



Nanoparticle-Enhanced Laser Induced Breakdown Spectroscopy for the noninvasive analysis of transparent samples and gemstones



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ABSTRACT

In this paper, Nanoparticle-Enhanced Laser Induced Breakdown Spectroscopy is applied to transparent samples and gemstones with the aim to overcome the laser induced damage on the sample. We propose to deposit a layer of AuNPs on the sample surface by drying a colloidal solution before ablating the sample with a 532 nm pulsed laser beam. This procedure ensures that the most significant fraction of the beam, being in resonance with the AuNP surface plasmon, is mainly absorbed by the NP layer, which in turn results the breakdown to be induced on NPs rather than on the sample itself. The fast explosion of the NPs and the plasma induction allow the ablation and the transfer in the plasma phase of the portion of sample surface where the NPs were placed. The employed AuNPs are prepared in milliQ water without the use of any chemical stabilizers by Pulsed Laser Ablation in Liquids (PLAL), in order to obtain a strict control of composition and impurities, and to limit possible spectral interferences (except from Au emission lines). Therefore with this technique it is possible to obtain, together with the emission signal of Au (coming from atomized NPs), the emission spectrum of the sample, by limiting or avoiding the direct interaction of the laser pulse with the sample itself. This approach is extremely useful for the elemental analysis by laser ablation of high refractive index samples, where the laser pulse on an untreated surface can otherwise penetrate inside the sample, generate breakdown events below the superficial layer, and consequently cause cracks and other damage. The results obtained with NELIBS on high refractive index samples like glasses, tourmaline, aquamarine and ruby are very promising, and demonstrate the potentiality of this approach for precious gemstones analysis.

1. Introduction

Laser Induced Breakdown Spectroscopy has proved a valuable tool for glass [1,2] and gemstone analysis [3–6], in particular for gem provenance studies [7] and to discriminate between different minerals [8]. The main advantages of using LIBS for glass and for gemstones analysis is that it is possible to have multispectral information just by a single shot, which enables fast multi-elemental analysis [9]. Moreover, the feasibility of calibration free approaches has also been demonstrated for these samples, which is especially useful when it is hard or expensive to produce matrix matched standards, like in the case of gemstones [10]. One of the crucial questions in applying laser ablation-based methods to the analysis of transparent samples is related to their high refractive index. This causes the laser pulse to penetrate beyond the superficial layer, thus inducing cracks and damage in the sample

itself [11,12]. This drawback prevents a straightforward application of LIBS to precious transparent samples such as gemstones or ancient glass although the use of UV laser pulse can limit the surface damage due to the better coupling of the laser with the matrix. Recently, the use of metallic NPs for controlling the laser-matter interaction has been proposed by the same authors of the present paper. It has been demonstrated for metallic samples [13] and microdrops of solutions [14] that the laser pulse, off-resonance with the NPs surface plasmons, can induce the collective oscillation of NP surface electrons, which in turn results in local field enhancement and in LIBS signal improvement. The use of NPs for enhancing the LIBS signal and analytical performance is named Nanoparticle-Enhanced LIBS, (NELIBS) [15]. In this paper, a NP layer was deposited on the transparent sample surface, in order to avoid the direct interaction of the laser pulse with the transparent medium. To prevent the direct laser interaction with the sample, a laser pulse in

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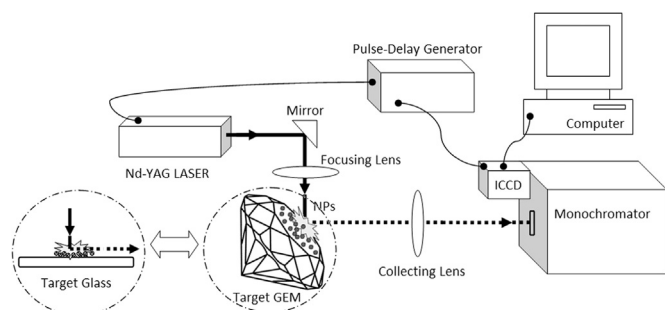


Fig. 1. Experimental set-up.

resonance with the surface plasmon of the NPs was employed, so that most of the laser energy was absorbed by the NPs. The preferential absorption of laser photons by the NPs allowed induction of the breakdown on the NPs layer deposited on the sample surface, rather than directly on the sample surface. As a consequence of this phenomenon and of the NP explosion, only a few superficial layers of sample were transported in the plasma phase. The main result was therefore not only to prevent the sample cracking, but also to avoid visible damage on the sample surface after the NELIBS measurement. Finally, in order to acquire an emission spectrum that was representative of the elemental composition of the sample without any interference, except for the emission lines of the metal of NPs, the NPs were synthesized in milliQ water by Pulsed Laser Ablation in Liquids (PLAL) [16] without any kind of stabilizer or chemical contaminant.

