

NANOPARTICLE DEPOSITION BY SPRAY COATING FOR ENHANCED ELEMENTAL MAPPING OF ROCK SAMPLES BY LASER-INDUCED BREAKDOWN SPECTROSCOPY

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Abstract

A novel method development of laser-induced breakdown spectroscopy (LIBS) uses nanoparticles deposition on the sample surface and achieves significant signal improvement (nanoparticle-enhanced LIBS, NELIBS). The present research aims at developing a reproducible method of nanoparticle deposition that would allow spatially resolved NELIBS elemental mapping of solid samples with an improved signal-to-noise ratio. The applicability of the method is demonstrated on a monzogranite rock sample.

Introduction

LIBS is a micro-analytical technique that uses short laser pulses as an energy source to produce a microplasma on the surface of a solid sample, which breaks down sample material and thermally excites the atoms generated to produce an atomic emission spectrum. Nowadays LIBS is being applied in many research fields due to its unique set of characteristics. It is a rapid, sensitive, versatile analytical method, which provides quantitative (ppm level) or qualitative information about the sample, is micro-destructive and requires practically no sample preparation, therefore allows fast and direct analysis of solid and liquid (even gaseous) samples in a non-contact manner. Furthermore, the application of chemical imaging methods or elemental mapping provides a spatial distribution of a single chemical species within a complex sample, obtaining information in the form of 2D (or 3D) images and also offering a high degree of discrimination between different sources [1-3].

Several novel approaches have been proposed for the signal enhancement in LIBS in recent years [3]. Some of them include instrumental arrangements, such as double- or multi-pulse LIBS, microwave assisted- or resonance-enhanced LIBS, but the nanoparticle-enhanced LIBS approach simply uses a deposition of plasmonic nanoparticles (NPs) on metal sample surfaces [4, 5]. The conceptual basis of this approach is that the plasmonic characteristics of the Au, Ag or Cu NPs will largely increase the electrical field strength of the laser pulse in their close vicinity, which leads to the field emission of electrons from the metallic NPs. These electrons will then facilitate the laser induced breakdown plasma generation as seeds, thereby significantly lowering the breakdown threshold and reserving more of the laser pulse energy for plasma heating, which eventually leads to higher analytical atomic emission signals. Figure 1 illustrates this effect [6].

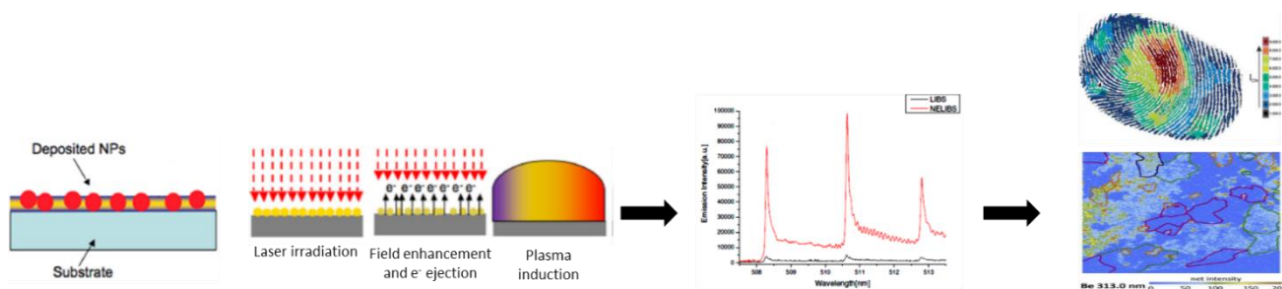


Figure 1. Sketch of NPs enhanced photoablation in metallic samples [5]

Although NELIBS has been successfully demonstrated as a useful signal enhancement approach for local analysis of solid and liquid samples [7, 8], when simple droplet deposition is applied. NELIBS elemental mapping has not yet been shown to work, due to known problems with the homogeneity of NP distribution with droplet deposition (coffee spot effect). At the same time, LIBS is recently being increasingly explored by geologists and the mining and mineral processing industry. LIBS geochemical analysis is generally directed towards quantitative analysis of the elemental contents of rocks/minerals and identification of the minerals (e.g. mapping of geochemical and mineralogical footprints) [9]. In the present work we set the goal of investigating the applicability of the spray coating nanoparticle deposition method for NELIBS elemental mapping on a monzogranite rock test sample.

Experimental

In the deposition experiments, a 0.05 mg/mL dispersion of Pelco NanoXact 30 nm Au NPs (Ted Pella, USA) was sprayed onto a 10 x 10 mm diced silicon wafer (Ted Pella, USA). The deposition was carried out by a commercial spray gun (DU-30 K) equipped with a 200 μm nozzle and by employing a 3 bar pressure of argon gas. Surface particle concentration was controlled by the spraying times: 10, 25, 50 and 100 s. The sample was kept at a distance of 25 cm from the nozzle and the spraying was followed by one-minute drying under an infrared lamp. Optical microscopy images of the deposition were taken afterwards with an Olympus BX-43 microscope.

