lasers with pulses with large bandwidth and high power are used to control several processes in physics where is necessary high fluencies, materials research and processing, plasmas, medicine and so on[22-26].

When the laser pulses reaches the solute, the nanoparticles can be evaporated, or fragmented, because of the Coulomb explosion as consequence of plasma dynamics. The colloid formed contain nanoparticles with specific sizes and shapes, dependent on radiation characteristics. This shows the importance of coherent control of phase characteristics of the

Nanophotonics VI, edited by David L. Andrews, Jean-Michel Nunzi, Andreas Ostendorf, Proc. of SPIE
Vol. 9884, 988439 · © 2016 SPIE · CCC code: 0277-786X/16/$18 · doi: 10.1117/12.2227759

incident pulses from the laser, because the specific selected plasmon excitation wavelength become possible the ensemble of metallic nanoparticles[17, 27].

In this paper it is demonstrated that the gold nanoparticles with different sizes and shapes production can be produced with different pulse energy distributions or changing the solution characteristics[28]. Therefore, the change of time irradiation and the concentration of the samples may influence on the average energy delivered to the clusters of gold nanoparticles.

2. EXPERIMENTAL

2.1. The femtosecond laser system

For the experiments it was used a CPA (Chirped Pulse Amplification) system, Figure 1, composed by a Ti:Saphire seeder (Mira, Coherent) with 550 mW and 78 MHz with pulses of 54 fs and 40 nm of bandwidth. There is a multistep Ti:Saphire amplifier (Odin, Quantronix) is pumped by a Nd:YLF 2ω laser, with 196 ns pulses and 18W of power (Falcon, Quantronix).

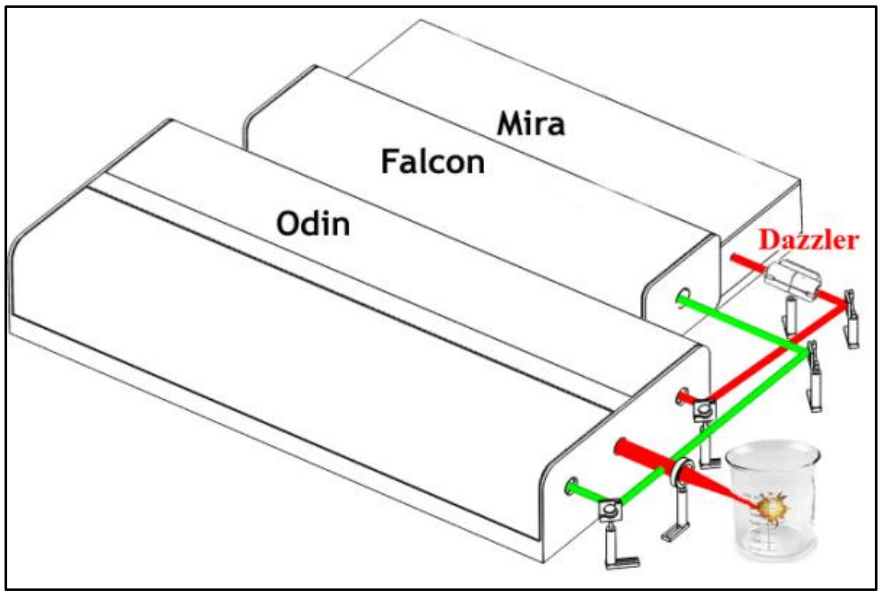

Figure 1. System components: Seeder laser Mira, Pump laser Falcon and Odin amplifier

The amplified beam on the Odin exit has pulses with 40 nm of bandwidth and approximately 36 fs FWHM, reaching 650 μJ of energy (Figure *2*). The repetition rate was 1 kHz and the pulses are centered at 800 nm. A 50 mm lens focused the beam in a gold nanoparticles solution localized inside of a cuvette with 10 mm of optical path.

