NANOSTRUCTURES ASSISTED TEA-CO_2 BASED LIBS: IMPROVEMENT OF THE LIMITS OF DETECTION

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ABSTRACT

We report preliminary results of an innovative approach based on nanomaterials deposition on the sample surface for the improvement of the limit of the detection of Laser-Induced Breakdown Spectroscopy (LIBS) analysis of trace elements in aluminum alloys known as Nanoparticle - Enhanced LIBS (NELIBS).[1] For this purpose, Ag-TiO_2 bimetallic nanoparticles were synthesized and used to enhance the emission signal of laser-induced plasma.

EXPERIMENTAL

With the Pulsed Laser Deposition (PLD) method thin film is prepared by the simultaneous ablation of two targets: silver and titanium dioxide. As the thin film substrate pure silica is used. PLD was performed in vacuum using 5 ns Nd:YAG laser operating at 1064 nm, 300 mJ of output energy and repetition rate of 5 Hz. Laser pulses were focused onto the target yielding laser fluence of about 30 mJ/cm^2.[2]

Silver-titanium dioxide bimetallic (Ag-TiO_2) nanoparticles were produced by the laser ablation method. A thin layer film obtained by PLD was placed in a glass and covered with 10 ml of bidistilled water. Laser applied was the picosecond Nd:YAG system, operating at 1064 nm with a 150-ps pulse length, pulse energy 40mJ pulse energy, and irradiation time of 30 minutes. The 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 zeta potential was measured at pH 5 at 25 ± 0.1 °C in a disposable zeta cell (DTS 1070) of a Nano ZS90 device.

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).[3]
The plasma was generated by focusing a pulsed TEA CO_2 laser that emits at 10.6 μm on the aluminum target with Ag-TiO_2 NPs on the surface at atmospheric pressure. All measurements were taken at the focal point. Applied laser energy was 200 mJ with a repetition rate of 1 Hz and the shot to shot fluctuation of its energy was about 5%.

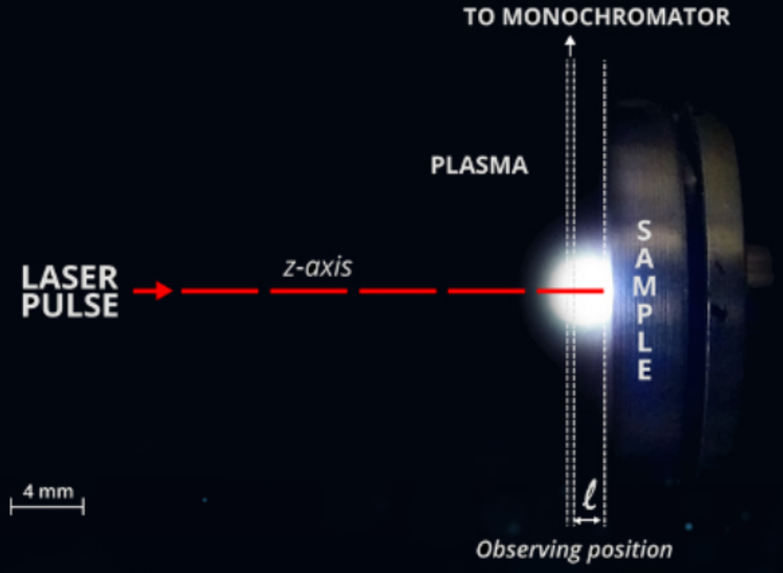

Figure 1: Photography of the plasma induced by focused TEA CO_2 laser beam at the aluminum alloy target in the air at atmospheric pressure with schematic representation showing sections of the plasma plume that were imaged onto the entrance slit of the monochromator.

RESULTS

Uniformity of the PLD thin film was confirmed by the LIBS method. Average spectra consist of several Ti I and Ti II lines and Ag I emission line, Figure 2.

