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Nanoparticle Enhanced Laser Induced Breakdown Spectroscopy: Effect of nanoparticles deposited on sample surface on laser ablation and plasma emission ☆

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ABSTRACT

In this paper the use of metallic nanoparticles (NPs) for improving Laser Induced Breakdown Spectroscopy (LIBS) is discussed. In the case of conductors an emission signal enhancement up to 1–2 orders of magnitude was obtained depositing NPs on the sample surface by drying a micro-drop of colloidal solution. The basic mechanisms of Nanoparticle Enhanced LIBS (NELIBS) were studied and the main causes of this significantly large enhancement were found to be related to the effect of NPs on the laser ablation process, in terms of a faster and more efficient production of seed electrons with respect to conventional LIBS. The characteristics of NELIBS-produced plasma were investigated by emission spectroscopy and spectrally resolved images. In spite of similar plasma parameters, the NELIBS plasma was found to have larger emission volume and longer persistence than the LIBS one. A method to determine NP concentration and size was also proposed, which involved depositing NPs on non-interacting substrates, and proved the feasibility of LIBS as a fast detection tool for a preliminary characterization of NPs.

1. Introduction

The potentialities of Laser Induced Breakdown Spectroscopy (LIBS) have been demonstrated in several applications [1–3] and LIBS has gained an important role in analytical chemistry as shown by the growing number of users in different fields of science, from cultural heritage [4] to geosciences [5], space exploration [6], and industrial process control [7]. In this frame, improving the sensitivity of LIBS is a priority. Many approaches have been proposed in the last decade, such as multi-pulse LIBS [8,9], resonance LIBS [10] and various hyphenated techniques [11]. These variants have been successfully applied, but they require complex experimental set-up and additional costs that decrease the LIBS' appeal for users, who generally use compact commercial systems and are not interested in developing deep expertise in laser-based techniques.

On the other hand, growing knowledge on nanotechnology is having a great impact on analytical chemistry, e.g. in mass spectrometric techniques, surface enhanced spectroscopic techniques, high resolution microscopy and gas sensors [12].

Starting from these considerations we have recently proposed Nanoparticle Enhanced LIBS (NELIBS) [13] in order to improve the sensitivity of LIBS on metals without changing the classical set-up and keeping the analysis operations easy and fast. As a matter of fact, in order to enhance the sensitivity of the technique it is necessary to increase the efficiency of the deposition of energy from the laser to the sample. This can be done up to a certain extent by controlling the laser parameters [14] (i.e. irradiance and photon energy) or changing the background environment [15] (by using double pulse techniques, including laser pre-spark, by changing the gas or by working in vacuum). On the other hand, when the laser source and experimental parameters cannot be changed the only way to improve the efficiency of the laser- target interaction is manipulating the sample itself. This is not trivial, because this manipulation should not change the chemical composition nor be time-consuming, in order not to lose typical LIBS advantages such as fast and straightforward analysis. Application of nanoparticles appears as the perfect solution for several reasons: first of all, they contaminate the target only in a negligible extent (less than 0.04%); they can be easily deposited on the sample surface and be completely removed during the laser irradiation [13]; their effect on the sample under laser irradiation is very large, thanks to their peculiar physical properties. In NELIBS a micro-drop of solution containing nanoparticles (NPs) is deposited on the sample surface in an area covering the focused laser spot. When the solvent evaporates, NPs adhere to the surface and change its properties, notably increasing the efficiency of laser energy deposition on the sample. As a main result, in the case of metals, the signal is enhanced up to 1–2 orders of magnitude.

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In this paper the fundamental aspects of NELIBS are discussed both for what concerns the effect on laser–sample interaction and the effect on plasma evolution and emission.

2. Experimental procedure

In this work a typical LIBS apparatus was used, which consists of one laser source for the ablation and plasma induction and one spectrograph for optical emission spectroscopy [2]. A Q-switched Nd: YAG nanosecond laser with energy up to 1.8 J/pulse and pulse duration of 8 ns at 1064 nm (Quanta System, model: Giant 770-10) was used as the laser source. The system for radiation detection comprises: a monochromator with spectral range 250–750 nm and a 1800 g/mm grating (Jobin Yvon Horiba TRIAX 550) coupled with an Intensified Charge Coupled Device (ICCD) (Jobin Yvon Horiba CCD-3000); a digital delay/pulse generator (Stanford Research Systems model: DG535) to synchronize the plasma production and the emission spectra acquisition; a computer to set via software the acquisition parameters (i.e. gate width, Tg, and delay time, Td, of ICCD aperture). The laser pulse was focused on the target by a lens of 100 mm focal length. The emitted light was reflected by an aluminum mirror of 50 mm diameter and the reflected emission light was collected through a 75 mm focal length biconvex UV fused silica lens directly on the monochromator entrance slit.