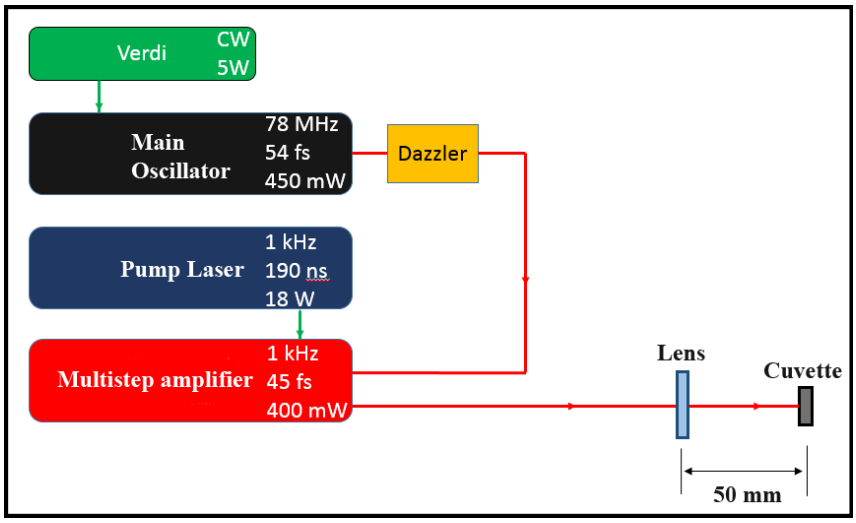

Figure 2. Complete laser system setup

2.2. The AOPDF (Acousto-optic programmable dispersive filter) system

To control the phase introduced on femtosecond pulses, used on the irradiations and decrease the pulse duration through the correction of laser residual second and third orders on phase, it was used a commercial AOPDF called Dazzler, from Fastlite, shown on Figure *3*. This filter uses an electric controlled piezo, to generate acoustic waves inside of a birefringent crystal of TeO_2. The frequency and the amplitude of acoustic waves can be controlled. It becomes possible to emulate a diffraction grating through the length of the crystal. This diffraction grating has different distances between the grooves and, therefore, each wavelength of the incident pulse, travels different distances inside the crystal, before it be disperse to another axis of propagation.

Figure 3. Fastlite Dazzler. Figure extracted of equipment manual.

3. METHODS

3.1. The measurement system

The Figure 4 shows the measurement setup. A 50 mm converging lens focuses the beam into a 1 cm optical path quartz cuvette. The position of cuvette was 1 mm sideways changed, every minute with a micrometer, to avoid the sludge accumulation on the entrance face of cuvette, as consequence of the laser incidence on samples.

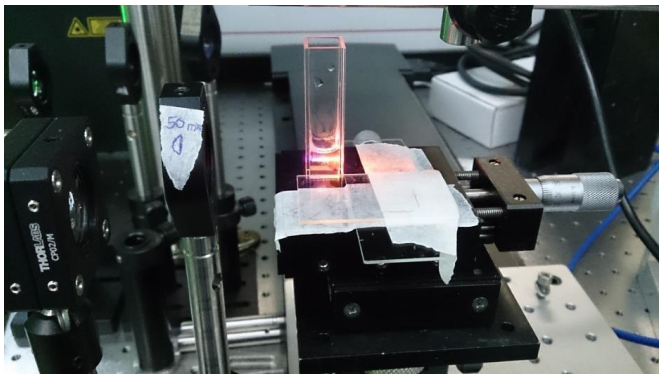

Figure 4. Irradiation setup

The use of Dazzler has the objective of change the gold nanoparticles average size, by the changing of temporal energy distributions of the laser pulses incident in the sample, as shown on Figure 5. This approach allows correcting the residuals third order phase components on the ultrashort pulses and decrease its duration. The result are pulses with approximately 43 fs FWHM.