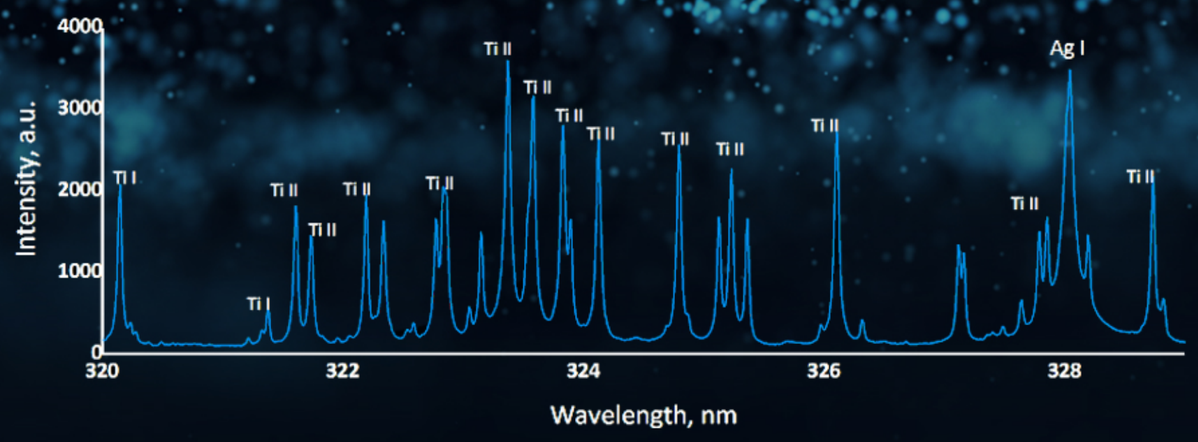

Figure 2: LIBS analysis of Ag:TiO_2 thin film

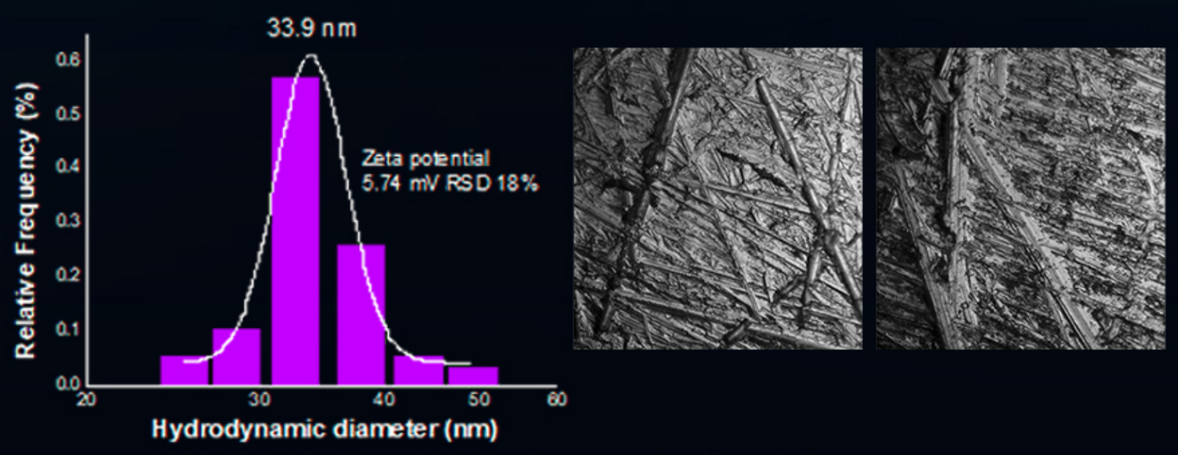

Figure 3: a) Size distribution of NPs; b) NPs dispersion layer applied on a sample surface (before and after, magnitude 80x)

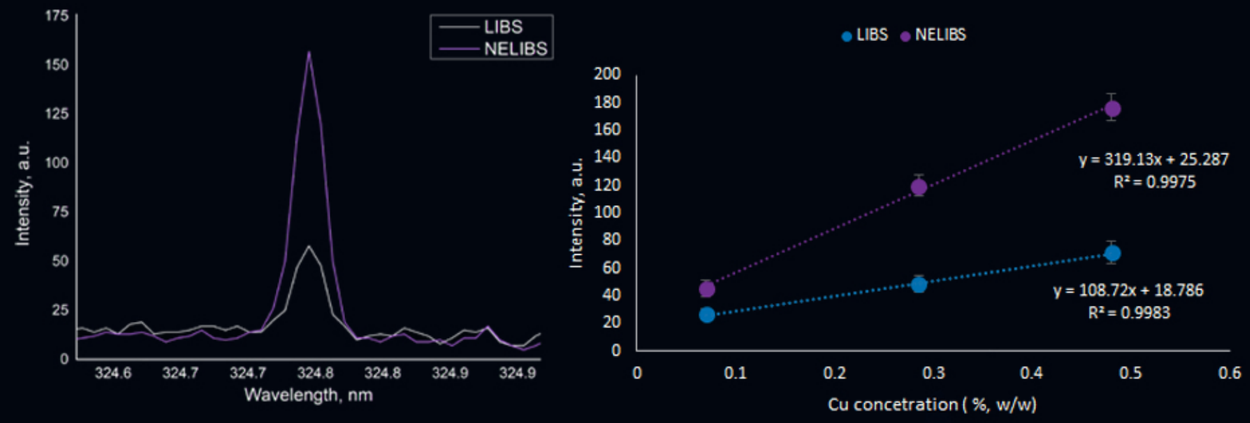

Figure 4: a) Segments of LIBS spectra with focus on Cu I 324.754 line; b) Calibration plots for two applied techniques

Using a formula LOD = 3σB/b, where σB is the standard deviation of background surrounding the selected emission line, and b is the sensitivity defined as the slope of the calibration curve, we estimated that $NELIBS_{LOD}$ is 2.5 times less than $LIBS_{LOD}$.

We believe that some methods could additionally lower the LOD: (1) optimized conditions to obtain thin film by PLD (2) the LIBS spectral characteristics will be improved by optimization dimensions of bimetallic nanoparticles. We will further study the above methods and present the results in our future publications.

References

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