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Dual photoacoustic monitoring in laser ablation synthesis of silver nanoparticles to find *in situ* their fluence threshold formation

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ABSTRACT

In this study, a dual pulsed photoacoustic technique was applied to monitor, in real time, the laser ablation synthesis in solution (LASiS) of silver nanoparticles. It was found that, at low optical fluence values, the ultrasound signal associated to the laser ablation process exhibited constant amplitude, independently of the ablation time. Further analysis confirmed that, under these conditions, the ablation process provided only suspended micro-sized Ag fragments. However, fluence values above 400 mJ cm^{-2} promoted the formation of nanoparticles, accompanied by amplitude changes in the photoacoustic signal. Determination of this threshold condition establishes a fingerprint in the photoacoustic signal that can be used to identify, *in situ* and in real time, the beginning of nanoparticle synthesis. Supplementary, the nanoparticle formation was also photoacoustically monitored during the ablation process introducing an additional laser pulse train of low fluence value propagating perpendicularly to the pulse train used for ablation. These laser pulses did not interfere with the nanoparticle LASiS process, but renders an ultrasound signal enhancement due to the surface plasmon resonance of metal nanoparticles. The characterization of the LASiS process through the photoacoustic technique can provide information about nanoparticle concentration and other synthesis features of interest.

Introduction

Metal nanoparticles (MNPs) have multiple applications in several fields such as thermotherapy [1], pollutant detection [2], biomarkers and contrast agents in bioimaging [3,4]. These MNPs change significantly their linear optical properties without a change in their chemical structure. For example, surface plasmon resonance of MNPs can be markedly shifted as a function of its shape, orientation or density keeping constant its metal composition. Therefore, methods for MNP synthesis have become an important research topic. Reprecipitation [5,6], chemical reduction [7], microwave assisted synthesis [8], and laser ablation [5,9–15] are widely used methods. In this regard, Laser Ablation Synthesis in Solution (LASiS) is a simple top-down physical approach to produce MNPs in a green fashion [9,10]. In the LASiS process, a metal target or suspended metal particles in different solvents are ablated by pulsed laser irradiation. The characteristics of the MNPs can be controlled by varying the wavelength, pulse duration, repetition rate, and fluence of the laser pulses; also, using specific solvents and temperature solution temperature [11,12]. In order to control size distribution and repeatability, the use of magnetic stirring and application of external fields during ablation synthesis has been proposed [13,14].

Among the several light-induced fluence-dependent phenomena taking place during the LASiS process under the thermal regime [15], spallation and phase explosion can lead to the generation of an ultrasound signal and a first shockwave, respectively [16–18]. In the high fluence regime, a second shockwave arise from the collapse of cavitation bubbles which have been identified as a diffusing mechanism of nanoparticles in the surrounding liquid to form a colloidal solution [19]. However, these two ultrasound signals can be clearly differentiated because of time scale, approximately 10 ns and 200 µs, respectively [20]. Recently, we demonstrated that the synthesis of organic NPs via LASiS can be monitored *in situ* by the generated photoacoustic (PA) signal [21]. Even when several non-radiative mechanisms were present, it was possible to determine the fluence ablation threshold and the exposure time at which the NPs undergo photodegradation under intense laser radiation [22].

Here, a novel pulsed PA technique to monitor the formation of silver nanoparticles (AgNPs) by the LASiS method is presented. It requires the

