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NANOPARTICLES ON A SAMPLE SURFACE AS LASER INDUCED BREAKDOWN SPECTROSCOPY ENHANCERS

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Abstract. Signal enhancement of Laser Induced Breakdown Spectroscopy in the presence of gold nanoparticles was studied. Nanoparticles were synthesised using pulsed laser ablation of the rotating Au target immersed in liquid mediums. Stability of nanocolloids was estimated. Nanosuspensions were applied to sample surface what enabled studies of Nanoparticle Enhanced Laser Induced Breakdown Spectroscopy. The effect of spectral line enhancement was observed under the optimised conditions both for neutral and ionic lines of the studied sample material.

1. INTRODUCTION

Laser Induced Breakdown Spectroscopy (LIBS) is emission spectroscopy technique that uses a short laser pulse to create plasma on the sample surface, and analyses formed plasma to gather information about the sample studied. Despite of all its advantages (fast response, no or minimal sample treatment, simple setup, requires only optical access to the sample), lower detection limit is the largest drawback of this technique. One way of signal enhancement is deposition of metallic nanoparticles on sample surface before laser irradiation. In this way, the order of magnitude enhancement of optical signal can be obtained [1,2].

In this work, nanoparticles (NPs) were synthesised using laser ablation of the bulk gold in liquid medium, and then applied on the surface of the sample. Surface prepared in such a way was than irradiated with the laser beam, Nanoparticle Enhanced LIBS (NELIBS) plasma was formed and spectra were recorded. It was shown that application of Au NPs on the target surface prior to laser induced breakdown leads to signal enhancement of sample's element optical emission.

2. EXPERIMENT

Experiment was conducted in several steps. Firstly, it was necessary to synthesize Au NPs, uniform by size and shape. Next, the size of the NPs needed

to be evaluated, based on the position of a Surface Plasmon Resonance (SPR) band maximum. In order to do that, absorption spectra of all produced colloids were recorded with spectrophotometer [3-5]. After that, synthesised colloids of NPs ought to be applied to analysed metal target (AlMgCu₅), where proper volume of the colloid drop and surface coverage had to be determined experimentally. As a final step, conditions for NELIBS spectra recordings had to be optimised.

Method of choice for NPs synthesis was laser ablation in different solutions. Experimental setup consisted of laser (Nd:YAG, 2nd harmonic 532 nm), mirror for guiding the laser beam (45° angle), focusing lens of 2.5 cm focal length and rotating table on top of which cuvette with a solution and immersed Au target were positioned., see Figure 1a. In order to find the optimal conditions for NPs generation, laser energy and wavelength were changed. Also, different distances between the target and lens were set, so different energy densities on the target surface were obtained, leading to the NPs of various sizes. Duration of ablation was varied in order to obtain different colloid concentrations. NPs were synthesized in water (distilled and deionized) and in different organic solvents (DMSO, Acetonitrile and Chloroform) [6]. Characterisation of formed nanocolloids was performed with measurements of SPR band using spectrophotometer Beckman Coulter DU720. Stability of formed solutions was also estimated.

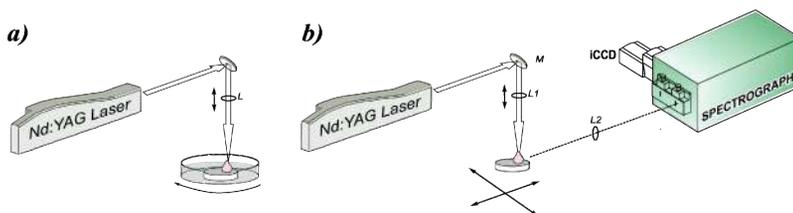


Figure 1. Experimental setup: a) for synthesis of Au nanocolloid; b) for NELIBS.

Experimental setup used for measurements of NELIBS spectra of prepared samples consisted of: laser (Nd:YAG, 2nd harmonic 532 nm), mirror (45° angle), focusing lens of 2.5 cm focal length (L_1) and lens for focusing NELIBS plasma (L_2 , $f=20\text{cm}$) onto the entrance slit of detection system (imaging spectrometer equipped with ICCD camera), see Figure 1b. Position of the projection lens L_2 with respect to the spectrometer was varied, i.e. different portions of the plasma volume were collected by optical system, which had prove to have direct consequence on the spectral line emission enhancement.

3. RESULTS AND DISCUSSION

When a metal particle is exposed to light, the oscillating electromagnetic field induces a collective coherent oscillation of conduction band electrons. The amplitude of the oscillation reaches maximum at a specific frequency, called surface plasmon resonance. The SPR induces a strong absorption of the incident light and thus can be measured using a UV-Vis

absorption spectrometer [5]. Based on the measured position of SPR band maximum, sizes of Au NPs were estimated, see Figure 2a. After few days, recordings were repeated in order to verify stability of solutions, Figure 2b. The variations in position of the SPR maximum were almost negligible after two days, leading to the conclusion that produced colloids are rather stable. Significant change in the SPR maximum position was only detected four days after the colloid synthesis.

