# Synthesis of Bimetallic Germanium-Copper Oxide Nanoparticles by Pulsed Laser Ablation in Liquids: Potential Application for LIBS Signal Enhancement

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## Abstract

In this work, signal enhancement of the original TEA $CO_2$ LIBS setup was studied. Bimetallic Germanium-Copper Oxide nanoparticles were synthesized, characterized and used for Nanoparticle-Enhanced Laser-Induced Breakdown Spectroscopy (NELIBS) of an aluminum sample.

Preliminary results have shown that an improvement in the analytical sensitivity for the detection of Mg in aluminum was yielded.

## Experimental

A thin germanium film was deposited onto a copper substrate by pulsed laser deposition (PLD) in vacuum, using an Nd:YAG laser (λ = 1064 nm, ≈300 mJ per pulse, 5 Hz repetition rate, 4 ns duration), with the target and substrate placed ~1 cm apart and rotated continuously for uniform coating, over 3000 pulses. The resulting material was then used to fabricate nanoparticles using the laser ablation technique in liquids.

This target was immersed in 3 ml of Milli-Q water, and the surface area of approximately 25 mm² was continually scanned by a pulsed laser beam to achieve homogeneous ablation of the sample using an Nd:YAG laser (7 mJ, 10 Hz, 150 ps pulse duration, wavelength of 1064 nm).

Characterization of the formed bimetallic nanocolloids was performed by measuring the SPR band using UV-VIS spectrophotometry and TEM microscopy.

Additionally, nanoparticles were used for Nanoparticle-Enhanced Laser-Induced Breakdown Spectroscopy (NELIBS) of an aluminum sample. LIBS measurements were performed using a TEA $CO_2$ laser-based setup with an Avantes spectrometer and optical triggering. A bimetallic nanocolloid solution was applied using the drop-and-dry technique [1].

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## References

[1] M. Momcilovic, J. Petrovic, M. Nemoda, J. Ciganovic, N. Krstulovic, M. Ognjanovic, S. Zivkovic, Appl. Phys. B 129, 62 (2023)..

## Results

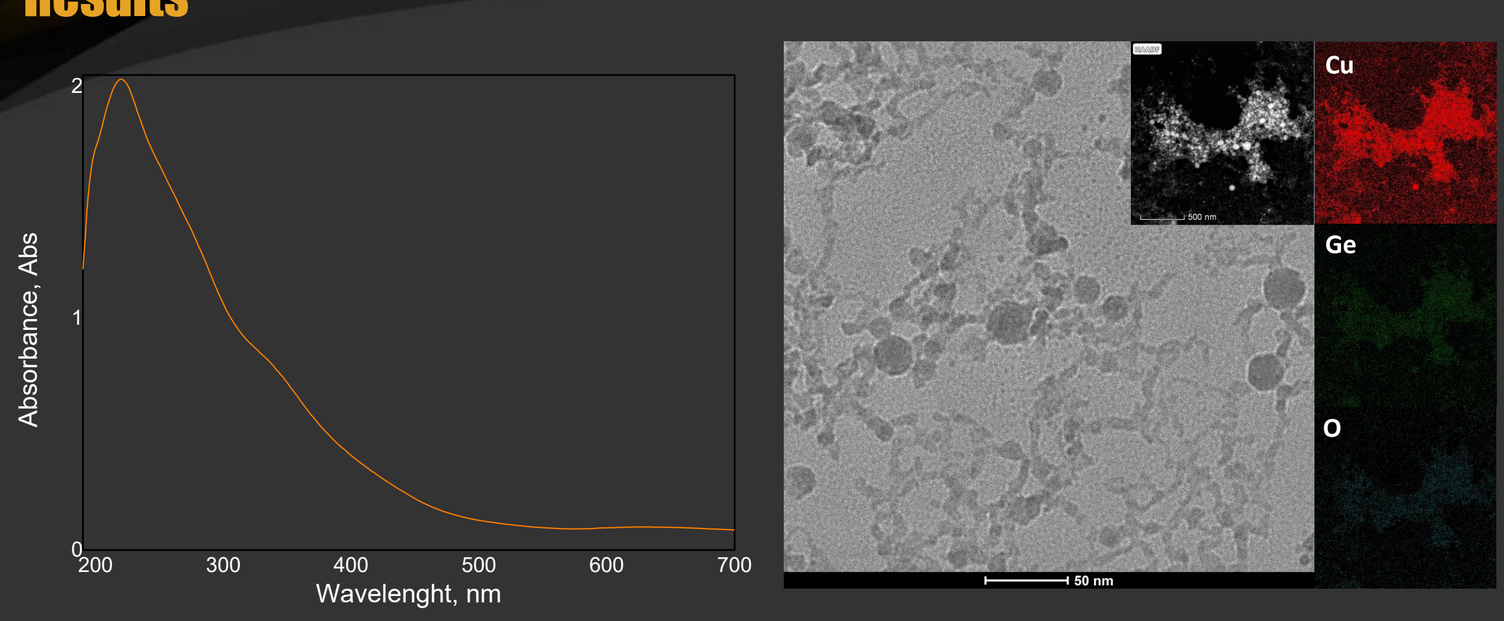


*Figure 1: Characterization of bimetallic nanoparticles: a) UV-VIS spectrum b) TEM micrograph with EDS layered images*

Formation of nanoparticles was confirmed by UV-VIS spectroscopy and TEM microscopy. The SPR band for copper oxide nanoparticles is typically observed in the UV-Vis spectrum between 250 and 600 nm, while the SPR of Ge nanoparticles can be observed in the NIR spectrum. EDS layered images confirmed that the obtained nanoparticles are bimetallic.