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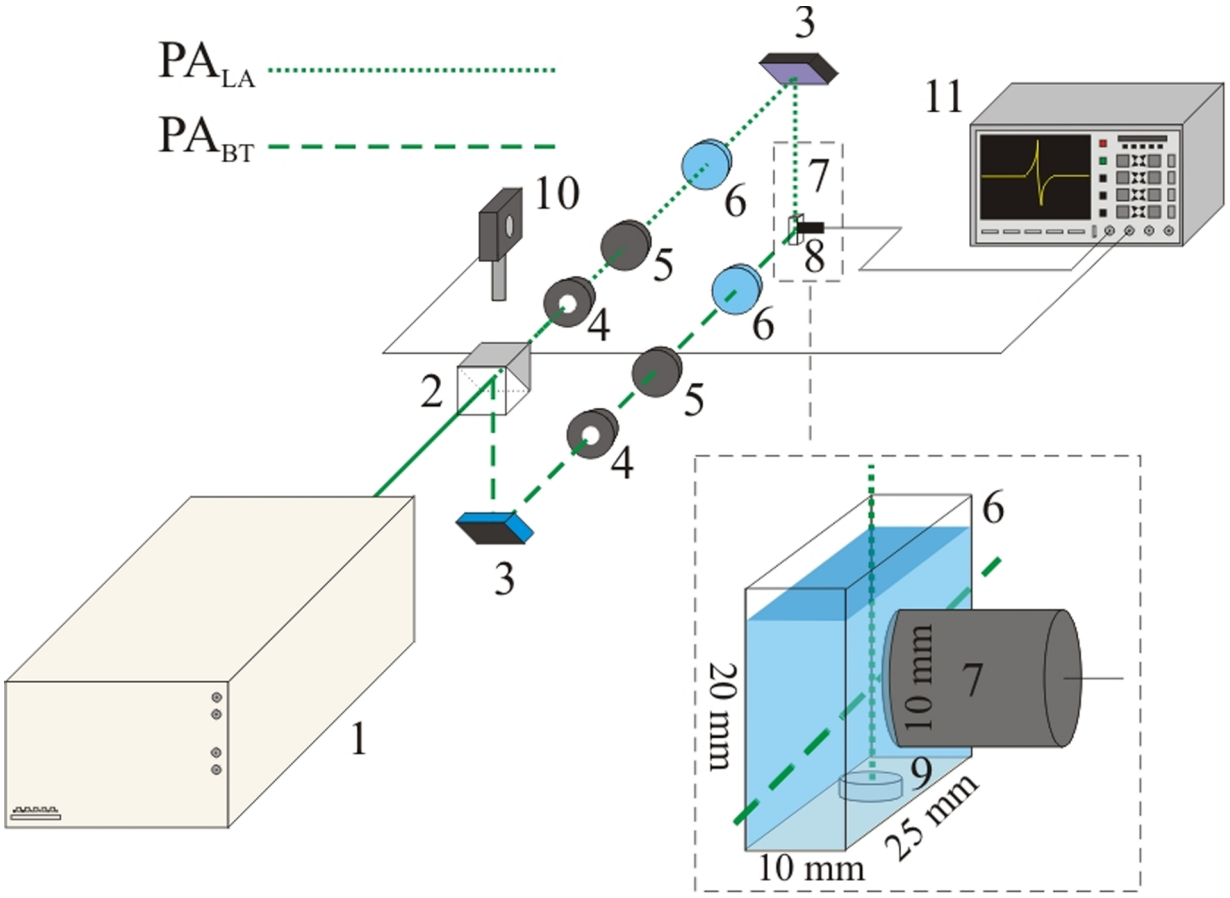

Fig. 1. Experimental setup: (1) pulsed laser, (2) beamsplitter, (3) mirrors, (4) iris, (5) variable neutral density filters, (6) positive lenses, (7) PA/LASiS chamber, (8) 3.5 MHz ultrasonic stress transducer, (9) Ag disk target, (10) photodiode sensing scattered light from experiment to trigger photoacoustic detection, and (11) oscilloscope.

acquisition of two pressure signals. The first one, the acoustic (shock) wave provided by the laser-metal interaction using pulse radiation with low (high) fluence values. The second one, the photoacoustic signal produced by the characteristic plasmonic resonance absorption of AgNPs. It was found that the latter signal is strongly dependent on the time of exposure to the laser radiation (ablation time). This finding was expected because the PA signal at low fluence values is directly proportional to the concentration of the sample that produces it [23]. UV–Vis absorption spectra of the AgNP colloidal suspension formed during ablation exhibit a specific pattern mainly due to the plasmonic properties of the material [24,25]. The generated PA signal also exhibits distinct characteristics for different sizes and shapes for bulk and AgNPs.

This new approach suggests that the PA technique could be used for real time monitoring of MNPs being synthesized by LASiS. This approach is as efficient as the well-established UV–Vis absorption spectroscopy, which provides information about whether the LA is producing Ag microparticles and/or AgNPs [26,27]. The advantage of this technique consists in the *in situ* LASiS monitoring provided directly by the PA signal derived from the laser interaction with the metal particle suspension.

Experimental apparatus and procedures

Sample preparation

The ablation target, a Ag disk 5 mm in diameter, was obtained from a pellet with 99.9% purity (EVMAG40QXQ-A, Kurt J. Lesker, Jefferson Hills, PA) after flattening with a hydraulic press to obtain a uniform thickness of 2 mm. The target sample was cleaned thoroughly with detergent (standard glassware), ethanol, triple distilled water, acetone, and finally sonicated for 20 min to remove any undesired residuals.

Experimental setup

LASiS/PA chamber

The experimental setup for NP LASiS process and PA signal detection is shown in Fig. 1. The LASiS/PA chamber consists of a plastic rectangular cuboid cell (25 mm × 8 mm × 21 mm) with glass windows on two lateral opposite walls designed *ad hoc* for the experiments. The cell contained 4 ml of aqueous solution using sodium citrate dihydrate at 0.8 mM (W302600; Sigma-Aldrich) as the solvent. The target Ag disk was placed at the bottom of the LASiS/PA chamber. The ultrasound transducer or hydrophone was attached through one lateral cell wall and pointing towards a perpendicular direction with respect to the line joining the glass windows.

Fluence control on laser beams

The second harmonic of a Nd:YAG-laser (Brillant; Quantel) was employed to provide laser pulses at 532 nm with pulse duration of 10 ns and repetition rate of 10 Hz. The laser energy was divided using an unbalanced beam splitter (95% transmission and 5% reflection). The LASiS process was initiated once the transmitted laser beam hits the silver (Ag) disk target. This optical beam is going to be called LA beam and the PA signal produced by it, PA_{LA} signal. The reflected beam by the beamsplitter (see Fig. 1, element No. 2), called BT beam was used,