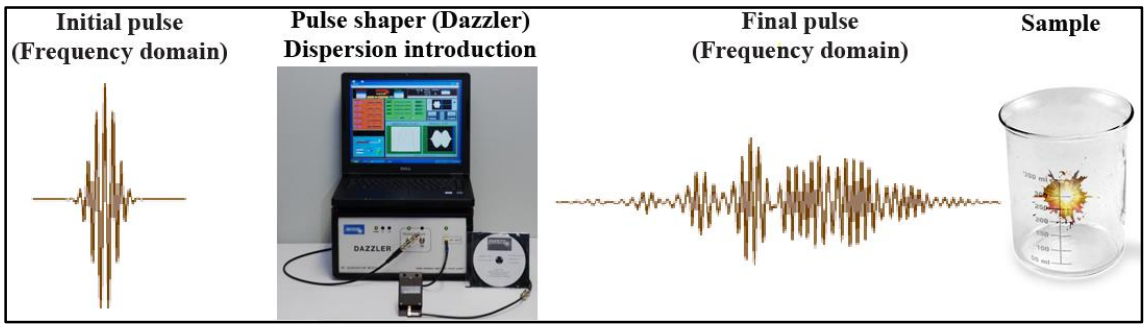

Figure 5. Dazzler change the pulses on the frequency, and consequently, on the time domain, changing the energy distribution incident on gold nanoparticles samples.

To measure the absorption spectra it was used a stabilized light from Ocean Optics model HL2000 and a source Czerny-Turner spectrometer (CCS 200 Thorlabs) and an optical fiber with 400 um of core.

3.2. The samples

The samples were produced with analytical grade. Agar-agar polysaccharide (A-7002) and the Chloroauric acid (HAuCl4) were purchased from Sigma-Aldrich.

The 150mg of agar-agar was diluted in 100 ml of distilled water at 70 °C, mixed with 30 mg of $HAuCL_4$, shacked for 5 minutes in a vortex and exposed to intense non-focused xenon lamp (*Cermax* with 300 Watts) light source, positioned at 10 cm from the sample.

After the gold nanoparticles production, the samples were irradiated by the laser pulses with 430 μJ and 40 nm bandwidth FWHM, centered at 800 nm, with approximately 43 fs. The pulses from seeder Mira were modified by the AOPDF to obtain pulses with the minimum experimental duration possible for the system. The residual third order phase component was minimized. It was added second order phase component values to decrease the pulse duration to close to Fourier Limited Transform value.

After diffracted by the Dazzler, the pulses were amplified by the Odin, and then, it goes to a lens to focalize it in the samples. The intensity promote non-linear phenomenon and high levels of pressure. The consequence is the ignition of the plasma into the sample generating high ionic temperatures. Occurs the Coulomb explosion as consequence of the ejection of the electron from the material and the charge of the nucleus of the atoms. This phenomenon fragmentizes the clusters of gold nanoparticles decreasing its sizes and it is highly dependent to the time energy delivery to the nanoparticles.

We made two experiments to observe the influence of the femtosecond laser irradiation on gold nanoparticles solutions. The first experiment was the change of the total time of irradiation (1, 2, 3, 5, 10, 20 and 30 minutes). The measurements used 1 ml of nanoparticles gold solution.

4. RESULTS

4.1. Irradiation Time

The results obtained after irradiating samples by (1, 2, 3, 5, 10, 20 and 30 minutes) are shown at Figure 6. Visually no color changes can be observed in the samples.

Figure 6. Gold nanoparticles irradiated for different times. From the left to the right: non irradiated and irradiated by, respectively, 1, 2, 3, 5, 10, 20 and 30 minutes.

The First Moment of absorption spectra, as function of irradiation times, are shown at Figure 7. For the times relatively shorts, ~ 3 minutes, the gold nanoparticles in solution was the smaller possible. After these values, the nanoparticles starting to agglomerate in higher clusters because of the heating of the samples in the region of focalization.

The local heating induced by laser on the sample, for very short time, initiates the process of Ostwald ripening[29]. The Ostwald ripening is a process where occurs the nanoparticle grows through the diffusion-coalescence dynamics[30-32]. The literature argues the increasing of temperature on the solvent and the rise of nanoparticles kinetic energy facilitates to overcome electrostatic repulsive forces the nanoparticles[33]. This complex process becomes possible the nanoparticles growth and occurs at millisecond and second scale.