2. Materials and methods

The experimental set up (Fig. 1) includes a second harmonic Nd:YAG laser, Quantel Q-smart 850 (532 nm, 6 ns duration, energy up to 500 mJ), a spectroscopic system consisting of a Czerny-Turner spectrograph (JY Triax 550) coupled with an ICCD (JY 3000) which was synchronized with the Pockels cell of the laser source by a pulse generator (Stanford DG 535). The sample was mounted on a micro-stage holder with adjustable angle with respect to the laser direction. The laser was focused 5 mm beyond the sample with a planoconvex lens with a 100 mm focal length, in order to avoid the breakdown on the sample surface. At this experimental condition the laser spot was around 1.5 mm of diameter. The laser was used in single shot mode and the parameters were as follows: delay time after the laser pulse was 800 ns and gate width was 10 μ s (virtually an integrated time LIBS measurement).

The AuNPs were prepared by Pulsed Laser Ablation in Liquid (PLAL) as described in Ref. [17]. PLAL allows ultrapure NPs to be produced in milliQ water without the use of any chemical stabilizers. This is an

important point in NELIBS applications because the emission signal of all the impurities of the colloidal solution are strongly enhanced and the spectrum of contaminants may affect the elemental analysis of the sample. The produced AuNPs, characterized with SPR (Surface Plasmon Resonance), TEM (Transmission Electron Microscopy), and DLS (Dynamics Light Scattering), had diameter of 15 ± 2 nm. The SPR of AuNPs deposited on quartz substrate after drying the drops of colloidal solution for the NELIBS experiment is reported in Ref. [14]. The concentration of the Au colloidal solution used in this work was between 0.05 and 0.6 g/l, depending on the experiment, as reported in the figure captions. The film of NPs on the sample surface were obtained by depositing and drying several drops of the colloidal solution until they formed a visible layer on the surface. The sample was placed on the holder and the angle between the laser direction and the sample surface was adjusted in order to have the maximum reflection at low laser energy below the breakdown threshold. Once the optimal angle was found, the energy of the laser was set up between 100 and 200 mJ in order to induce the breakdown of the deposited NP film.

Optical microscope images of glass and gemstones were acquired with Dino-Lite pro (AM431ZTA).

The following samples were tested: microscope glass slides (7101 Pearl); Pyrex glass; standards of di-lithium tetraborate doped with Cr_2O_3 with Cr concentration varying from 0.0017 to 0.1 wt% provided by CRITT Matériaux Alsace – Schiltigheim – France; tourmaline from the Royal Mineralogical Museum of Naples; aquamarine and ruby provided by Centro di Analisi Gemmologiche “Masterstones” of Rome.

2.1. Glass samples

Glass slides of different typologies were tested with NELIBS with the laser beam perpendicular to the sample surface. A gold colloidal solution was deposited on the glass, in order to obtain a thin layer of NPs. The laser was focused beyond the sample surface in order to have a laser spot of 1.5 mm and a fluence of 1.5 J cm^{-2} , as shown in Fig. S1 of Supplementary material. This energy was below the breakdown threshold of the sample and without the deposition of NPs the laser would pass through the sample without inducing any breakdown. On the contrary, when the sample was covered with the AuNPs, the efficient laser absorption by the NP surface electrons produced the breakdown of the NP layer, and the emission spectrum of the NPs and of the underlying portion of sample was obtained, as reported in Fig. 2. Unlike in previous NELIBS applications [13,14], in this case, in order to maximize the photon absorption of the Au-NPs, whose surface plasmon resonance is around 523 nm (Fig. S2 of Supplementary material), we used the second harmonic of the Nd:YAG, 532 nm, to obtain an effective match with the NP band absorption. The efficient laser absorption from the NPs allows the laser pulse to induce the breakdown directly on the NPs, avoiding the direct interaction of the laser pulse with the sample.

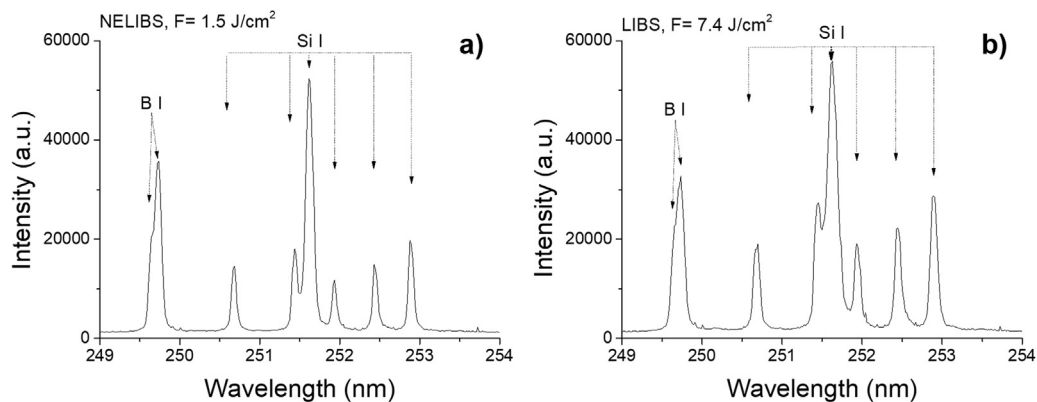


Fig. 2. a) NELIBS and b) LIBS spectra of borosilicate glass. Different laser fluences were employed in order to obtain comparable emission spectra: 1.5 J cm^{-2} and 7.4 J cm^{-2} respectively, in the case of NELIBS 3 drops of 2 μ l of AuNPs solution 0.05 g/l.

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