Particle distribution of Au NPs resulting from spray deposition were characterized by scanning electron microscopy (SEM, S-4700, Hitachi, Japan). The quantification of the surface mass concentration of NPs was determined by inductively coupled plasma mass spectrometry (ICP-MS, 7700x, Agilent Technologies, USA). 1 cm x 1 cm Si chips were masked with electrical adhesive tape before the deposition experiments in order to ensure that only the exposed, known surface of the substrate were covered by NPs. After the deposition the chips were subjected to aqua regia (trace quality cc. hydrochloric and cc. nitric acids, VWR Chemicals) treatment, which dissolved the gold NPs. Matrix-matched calibration for the surface area quantification was performed using certified calibration standards (IV-ICPMS-71A and IV-ICPMS-71C, Inorganic Ventures, USA) in the range of 0 ppb – 100 ppb, with the application of ^{209}Bi as internal standard. All measurements were carried out by monitoring the signal of the ^{197}Au isotope.

The rock samples were prepared in such a way that from each sample, a 30 mm thin section was cut employing a diamond cutter (Struers DiscoPlan) to form 35 x 20 x 10 mm rectangular bodies for mineral identification by optical microscopy (Olympus BX-43) and the remaining part of the bulk sample was diamond-polished for LIBS analysis. The elemental map was recorded using a J-200 tandem LA/LIBS instrument (Applied Spectra, USA), with a laser spot size of 40 μm , 266 nm laser wavelength and 17.5 mJ pulse energy. Stepwise scanning was employed and the emission spectrum in the 190 to 1040 nm range was collected. The number

of repeated measurements in one sampling location (without translation) was ten. Measurements were performed at 4–5 sampling points in each mineral grain.

Results and Discussion

Spraying, as a general technical coating procedure, produces a relatively homogenous distribution of droplets on the surface of a solid target (Figure 2, left), consequently we also expected a homogeneous distribution of NPs on the surface after drying, but we carried out a detailed morphological investigation of the depositions. SEM revealed that there is a tendency of NP aggregation (Figure 2, right), which results in an „island-like“ deposition pattern. This has already been observed for spray coating in the literature [10], and key factors were also identified that determine the quality of a spray-coated „layer“. These are the size and dimensional uniformity of droplets in the spray and the droplet impact velocity. Due to the presence of the liquid phase, there still is a chance that the deposited microdroplets coalesce before they dry, which strongly increases the probability of particle aggregation. It also has to be added that the intuition to strongly lower the NP concentration in the sprayed liquid would result in a longer spraying time in order to achieve the required surface mass concentration, which again would increase the probability of microdroplet coalescence, due to the action of surface tension and gravity.

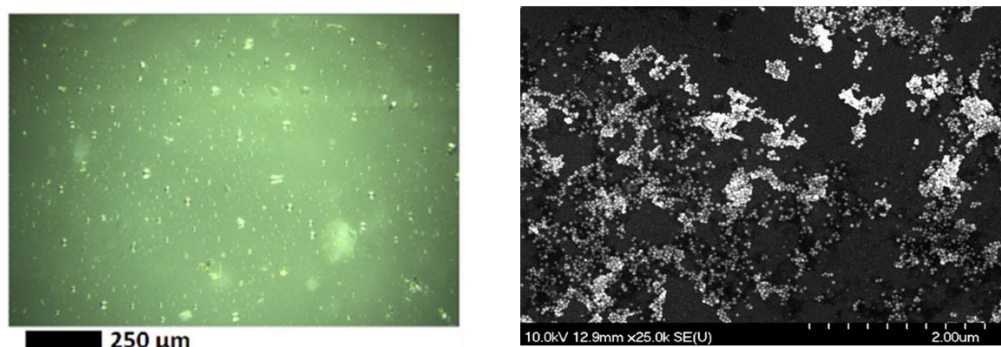


Figure 2. Optical microscopy (left) and SEM image (right) of a solid sample surface spray-coated with NPs. Please note that the left image shows the droplets deposited before drying, whereas the right image was taken after drying.

Optimization of NELIBS conditions requires a control of the surface mass concentration of deposited nanoparticles [4, 5]. For spray coating the control parameter is the nanodispersion concentration and the spraying time. As it can be seen in Figure 3, the surface concentration range we achieved was from 0.287 to 0.942 $\mu\text{g}/\text{cm}^2$. As the time increased, the surface density of NPs increased monotonously, following a linear function for the spray coating deposition. The regression coefficient was 0.7 which indicates a low control of surface concentration, which is probably due to the random coalescence or dripping of the deposited microdroplets. Nevertheless, the optimal mass concentration suggested in the literature [4, 5] could be set on the surface by this process.

