NANOPARTICLE ENHANCED LASER INDUCED BREAKDOWN SPECTROSCOPY: FUNDAMENTALS AND PERSPECTIVES

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1. INTRODUCTION

It has been recently proposed to use metallic nanoparticles for improving the sensitivity and the capabilities of laser ablation analytical techniques, such as LA ICP MS and LIBS (named respectively NE-LA-ICP-MS and NE-LIBS, NE stands for Nanoparticles Enhanced). Metallic NPs allow modulation and enhancement of the incoming laser pulse with the ignition of a surface plasmon resonance (SPR). These enhanced techniques present different advantages: the ablation occurs mainly on the NPs deposited on the surface of the sample which leads to few damages on this one and thus is interesting for numerous domain of applications [Dell'Aglio 2018]. In addition, sensitivity is hugely increased in the case of LIBS allowing the detection of ultra-traces in the range of ppb level [De Giacomo 2013, De Giacomo 2016] whereas, signal from LA-ICP-MS mediated by NPs is also increased, but in a more moderate way, achieving enhancement between 2 to 10 [Mangone 2020]. Mechanisms that relies behind this enhancement are not yet completely understood. In addition, it seems that, mainly, the NPs play a role on the plasma emission in the case of NE-LIBS [De Giacomo 2020], and on laser ablation and elemental fractionating in the case of NE-LA-ICP-MS [Holá 2018], which are two complete different processes.

2. EXPERIMENTAL

NE-LIBS experiments do not need any tuning setup, and in that way, experimental setup is a classical homemade LIBS setup with a pulsed Nd:YAG laser, 6 ns pulse duration, of fundamental wavelength 1064 nm, (Q-SMART 850, Quantel). Laser pulse is focalized on the target using a focal lens of various focal distance depending on the desired spot size and can be replaced by a microscope objective for conducting μ-LIBS experiment. Plasma emission light is collected with a fiber into a spectrometer (TRIAX 500, Andor) coupled with a CCD camera. Additional laser module can be used to change the laser wavelength into the 2^{nd} and 3^{rd} harmonics, respectively 532 and 354 nm, in order to fit perfectly the resonance band of the NPs system.

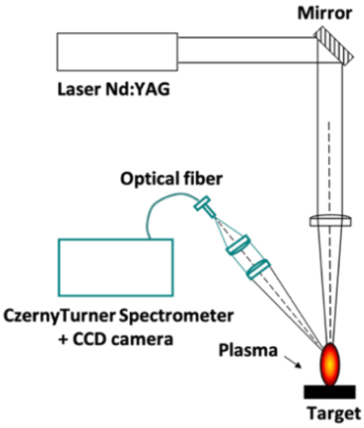

Figure 1. Experimental setup for typical LIBS and NE-LIBS measurement.

Various kind of NPs can be employed, of all different shapes, even if platinum, gold and silver spherical NPs are most commonly used. Sample preparation is quite fast and easy: µL drops of NPs colloidal solution are deposited on the sample surface and gently dried. The NPs size effect will be discussed below. It is important to notice that NE-LIBS effect can only occurs under specific conditions. First, the spot size must be large enough to ablate a large amount of NPs. Secondly, the laser fluence should be relatively low, so the NPs are not destroyed during the ablation. Finally, NPs should not aggregate during the deposition or inside the colloidal solution. This latter point is crucial in order to have a stable and reproducible signal. If all these conditions are fulfilled, NE-LIBS effect can occur and signal enhancement of some orders of magnitude can be reached.

3. Results and discussion

3.1. Analytical performance

Briefly, NE-LIBS can achieve a sensitivity close to the ppb level, and an enhancement of some order of magnitude between LIBS and NE-LIBS signal can be observed, especially on metallic target.

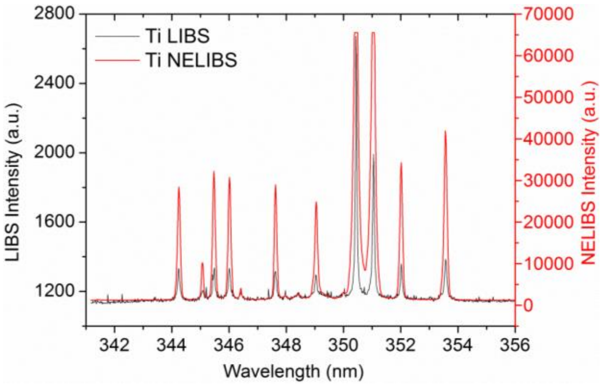

Figure 2. Typical NE-LIBS spectra obtained on a titanium target.

Even if NE-LIBS provides astonishing results on metallic target as shown in Figure 2, it can be used for a wide area of application, as seen in Table 1, including analysis of biological sample, liquids or even crystal and precious sample.