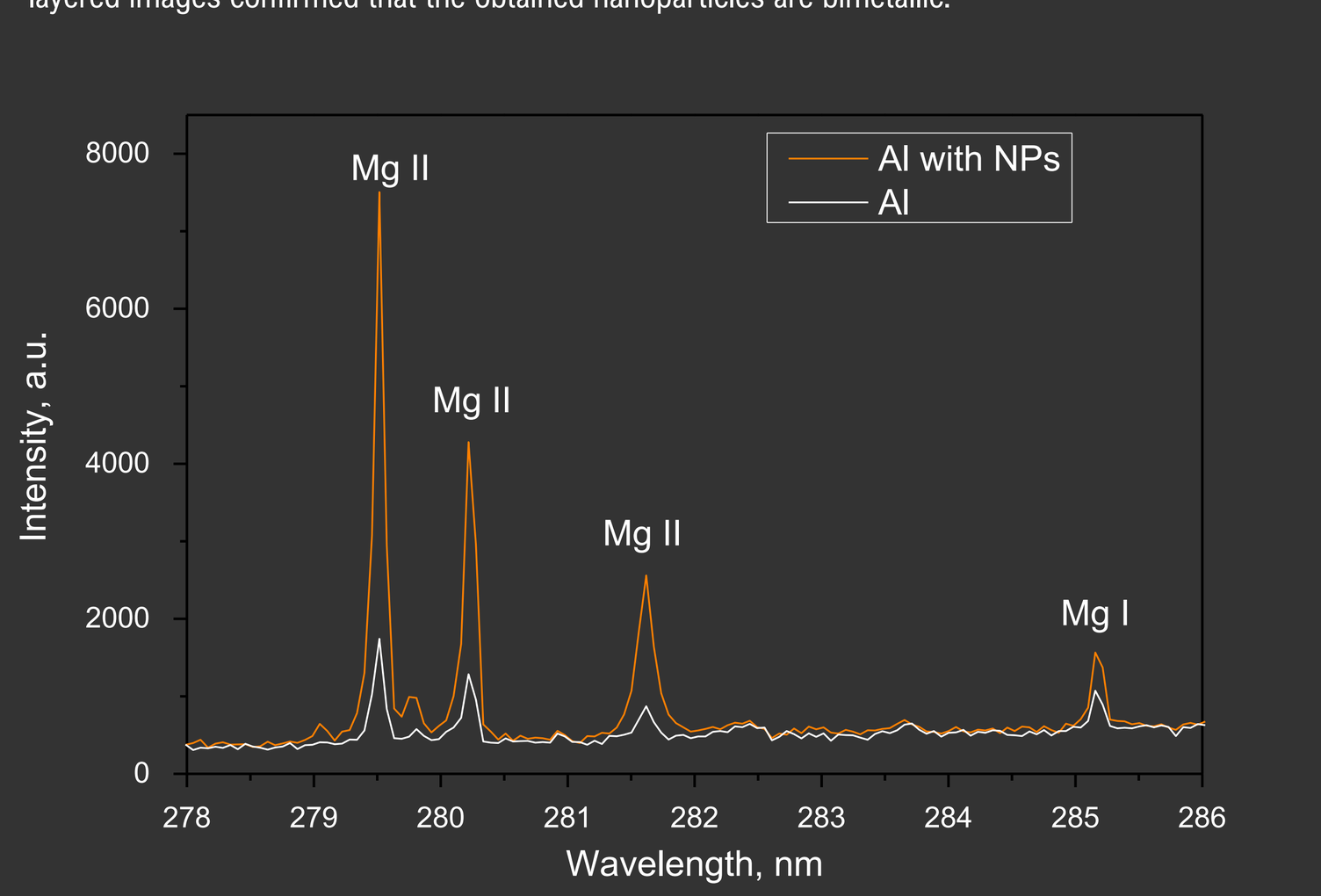


*Figure 2: LIBS spectra of the analyzed aluminum sample*

The LIBS spectra segments of the analyzed sample, with a focus on the Mg lines are shown in Figure 1.

The limit of detection (LOD) was calculated using the formula LOD = (3 × c) / SNR, and we estimated that NELIBS with bimetallic nanoparticles can produce an enhancement of the analyte emission signal up to 5 times. Furthermore, based on the calculated LODs, this method can lower the limits of detection from 181 to 36 mg/kg.

## Conclusions

The obtained results showed that Bimetallic Germanium-Copper Oxide nanoparticles can be applied for the enhancement of the emission signal of magnesium emission lines.

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