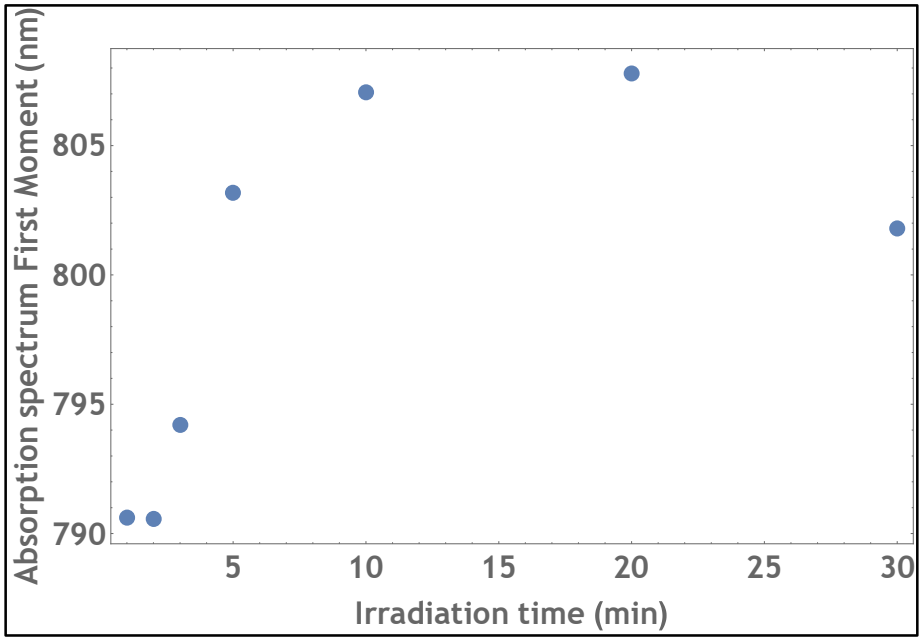

Figure 7. First Moment of Relative absorption spectra as function of Irradiation time for 1, 2, 3, 5, 10, 20 and 30 minutes.

4.2. Gold sample concentration

The influence of the solution concentration and the time of irradiation in the nanoparticles sizes was studied.

The top Figure *8* shows the samples irradiated by the laser with the different dilutions. The sample non irradiated is shown on First tube at left on the top of the figure. The other tubes contain the solution of nanoparticles diluted in water. The second tube contain 10% of original sample of nanoparticles and 90% of water. The other tubes have 20%, 30%, 40%, 50%, 60%, 80% and 100%, respectively, of nanoparticles sample. The water quantity is the complementary value at each case, i. e., 80%, 70%, 60%, 50%, 40%, 20% and 0%, respectively. On the bottom of the figure, the samples irradiated were diluted to be measured by the spectrometer and avoid the equipment signal saturation. The color changing is evident, showing the macroscopic effect of laser irradiation on the samples, and it is an indicator of gold nanoparticles dimensional and geometric change.

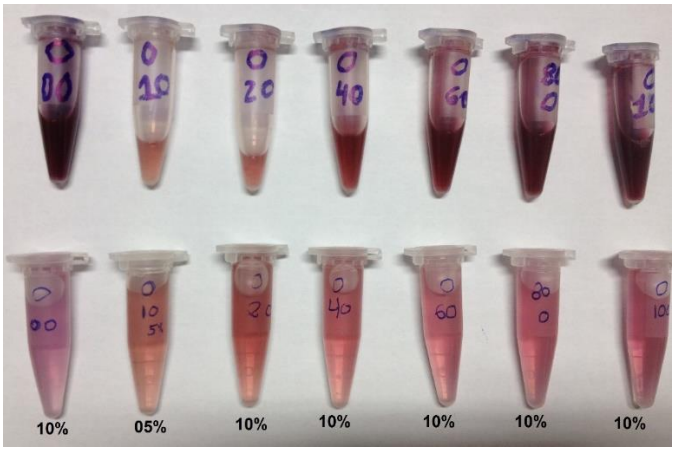

Figure 8. On the top: Samples with different dilutions irradiated by femtosecond laser for 5 minutes. On the bottom: samples diluted to 10 % to measure its absorbance spectra.

