

Synthesis of silver nanoparticles by Double Pulse Laser Ablation in liquids

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Silver nanoparticles (Ag NPs) with diameter in the range of 5-10 nm have been produced by laser ablation in liquid (LAL) at atmospheric pressure and room temperature by using the second harmonic (532 nm) of two Nd:YAG lasers and varying the delay time between them (interpulse delay). The double pulse (DP) technique offers a good control on the particle formation process and can enhance remarkably the production yield by selecting the appropriate interpulse delay with respect to single pulse method (SP). This implies that by using different interpulse delays, a different effect can be induced on the process of NPs generation. In this work, a correlation has been found between the emission lines of Ag atoms from the Laser-Induced Plasma (LIP) and the absorption maxima of the surface plasmonic resonance (SPR) of the NPs in solution. However, Different techniques have been used to understand the different phenomena occurring in the DP-LAL process : Optical Emission Spectroscopy (OES) has been employed to investigate the plasma induced by the second laser pulse, fast camera shadowgraph has been applied for studying the cavitation dynamics, and the produced Ag NPs have been analyzed by (SPR) absorption spectroscopy.



Experimental set-up

The dashed boxes show the two different detection systems used for the optical emission spectroscopy and shadowgraph measurements, and the cuvette for the realization of Ag colloidal solutions at controlled concentration





Surface Plasmon Resonance absorption spectra of the AgNPs in water obtained by SP-LAL and by DP-LAL at three representative interpulse delays



OES measurement of plasma emission produced by the second laser pulse during a DP experiment on Ag target in water 🛛 Emission intensity of Ag I spectral line (520.9 nm) and \square electron number density as function of the delay time between the two laser pulses. The \square bubble radius temporal evolution





SPR peak wavelength and its absorbance of AgNPs in water as function of interpulse delays prepared by DP-LAL. The first point of graphics corresponds to an AgNPs solution prepared with SP-LAL at the same Experimental conditions of DP-LAL. Bubble radius is reported for comparsion



Time-resolved shadowgraph images of bubbles induced by double laser pulses on Ag target in water. The image with yellow square represents the incoming time of the second pulse.

SPR, OES and shadowgraph results clearly shows that the larger the second laser pulse energy fraction arriving to the target, the higher the yield of the process. On the contrary the lower the pulse energy reaching the target, the higher the fraction spent in interacting with the NPs produced by the first pulse, which leads to increased fragmentation. So:

- 1. considering the proportionality of the SPR wavelength with the NP size, smaller NPs are obtained at interpulse delay times corresponding to the early expansion and late collapse of the cavitation bubble.
- 2. considering that the scattering contribution can be neglected for NPs smaller than 20 nm (that is the case of this study) absorbance obeys the Lambert Beer law and it is related to NPs concentration. Therefore higher concentration of NPs is obtained with DP-LAL when the laser pulses are shot at interpulse delay corresponding to the maximum of bubble expansion.

a) SPR peak wavelengths and b) SPR peak width of AgNPs solution obtained by ■ SP and DP-LAL at three representative interpulse delays • 10µs, \blacktriangle 80 μ s and \blacksquare 160 μ s respectively, as function of time after laser ablation.

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