

ENHANCEMENT OF THE TEA CO₂ LIBS EMISSION USING Ag AND Ag/Zn NANOSTRUCTURES

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1. INTRODUCTION

Nanoparticle-Enhanced Laser-Induced Breakdown Spectroscopy (NELIBS) that is firstly introduced by *de Giacomo et al.* has gained much attention due to its capability of improving the spectral intensity and detection sensitivity [De Giacomo 2013]. The presence of nanotechnology in today's scientific world is increasing, as well as their various application. This new approach uses a deposition of nanoparticles on the sample to increase the emission signal of the LIBS plasma. There are various methods of preparation of different types of nanoparticles and different materials of the sample that is analyzed. The possibility of using nanoparticles in different fields increases the need for their production in stable states and environmentally acceptable processes. Several researchers have studied the new approach of NELIBS from both fundamental and application point of view [Palásti 2020, Poggialini 2020].

Enhancement of the LIBS emission signal by deposition of Ag/Zn nanoparticles prepared by laser ablation and silver nanoparticles prepared by chemical synthesis on the surface of the aluminum sample has been investigated. The great potential of the use of nanoparticles in analytical LIBS is shown, by obtained results and the further possible development of this technique is suggested.

2. EXPERIMENTAL

2.1. Synthesis of nanostructures

Silver and bimetallic Ag/Zn nanoparticles were produced by chemical and by the laser ablation method. A pure metal of the Zn sample was placed in a glass and covered with 6 mL of previously synthesized Ag colloidal solution. Laser applied was the picosecond Nd:YAG system, operating at 1064 nm with a 150-ps pulse length, pulse energy 40 mJ pulse energy, and irradiation time of 15 minutes.

For the preparation of silver nanoparticles by the chemical method 1.98×10^{-2} M NaBH_4 , 3.8×10^{-3} M AgNO_3 , 0.1 M NaOH , and citric acid were used. A 30 ml 1.98×10^{-2} M NaBH_4 was poured into a glass, 0.1 M NaOH was added and the pH of the solution was adjusted to pH 10.5. Then the solution was placed in an ice bath and was stirring for 20 minutes. After that 10 ml of 3.8×10^{-3} M aqueous solution of AgNO_3 was added drop-wise into the cooled solution of NaBH_4 . Stirring was stopped immediately when the solution of AgNO_3 was being added. Finally, 0.008 g of citric acid was added into the Ag NPs solution.

The hydrodynamic size distribution of the obtained colloid solution of nanoparticles was analyzed by dynamic light scattering (DLS) technique using a Zetasizer Nano ZS90 (Malvern, UK) with 633-nm He-Ne laser and 90° detection optics. The concentrations of Ag, Zn, and Cu in these solutions were determined by the ICP-OES technique.

2.2. LIBS measurements

LIBS measurements were conducted using a unique developed LIBS system based on pulsed gas TEA CO_2 laser and time-integrated spatially resolved spectroscopy (TISR). In our previous study, we reported that aluminum alloy samples need to be mechanically treated with corundum abrasive paper to increase the absorptivity of applied TEA CO_2 laser wavelength before the LIBS analysis [Zivkovic 2017]. In this study, all aluminum samples were cleaned from the impurities on the sample surface, and after that samples were coated with a thin layer of nanomaterial dispersion droplets and dried at the end.

The plasma was generated by focusing a pulsed TEA CO_2 laser that emits at $10.6 \mu\text{m}$ on the aluminum target with deposited NPs on the surface at atmospheric pressure. All measurements were taken at the focal point. Applied laser energy was 170 mJ with a repetition rate of 1 Hz and the shot to shot fluctuation of its energy was about 5%. Optical emission from the induced plasma was collected on the entrance slit of a Carl Zeiss PGS2 monochromator by using an achromatic lens with magnification 1:1. LIBS analysis was conducted in time-integrated mode during 5 s using CCD Apogee Alta F1007 camera as a detector. The TISR measurements were performed at the atmospheric pressure in the air. All measurements were carried out in triplicate and obtained spectra present average values of line intensities from 3 different parts of the sample surface.

3. RESULTS AND DISCUSSION

3.1. Characterization of nanostructures

Obtained concentration from ICP-OES analysis for the used nanostructures alongside the size distribution are given in **Table 1**. In both cases, measurement uncertainties were calculated as the standard deviation.

Ag				Ag/Zn			
Size [nm]	Ag [ppm]	Zn [ppm]	Cu [ppm]	Size [nm]	Ag [ppm]	Zn [ppm]	Cu [ppm]
1.9 ± 0.7	29.1 ± 0.2	0.8 ± 0.1	< 0.002	574±45	3.5 ± 0.5	35.1 ± 0.1	< 0.002

Table 1. DLS (size) and ICP-OES (composition) results obtained for Ag and bimetallic Ag/Zn dispersions.

3.2 NELIBS analysis of aluminum samples

The LIBS spectra segments of the analyzed sample with a focus on the copper line are shown in **Figure 1**. Each spectrum represents an averaged spectrum from 5 laser pulses while the distance between the focusing lens and a target was constant at 1 mm in front of the target. When the pure sample was analyzed, not even one emission line was detected. At the same time, when the same sample has deposited nanoparticles on it, the emission lines of Ti and Cu from the sample were detected.