Each emission spectrum was acquired in single shot mode. Before each LIBS measurement a set of laser shots was focused on the sample in order to keep the surface conditions similar among different experiments. In the case of NELIBS, a drop of solution of metallic colloids was deposited on the treated sample surface. A standardized adjustable volume micro-pipette was used to put on the target surface 0.5 μL drops of either 20 nm certified spherical Ag NP dispersions (0.02 mg/mL in aqueous citrate buffer, Sigma Aldrich Co.) or NPs of different metals produced by Pulsed Laser Ablation in Liquid (PLAL) as described in Ref. [16]. The solution was then evaporated to form a coating layer of NPs on a circular area of 2.5 mm of diameter. To investigate the effect of particle sizes on NELIBS enhancement we also performed a set of experiments by using certified spherical Ag NP dispersions of both 20 nm and 10 nm (0.02 mg/mL in aqueous citrate buffer, NanoComposix, Inc.) particle sizes, as well as Ag, Au, Pt and Cu-NPs produced by PLAL [16]. It is important to underline that, as demonstrated in Ref. [13] the NELIBS enhancement is not very sensitive to NP concentration within a given range and to particle size within the range 8–20 nm diameter. The latter question is really important from the practical point of view because it means that mono-dispersed nano-fluids are not required. The little effect played on emission intensity by NP concentration and size implies that temperature and volume of drops, as well as the whole experimental procedure, do not need to be strictly monitored for carrying out the experiment.

3. Effect of NPs on the ablation process

In a previous work [13] it was shown that, when 20 nm Ag NPs were deposited on the sample surface, the breakdown threshold of metals decreased in a percentage depending on the metal sample (33% for copper, 35% for titanium, 36% for iron etc.). On the contrary, no evident effect was observed in the case of an insulator, i.e. Teflon, and a semiconductor, i.e. silicon. These observations suggest that the induction of free electrons on the sample plays an important role in NELIBS. It is well-known that surface roughness and the presence of flakes on the surface can improve the ablation efficiency by decreasing the ablation threshold, as a consequence of the lower thermal conductivity of small-sized objects under laser irradiation [17]. Thus, NPs can be considered as ideal thermally-insulated defects able to lower the breakdown threshold. Anyway, surface defects can significantly affect the breakdown only at low laser irradiance. Instead, when irradiance is well above the breakdown threshold, multiphoton processes are so efficient that they are not evidently affected by defects [18]. On the contrary, high-energy laser pulses can induce electric fields strong enough to produce direct emission of electrons from the surface [19,20]. This phenomenon, well-known in electrical discharges in vacuum [21], can occur under laser irradiation when the metallic surface is covered with nanostructures, thanks to the large local increase of the electromagnetic field (1–4 orders of magnitude) of the incident light [19,20]. In the present experiment, irradiance between 0.3 and 1.3 GW/cm^2 is used, and the corresponding electric field amplitude is in the order of tens of MV m^{-1}. The sample can be considered as a flat surface with spheres with diameter in the order of tens nanometers deposited on its surface. These can enhance the field up to a factor of 10^3 [20], thus inducing instant field electron emission and producing several seed electron sources in the laser spot.

The competition between multiphoton ionization and field emission has been studied intensively in the last decades in connection with many nano-technological applications. The Keldysh parameter allows quickly estimating if the ionization of atoms in the sample proceeds by absorption of photons, that is, if electrons escape through direct or indirect paths of ionization, or by tunneling the work function barrier through field emission. The original formalism of the Keldysh parameter is given by the following equation [22]:

$$\gamma = \omega \frac{\sqrt{m_e V_B}}{eF} \quad (1)$$

where V_B is the potential energy of the barrier (i.e. the work function potential), F is the electric field intensity, ω is the laser frequency, and m_e and e are the electron mass and charge, respectively. The main contribution to sample ionization is multiphoton ionization if $\gamma > 1$, and field emission if $\gamma < 1$. In the present experiments, during LIBS of titanium with laser irradiance 3×10^8 W/cm^2, F = 10 MV m^{-1} and V_B = 4.33 eV, γ exceeds 10^2 and, as usual in LIBS, multiphoton ionization is the mechanism determining the production of free electrons. On the contrary, during NELIBS the laser field is enhanced of a 10^3 factor [20] as a result of plasmon coupling, thus γ decreases to 0.14 and field emission becomes the main mechanism of free electron production.

During the field emission, sample heating and electron acceleration by inverse Bremsstrahlung cause the electron flow to further increase by Schottky effect [23], which results in an extremely efficient breakdown.

In order to investigate the effect of NPs on sample ablation, Scanning Electron Microscopy (SEM) was employed. The images of a portion of the laser crater after LIBS and NELIBS are shown in Fig. 1a) and b). Observing the figure it is clear that with conventional LIBS a flat surface produced by a melted and resolidified layer of sample is found after the ablation process. On the other hand, with NELIBS the crater appears characterized by irregular surface, with many burst cavities whose dimensions are in the order of several hundreds of nanometers to few micrometers. These images resemble the typical morphology of arc cathode spot [21] and suggest that: 1) the role of deposited NPs is acting like multiple ignition points, each behaving as a source of seed electrons by field emission; and 2) these sources are localized in all the irradiated portion of sample. Although in the case of laser ablation in nanosecond regime it is not possible to clearly establish the contribution of the various mechanisms to the ablation process, a hypothetical sketch of what occurs during NELIBS is reported in Fig. 2: when laser irradiation occurs, seed electrons are immediately (t < 1 fs) provided by field emission at the NP position; due to electron ejection and multiphoton ionization (the latter on a longer time scale, in the order of few tens of fs), ionization and consequent sample breakdown take place; breakdown and heating of electrons by inverse Bremsstrahlung lead to the formation of the typical laser induced plasma; after plasma evolution and sample cooling, the melted sample portion next to the ablated one resolidifies, giving the crater surface the shape shown in Fig. 1b), where burst holes can be observed, located where NPs were at the moment of laser irradiation. Together with the multi-point ignition effect, other