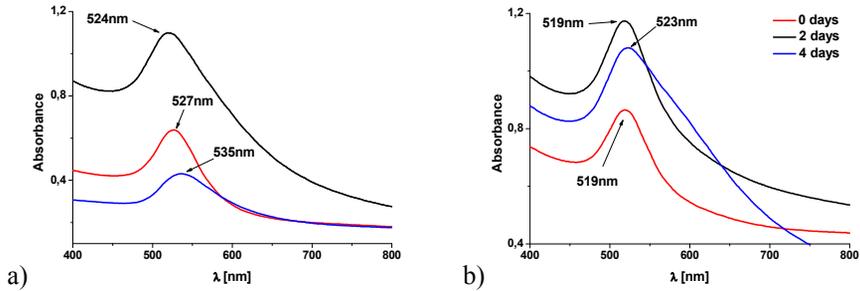


Figure 2. SPR band of formed solutions: a) size estimation; b) stability check.

Estimated sizes of Au NPs (30 ± 5 nm) [3] were in the range of sizes that have already been reported to produce NELIBS effect [1], even two days after synthesis. Besides NPs size, important parameter for line intensity enhancement is the NP surface concentration. It was found that after certain limit, further increase of concentration does not contribute to signal enhancement [2]. In order to test that, nanocolloid was first applied on the sample surface in a form of large droplets ($\sim 10 \mu\text{l}$). In this case, the deposition of colloid was inhomogeneous such that the concentrations at the edges were higher than at the center, i.e. “‘coffee-ring” effect [7], resulting in noticeable enhancement only when particular place on a drop was irradiated. This indicates that, with the large droplets, surface concentration of NPs was above critical, leading to decreased NELIBS performance [7]. Since enhancement is strongly dependent on the total amount of colloid, smaller droplets should be used. Having this in mind, further on microdroplets ($0.5 \mu\text{l}$) were applied with micropipette on the previously irradiated surface of the target.

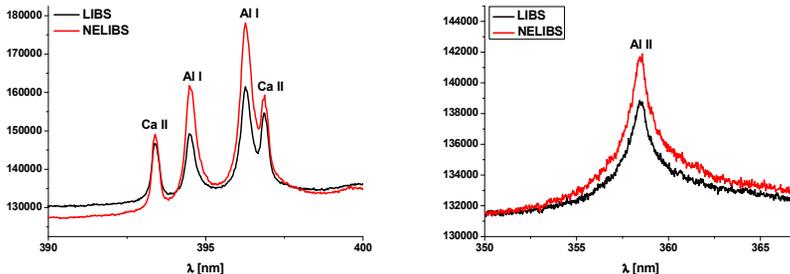


Figure 3. Comparison of LIBS and NELIBS spectra for neutral and ionic lines of main target constituent.

Spectra obtained with microdroplets are shown in Fig. 3. All presented spectra were recorded with single shot. Further enhancement of optical signal could be obtained if signal accumulation was performed. Increase of signal intensity was present in both neutral and ionic lines. Enhancement of spectral line intensity was more pronounced in case of neutral lines, possible due to larger emission volume of NELIBS plasma. Since LIBS and NELIBS plasma have similar plasma parameters [1], larger emission volume of NELIBS plasma means more contributions from "colder" layers which are emitters of mostly neutral lines. It is important to emphasize this was the reason why lens L_2 was positioned in such a way that complete plasma volume was focused to the spectrometer. This configuration corresponds to the maximum signal enhancement.

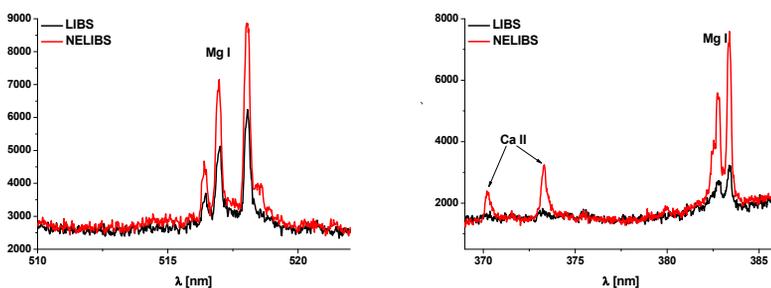


Figure 4. Comparison of LIBS and NELIBS spectra of minor elements in sample.

Fig. 4 illustrates intensity increase of spectral lines of magnesium which is minor sample constituent. Also, lines of Ca appeared in NELIBS spectra. Calcium can be present in $AlMgCu_5$ in small amounts, but also can come from water used as a medium during the NPs synthesis. Because of this uncertainty, it can be concluded that this method is not reliable for investigations of calcium containing samples.

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REFERENCES

- [1] A. De Giacomo et al, *Spec. Acta Part B* 98, 19 (2014)
- [2] A. De Giacomo et al, *Anal. Chem.* 88, 9871 (2016)
- [3] S. Link and M. A. El-Sayed, *J. Phys. Chem. B* 103, 4212 (1999)
- [4] V. Amendola et al, *J. Phys.: Condens. Matter* 29, 203002 (2017)
- [5] X. Huang and M. A. El-Sayed, *J. of Adv. Research* 1, 13 (2010)
- [6] V. Amendola et al, *J. Phys. Chem. B* 110, 7232 (2006)
- [7] C. Zhao and D. Dong, *Anal. Chem.* 88, 9869 (2016)