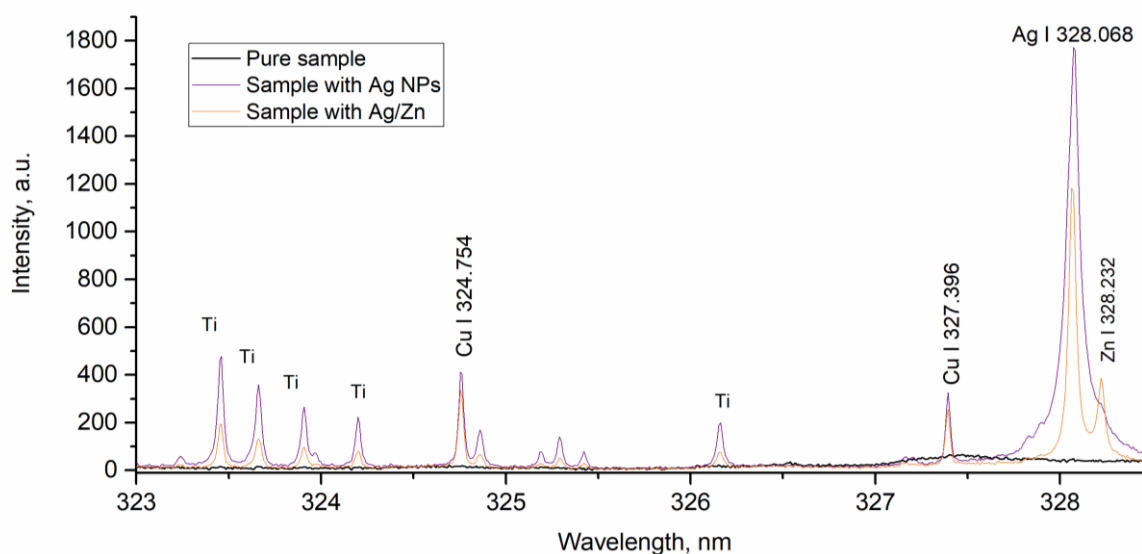


Figure 1. LIBS spectra obtained by analysis of: a) untreated sample; b) sample with Ag nanoparticles; and c) sample with bimetallic dispersion of Ag and Zn.

For determination limits of detection (LOD) of the applied technique, the standard calibration method was chosen. The linear dependency of measured LIBS intensity towards the concentration of Cu in samples was obtained, **Figure 2**. It shows the incensement of a slope when are 2 nm nanoparticles of silver were used, which corresponds to the incensement of method sensitivity. Using a formula $LOD = 3\sigma B/b$, where σB is the standard deviation of the background surrounding the selected

emission line, and b is the sensitivity defined as the slope of the calibration curve, we estimated that the limit of detection of Cu by NELIBS was 70 ppm.

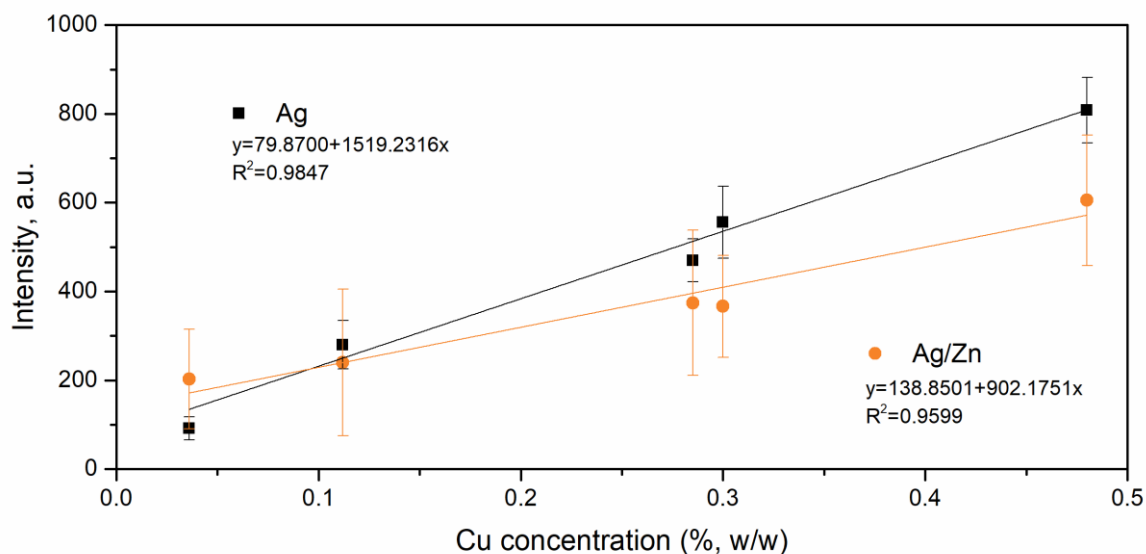


Figure 2. Calibration plots obtained from: a) LIBS analysis of Ag deposited onto Al sample (black); b) LIBS analysis of Ag/Zn deposited onto Al sample (orange).

4. CONCLUSIONS

In our experiment, the influence of nanoparticles application on a signal amplification in the LIBS spectrum was investigated. Nanoparticles were prepared in two ways, by chemical synthesis and laser ablation with Nd:YAG laser. The obtained nanoparticles were deposited to an aluminum target and exposed to TEA CO₂ laser radiation at atmospheric pressure. The recorded spectra show more signals from material with nanoparticles than from clean material. As shown in **Figure 1.**, a better emission signal was acquired using chemically obtained Ag nanoparticles. The developed and improved NELIBS technique for obtaining better emission signals has proven to be compact, easy to use and relatively stable, which can be applied in the analysis of materials.

5. ACKNOWLEDGEMENTS

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6. REFERENCES

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