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PERSPECTIVE ON THE USE OF NANOPARTICLES TO IMPROVE THE TEA CO_2 BASED LIBS ANALYTICAL PERFORMANCES: COPPER NANOPARTICLES FOR NELIBS ANALYSIS OF POLYPROPYLENE

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Abstract. In this work, signal enhancement of the original TEA CO_2 LIBS setup was studied. Two different methods for copper nanoparticle synthesis were applied. Obtained nanoparticles were characterized and then used for Nanoparticle-Enhanced Laser-Induced Breakdown Spectroscopy (NELIBS) of plastic polypropylene. Preliminary results have shown that improvement in the analytical sensitivity for the detection of Cr in plastic materials was achieved.

1. INTRODUCTION

Laser-Induced Breakdown Spectroscopy (LIBS) is a modern method of analytical chemistry that uses an optical signal from laser-induced plasma to study the elemental composition of materials. Thanks to its unique features, LIBS has found numerous and diverse applications, from control of industrial processes, through diagnostics of cultural heritage objects and biomedicine to space research. On the other hand, application of LIBS is limited with respect to other standard spectrochemical techniques (ICP-OES, AAS) by a strong matrix effect, poor repeatability, and relatively weak sensitivity and therefore much effort has been put into improving the capabilities of LIBS in recent years. Recently, a new method of signal enhancement has emerged as a possible solution. This promising variant of the LIBS technique, namely Nanoparticle-Enhanced LIBS (NELIBS) is based on the use of nanoparticles (NPs), which can be used to control the laser-matter interaction by directly affecting better coupling of incoming laser electromagnetic

field with the irradiated material. In this work, Cu nanoparticles, synthesized by chemical method and by laser ablation in liquids, were applied to the analysis of Cr in polypropylene sample.

2. EXPERIMENTAL

2.1. Copper nanoparticles synthesis

Chemical method: For the synthesis of copper nanoparticles, 50 mL of 0.2 M $CuSO_4x5H_2O$ and 0.4 M $NaBH_4$ were prepared. Using NaOH, the pH was adjusted to 12 for these two solutions. PVP was used as a stabilizer, which helps prevent direct contact of particles and their aggregation when the conditions of the solution change or when the particles dry on the substrate. Therefore, 1% PVP (40 kDa) was made and added to the previously prepared $CuSO_4$ solution. The $NaBH_4$ solution was then added dropwise to the $CuSO_4$ solution in a beaker on a magnetic stirrer at 40 °C. The stirring continued for the next hour. The color of the mixture changed from blue to brown during heating and stirring, indicating that Cu nanoparticles precipitated.

Laser ablation in liquids: A pure copper target was immersed into the 25 ml of Milliq water and placed about 2.5 cm under the water surface. The surface of approximately 1 cm^2 in size was continually scanned by a pulsed laser beam in order to achieve homogenous ablation of a sample. The total number of pulses for irradiation of each sample was 5000 using the Nd:YAG laser (300 mJ, 5 Hz, 5 ns pulse duration, wavelength of 1064 nm, Quantel, Brilliant). The laser beam was focused by 10 cm lens in order to enhance ablation.
Characterization of formed nanocolloids were performed with the measurement of SPR band using a UV-VIS spectrophotometer (*LLG-uniSPEC 4 UV/VIS-Spectrophotometer*). Also, NP concentration as an important parameter for signal enhancement was determined by ICP-OES spectrometer (*Thermo Scientific iCap 7400 duo*).

2.2. LIBS setup and NELIBS experiments

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). The polypropylene sample was prepared in duplicate. With a micropipette, the same amount of nanoparticles was added in a thin layer to each sample and then dried. The plasma was generated by focusing a pulsed TEA CO_2 laser that emits at 10.6 μm on the sample with copper NPs on the surface at atmospheric pressure. Applied laser energy was 170 mJ with a repetition rate of 1 Hz and the shot-to-shot fluctuation of its pulse 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 achromat objective with a magnification of 1:1. LIBS analysis was conducted in time-integrated mode during 3s using CCD Apogee Alta F1007 camera as a detector. The TISR measurements were performed, and all measurements were carried out in triplicate. The obtained spectra present average values of line intensities from 3 different parts of the sample surface.

3. RESULTS AND DISCUSSION

The LIBS spectra segments of the analyzed sample with a focus on the chromium line are shown in Figure 1. The reason for the monitored chromium in the polypropylene sample is that it appears as one of the elements in the Ziegler-Natta catalyst for the synthesis of polypropylene for a variety of applications. Considering that TISR method utilizes the fact that intense continuum emission is mostly emitted from a region close to the sample surface, the best signal to background (SBR) value was achieved by changing the viewing position of plasma along its expanding direction toward the laser beam. Distance between the focusing lens and a target was constant and optimal SBR ratios were obtained at 0.5 mm in front of the target.

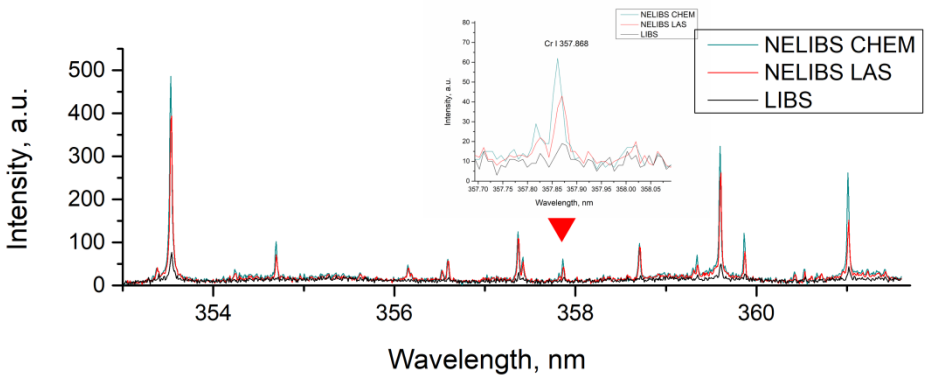

Figure 1: LIBS spectra of analyzed polypropylene sample

The limit of detection (LOD) was calculated using the formula LOD = (3 × c) / SNR, where c is a known analyte concentration of Cr obtained by the ICP-OES method, and signal-to-noise ratio (SNR) is the absolute intensity of the integrated peak area A, divided by the width of the peak area w, times the absolute value of the rms noise, SNR = A / (w × rms). Based on the results, we estimated that NELIBS based on chemical NPs can produce enhancement of the analyte emission signal up to 4.6 times, while laser NPs can produce up to 3.2 times. Furthermore, based on the calculated LODs, this method can lower the limits of the detection up 5 or 3 times, respectively. In our future publications, we will study in detail the improvement of analytical possibilities for multielement analysis by optimization of size and concentrations of NP and as well as deposition of NP on the plastic surface.

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