The Figure 9 shows the SPR gold nanoparticles peak position as function of sample concentration, using the First Moment Method. If x_i and y_i are the coordinates to each element of area measured, the First Moment of the Area, in y and x direction is given by, respectively, equations 1 and 2:

$$\mathrm{Sy} = \sum_{i=1}^{n} x_i \; dA_i = \int_A \; xdA \qquad (1)$$

$$\mathrm{Sx} = \mathrm{A}\bar{y} \sum_{i=1}^{n} y_i \; dA_i = \int_A \; ydA \qquad (2)$$

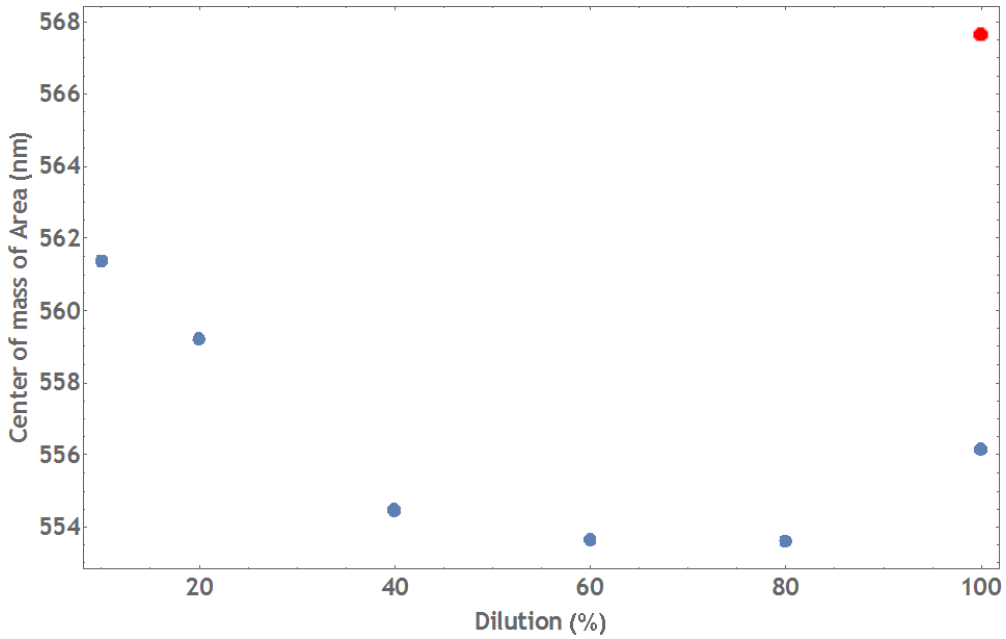

Figure 9. Spectrum peak position, in nm, for different concentrations samples, using the First Moment Method. The red point is the initial sample

The results show the saturation localization in a concentration of 60%, approximately. The initial value for the non-irradiated sample was 550 nm in the Find Extreme algorithm and 561 nm for the First Moment Method.

5. CONCLUSIONS

The results show the importance of laser irradiation control to change the size of clusters containing gold nanoparticles. The best times to obtain smaller nanoparticles were 1 to 3 minutes. After these values, the sizes of nanoparticles increases and show the heating of samples responsible by aggregation of nanoparticles clusters.

The concentration experiment show that is better to dilute the samples containing gold nanoparticles. The best proportion is 40% of water and 60% of gold nanoparticles. These parameters are the ideal condition to the distribution of energy between the gold nanoparticles clusters for obtain the smaller nanoparticles.