Target	Elements	NPs	Enhancement/LOD
Titanium	Ti	Ag, Au	En > 100
Steel	Fe	Ag	En = 5
Cu-based alloys	Pb, Sn,Mn	Au, Ag, Pt, Cu/CuO	En ~ 50
Al-based alloys	AlO, Ti,Fe	Au	En ~ 10
$CuSO_{4\,(aq)}$	Cu	Au	ppt level in 100 µl
$CuSO_{4\,(aq)}$, $NaF_{(aq)}$	Cu, F	Au	En = 3.5 For F LOD ~ 0.1% ppm in 20 µl
$AgNO_{4\,(aq)}$ $PbCl_{2\,(aq)}$, $PbSO_{4(aq)}$	Ag, Pb	Au Au	LOD <ppb in 2 µl En >10
Blood	Pb	Au	LOD ~ 10 ppb in 2 µl
RC Protein solution	Li	Au	En ~ 20
$CuSO_{4\,(aq)}$, $Cr(NO_3)_{2\,(aq)}$ $Pb(NO_3)_{2\,(aq)}$	Cu, Cr, Pb	ultrafine fibers +Au NPs	En ~ 4
Leaf	Fe, Mn, K, Ca, Mo	Au, Ag	En = 5
SiO_2 crystal	Si	Au	En = 30
ZnO pressed pellets of NPs	No plasmonic enhancement	ZnO	2<En<120
Tourmaline	Mn, Fe	Au	En ~ 10

Table 1. Analytical performance of NE-LIBS taken from [Dell'Aglio 2018].

3.2. Understanding the NE-LIBS effect

NPs play a double role during laser-induced plasma experiment: first during the ablation and then on the plasma phase. During the ablation, if the laser wavelength matches the absorption band of the NPs system, plasmonic effects will occur : a coherent and collective oscillation of the NPs system will be created and NPs electrons will be able to move freely between the NPs system and the plasma phase. In addition, NPs will be shielded during the ablation, and the laser pulse will be focused in the space between themselves, leading to multiple ignition point and thus to a more efficient ablation.

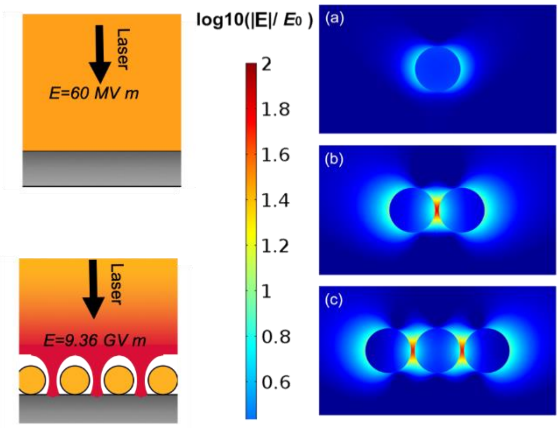

Figure 3. Laser-NPs interaction during laser ablation experiment.

After the laser pulse, NPs will survive the ablation and will be ejected at the top of the plasma. During its expansion, the plasma will slowly take in the NPs and vaporize them. It was shown that the NPs size was not affecting the global enhancement, but rather the temporal evolution of the signal instead.

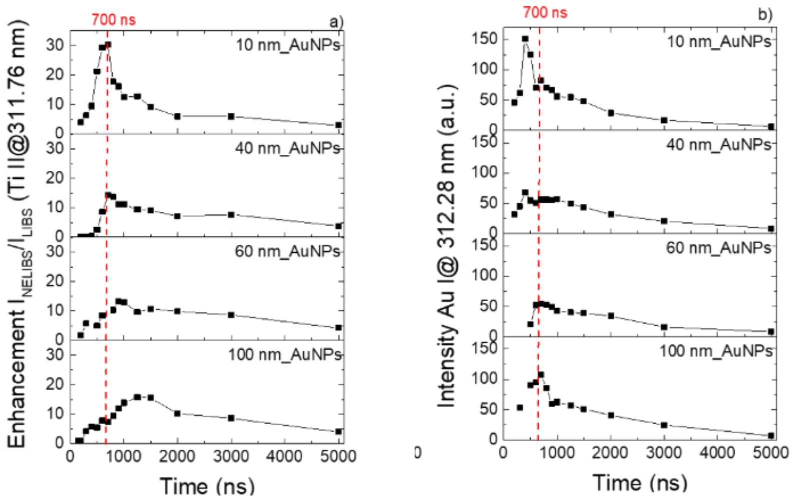

Figure 4. Temporal evolution of signal enhancement and gold (NPs) signal.

Finally, the NPs role on the plasma during its expansion is not yet fully understood. Only a small portion of the ablated mass will take part into the emission processes and it is supposed that the NPs can convert a part of the "sleeping mass" into emissive mass, and thus leading to a higher emission efficiency.

4. Conclusions

NE-LIBS has shown astonishing capabilities in term of emission efficiency, signal enhancement and sensitivity. NPs can be used for all kind of experiments and their use is not time consuming and no setup tuning is needed. In order to fully optimize the NE-

LIBS effect, there is a crucial need to understand all the fundamental processes which relies behind this enhancement. So far, the NPs are acknowledged to play a role during the ablation and on the plasma phase.

6. References

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