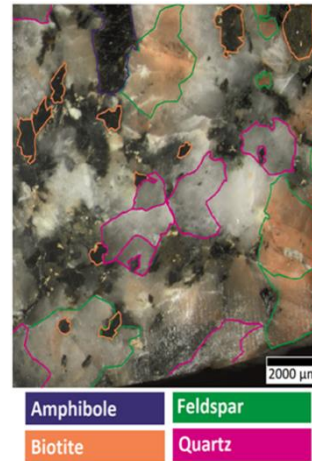
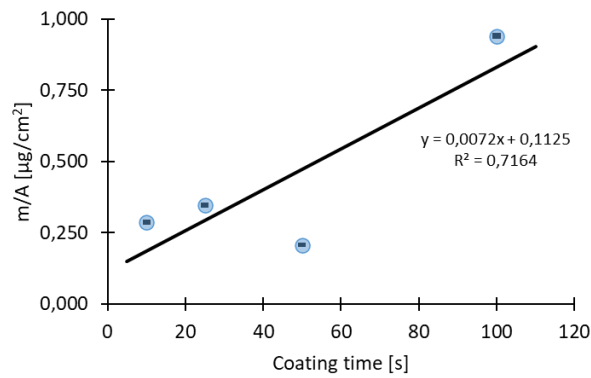


Figure 3. Control of the surface concentration of deposited NPs by spray coating, as quantified by ICP-MS analysis.

Figure 4. Reflective optical microscopy image of the rock sample with four minerals indicated by colors.

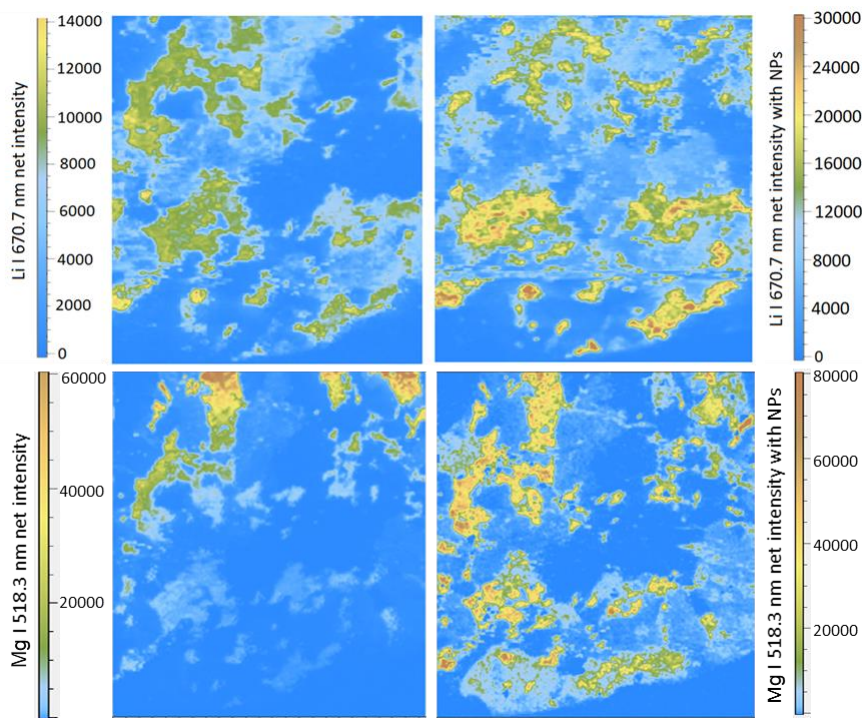


Figure 5. Intensity-based LIBS elemental maps of a granitoid rock (10 x 15 mm area). Showing Li I 670.7 nm and Mg I 518.3 nm elemental maps of sample without NPs (left side) and with NPs (right side).

Granitoid rocks are of industrial interest, as they contain mineral grains with mining-worthy concentrations of Li [9]. The four most common mineral grains in the sample were identified as amphibole, feldspar, biotite and quartz (Figure 4). Subsequently, we tested the optimized spray deposition process (a dispersion of 0.05 mg/mL of Au NPs, spraying in five repetitions each consisting of five seconds of spraying, with a NP surface concentration of 0.347 $\mu\text{g}/\text{cm}^2$ on the rock). In order to ensure comparability of the two maps, we first recorded

the LIBS map and then applied the spray deposition of gold NPs and performed the NELIBS mapping.

We present two elemental maps for the studied rock sample in Figure 5; the Li map is shown for the spectral line of Li I 670.78 nm, whereas the Mg map is shown for Mg I 518.3 nm. As can be seen, the LIBS mapping of the granitoid rock provides information about the distribution of Li and Mg within the mineral rock; therefore, it is possible to identify the type of mineral that contains most of the targeted trace elements. By the comparison of Figure 4 and 5, it can be observed that biotite and amphibole minerals contain the most Li and Mg. These results suggest that mining for Li in granitoid rocks should be aiming for biotite and amphibole grains. An about two-fold signal enhancement could be achieved by NELIBS. The signal enhancement allowed us to detect mineral grains with smaller concentration of the elements too. For example, quartz, feldspar and biotite grains with low Mg content would also be detected (in the lower left quadrant of the image) when the NELIBS approach was used.

Acknowledgements

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