The nanoparticles growth it was observed as consequence of ripening kinetics process caused by the heating of the solvent and the increase of nanoparticles kinetic energy.

6. ACKNOWLEDGEMENTS

The authors thanks the FAPESP (2013/26113-6), Capes and CNPq agencies for the structural and financial support for this work.

7. REFERENCES

[1] X. Huang, P. K. Jain, I. H. El-Sayed *et al.*, "Gold nanoparticles: interesting optical properties and recent applications in cancer diagnostic and therapy," Nanomedicine, 2(5), 681-693 (2007).

[2] R. M. Amin, M. B. Mohamed, M. A. Ramadan *et al.*, "Rapid and sensitive microplate assay for screening the effect of silver and gold nanoparticles on bacteria," Nanomedicine, 4(6), 637-643 (2009).

[3] S. E. Skrabalak, J. Chen, Y. Sun *et al.*, "Gold Nanocages: Synthesis, Properties, and Applications," Accounts of Chemical Research, 41(12), 1587-1595 (2008).

[4] M. G. Warner, G. L. Succaw, and J. E. Hutchison, "Solventless syntheses of mesotetraphenylporphyrin: new experiments for a greener organic chemistry laboratory curriculum," Green Chemistry, 3(6), 267-270 (2001).

[5] R. A. de Matos, T. d. S. Cordeiro, R. E. Samad *et al.*, "Synthesis of silver nanoparticles using agar-agar water solution and femtosecond pulse laser irradiation," Colloids and Surfaces a-Physicochemical and Engineering Aspects, 423, 58-62.
[6] H. Z. Huang, and X. R. Yang, "Synthesis of polysaccharide-stabilized gold and silver nanoparticles: a green method," Carbohydrate Research, 339(15), 2627-2631 (2004).
[7] V. K. Sharma, R. A. Yngard, and Y. Lin, "Silver nanoparticles: Green synthesis and their antimicrobial activities," Advances in Colloid and Interface Science, 145(1-2), 83-96 (2009).
[8] Y. Wang, S. K. Eswaramoorthy, L. J. Sherry *et al.*, "A method to correlate optical properties and structures of metallic nanoparticles," Ultramicroscopy, 109(9), 1110-1113 (2009).
[9] J. Zhao, X. Zhang, A. J. Haes *et al.*, [Localized surface plasmon and molecular resonance: fundamental study and application - art. no. 63231B], (2006).
[10] J. H. Hodak, A. Henglein, and G. V. Hartland, "Photophysics of nanometer sized metal particles: Electron-phonon coupling and coherent excitation of breathing vibrational modes," Journal of Physical Chemistry B, 104(43), 9954-9965 (2000).
[11] T. Vo-Dinh, A. Dhawan, S. J. Norton *et al.*, "Plasmonic Nanoparticles and Nanowires: Design, Fabrication and Application in Sensing," Journal of Physical Chemistry C, 114(16), 7480-7488.
[12] R. A. de Matos, T. d. S. Cordeiro, R. E. Samad *et al.*, "Green synthesis of stable silver nanoparticles using Euphorbia milii latex," Colloids and Surfaces a-Physicochemical and Engineering Aspects, 389(1-3), 134-137.
[13] M. D. Malinsky, K. L. Kelly, G. C. Schatz *et al.*, "Nanosphere lithography: Effect of substrate on the localized surface plasmon resonance spectrum of silver nanoparticles," Journal of Physical Chemistry B, 105(12), 2343-2350 (2001).
[14] P. K. Jain, S. Eustis, and M. A. El-Sayed, "Plasmon coupling in nanorod assemblies: Optical absorption, discrete dipole approximation simulation, and exciton-coupling model," Journal of Physical Chemistry B, 110(37), 18243-18253 (2006).
[15] E. Hutter, and J. H. Fendler, "Exploitation of localized surface plasmon resonance," Advanced Materials, 16(19), 1685-1706 (2004).
[16] A. V. Kabashin, M. Meunier, and J. H. T. Luong, "Femtosecond laser ablation of gold in aqueous biocompatible solutions to produce colloidal gold nanoparticles," Photon Processing in Microelectronics and Photonics Ii, 4977, 609-614 (2003).
[17] S. Besner, A. V. Kabashin, and M. Meunier, "Fragmentation of colloidal nanoparticles by femtosecond laser-induced supercontinuum generation," Applied Physics Letters, 89(23), (2006).
[18] A. Podlipensky, A. Abdolvand, G. Seifert *et al.*, "Femtosecond laser assisted production of dichroitic 3D structures in composite glass containing Ag nanoparticles," Applied Physics a-Materials Science & Processing, 80(8), 1647-1652 (2005).
[19] A. Hahn, S. Barcikowski, and B. N. Chichkov, "Influences on Nanoparticle Production during Pulsed Laser Ablation," Journal of Laser Micro Nanoengineering, 3(2), 73-77 (2008).
[20] S. Besner, and M. Meunier, "Femtosecond Laser Synthesis of AuAg Nanoalloys: Photoinduced Oxidation and Ions Release," Journal of Physical Chemistry C, 114(23), 10403-10409.
[21] A. Menendez-Manjon, and S. Barcikowski, "Hydrodynamic size distribution of gold nanoparticles controlled by repetition rate during pulsed laser ablation in water," Applied Surface Science, 257(9), 4285-4290.
[22] K. Konig, "Femtosecond laser application in biotechnology and medicine," Fifth International Symposium on Laser Precision Microfabrication, 5662, 255-267 (2004).
[23] H. Nishiyama, "Femtosecond-laser nanolithography for photonic applications," Journal of Nanophotonics, 3, (2009).
[24] G. Della Valle, R. Osellame, S. Taccheo *et al.*, "Advanced waveguide lasers fabricated by femtosecond laser writing in an Er : Yb-doped phosphate glass - art. no. 64690J," Optical Components and Materials IV, 6469, J4690-J4690 (2007).
[25] T. Juhasz, G. Djotyan, F. H. Loesel *et al.*, "Applications of femtosecond lasers in corneal surgery," Laser Physics, 10(2), 495-500 (2000).
[26] V. V. Lozovoy, and M. Dantus, "Coherent control in femtochemistry," Chemphyschem, 6(10), 1970-2000 (2005).
[27] S. Link, Z. L. Wang, and M. A. El-Sayed, "Alloy formation of gold-silver nanoparticles and the dependence of the plasmon absorption on their composition," Journal of Physical Chemistry B, 103(18), 3529-3533 (1999).

[28] R. A. de Matos, T. d. S. Cordeiro, R. E. Samad *et al.*, "Green synthesis of gold nanoparticles of different sizes and shapes using agar-agar water solution and femtosecond pulse laser irradiation," Applied Physics a-Materials Science & Processing, 109(3), 737-741.
[29] B. Goekce, D. D. van't Zand, A. Menendez-Manjon *et al.*, "Ripening kinetics of laser-generated plasmonic nanoparticles in different solvents," Chemical Physics Letters, 626, 96-101 (2015).
[30] A. Bhakta, and E. Ruckenstein, "OSTWALD RIPENING - A STOCHASTIC APPROACH," Journal of Chemical Physics, 103(16), 7120-7135 (1995).
[31] A. Kabalnov, "Ostwald ripening and related phenomena," Journal of Dispersion Science and Technology, 22(1), 1-12 (2001).
[32] V. P. Zhdanov, "Ostwald ripening of charged supported metal nanoparticles: Schottky model," Physica E-Low-Dimensional Systems & Nanostructures, 71, 130-133 (2015).
[33] S. Jendrzej, B. Goekce, V. Amendola *et al.*, "Barrierless growth of precursor-free, ultrafast laser-fragmented noble metal nanoparticles by colloidal atom clusters - A kinetic in situ study," Journal of Colloid and Interface Science, 463, 299-307 (2016).