

Optimization of Laser-Induced Breakdown Spectroscopy (LIBS) for Determination of Quantum Dots (QDs) in Liquid Solutions

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Abstract—Here we report on the utilization of Laser-Induced Breakdown Spectroscopy (LIBS) for determination of Quantum Dots (QDs) in liquid solution. The process of optimization of experimental conditions from choosing the carrier medium to application of colloid QDs is described. The main goal was to get the best possible signal to noise ratio.

The results obtained from the measurements confirmed the capability of LIBS technique for qualitative and afterwards quantitative determination of QDs in liquid solution.

Keywords—Laser-Induced Breakdown Spectroscopy, liquid analysis, nanocrystals, nanotechnology, Quantum dots.

I. INTRODUCTION

QDs are light-emitting semi-conducting nanocrystals with great potential for utilization in imaging protocols [1]. QDs are commonly studied using standard optical devices. However, Laser-Induced Breakdown Spectroscopy (LIBS) analytical technique [2] has not been used for this purpose in spite of the fact that LIBS could cast the light on qualitative and quantitative properties of produced nanoparticles. In this study, we focused on Double Pulse LIBS (DP LIBS) analysis of CdS and CdTe quantum dots using Nd/YAG laser. Based on the optimization steps, spectral lines 508.58 nm for cadmium and 276.67 nm for tellurium were selected in our experiments.

After we optimized experimental conditions, we compared qualitative and quantitative occurrence of elements in materials used as matrices for our experiments such as silica

gel spread on aluminum foil, nitrocellulose, polyvinylidene fluoride membrane, chromatographic paper, filtration paper, pure cellulose and paper. Chromatographic paper demonstrated the most suitable properties for further experiments due to higher signal to noise ratio and lowest content of contaminants. Furthermore, application of colloid QDs was carried out under vacuum into strictly defined raster (96 spots for samples) using the dot blot system. For the uniform distribution of sample and for the determination of dependence of emission intensity on applied volume, 1, 2 and 5 μ l volumes of CdS and CdTe QDs samples were tested.

II. EXPERIMENTAL SETUP

The necessary instrumentation can be summarized as a short duration pulsed laser, a focusing lens, collecting optics for the emitted radiation, a wavelength analyzer and a detector, all computer controlled [3]. One of the suggested approaches to improve LIBS sensitivity is the double pulse configuration. The aim of the double-pulse approach is to increase LIBS performance through better coupling of laser energy to the target and ablated material, leading to more efficient production of analyte atoms in the excited state.

As mentioned above, we used two different experimental arrangements using double-pulse LIBS technique in our investigations. Both arrangements use two Q-Switched Nd:YAG lasers, however, different laser wavelengths, collimating system and type of spectrometer were used.

Experimental setup at Masaryk University

The first laser, which irradiates the sample surface was Nd:YAG laser operating at fourth harmonic frequency 266 nm (New Wave, UP-266 MACRO) with the energy of 10 mJ per pulse. This laser ablation device incorporates 30 to 750 μ m expandable, aperture-imaged beam delivery system. The laser system UP-266 MACRO was equipped with a sample holder with software-controlled movement in x,y direction and hand-controlled z direction movement. The slide with a sample was firmly fixed on the holder and measured in the air at atmospheric pressure. As the second, re-heating laser system, that propagates beam parallel to the sample surface was used Quantel, Brilliant Nd:YAG laser at fundamental wavelength 1064 nm and energy 100 mJ per pulse. This laser was focused by 80 mm focal length glass lens to intersect the path of the first laser beam and finally to create a coincident spark about 0.5 mm above the sample surface.

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Both lasers were externally triggered by two delay generators (Stanford Research Systems, DG 645). The first generator initialized with the control pulse from the flash lamp of UP-266 MACRO laser module was used to trigger the flash lamp of the first laser (UP-266 MACRO) and the second laser (Quantel, Brilliant). The second generator was handled by Q-switch control pulse of UP-266 MACRO laser module and was utilized to trigger Q-switches of both lasers. The delay of opening the second laser's Q-switch after the first one determines the inter-pulse delay. For our samples 500 ns was established as the optimal inter-pulse delay. The second generator was also used for ICCD detector triggering. The energy of the laser was measured with laser power/energy meter (Nova, Ophir). The plasma emission was collected and transported by means of 3 m long optical fiber into the entrance of a monochromator (JobinYvon, TRIAX 320) (grating 2400 grooves. mm^{-1} , 50 μm entrance slit) and detected with the ICCD detector (JobinYvon, Horiba). The delay of the ICCD detector was 10 μs and the integration time was 1 μs . The spectral resolution of JobinYvon TRIAX with this grating was 0.028 nm.

Experimental setup at Brno University of Technology

Geometric configuration of laser pulses was orthogonal like at Masaryk University. The beam of ablation laser was directed normal to the surface sample by mirrors and focused onto the sample surface by a 30 mm focal length glass triplet. The beam of second laser was directed parallel to the sample surface to the plasma using mirrors and focusing lens of 40 mm focal length. The setup is composed of two Q-switched Nd:YAG lasers both operating at 10 Hz. LQ 529a (SOLAR, BY) operated at the second harmonic (532 nm) with pulse width ~ 10 ns was used as the ablation source and Brilliant B (Quantel, FR) at first harmonic (1064 nm) with pulse width ~ 6 ns was used for reheating the plasma. The energy of primary/ablation laser pulse was 12 mJ per pulse and the energy of secondary/re-excitation laser pulse was 110 mJ per pulse.

The sample was mounted on a stage with precision movements (2 μm resolution) inside the ablation chamber (Tescan.s. CZ). The ablation spot was targeted and controlled by a CCD camera placed outside of the ablation chamber.

The LIBS plasma radiation was collected with UV-NIR achromatic collimating mirror system, the CC52 (ANDOR, UK) and transported by a fiber optic system (25 μm in diameter) onto the entrance of spectrometer in echelle configuration (ME5000, Mechelle, ANDOR, UK). As the detector ICCD camera (iStar 734i, ANDOR, UK) was employed.

The time-resolved studies were performed by controlling the gate width t_w (time during which the spectra are integrated), the gate delay time t_d (time at which the spectra are acquired by the detector) and the delay between the two pulses Δt . Both lasers and ICCD camera were triggered by delay generator (DG535, Stanford Research System, US) and specially developed electronic switch and controlled via computer equipped with laboratory-made software.

In this case the time was optimized to obtain the best signal to noise ratio and adjusted at $t_w = 16 \mu\text{s}$, $t_d = 1.5 \mu\text{s}$ and $\Delta t = 1.5 \mu\text{s}$.

III. RESULTS AND DISCUSSION

A. Selection of Carrier Medium

The LIBS target/sample can be solid as well as liquid or gas[3].

QDs are prepared as particles floating in liquid medium so it has to be ensured that they are deployed equally during the time of experiment in the whole volume. There are two possibilities how to achieve this: circulate the medium or deposit the liquid medium on some kind of carrier medium.

For circulation of medium it is necessary to have relatively big amount of liquid (~ 20 ml). On the contrary, application of liquids on suitable carrier medium needs small amount of sample ($\sim 1 \mu\text{l}$) and also it can be more easily manipulated.

Materials suitable for carrier medium have to comply with following parameters – chemical stability, high absorption, well-defined elemental composition (the most important is that any spectral line of included elements does not interfere with spectral lines of elements of interests), low costs and easy manipulation.

In this work we focused on following materials: polyvinylidene fluoride membrane, nitrocellulose chromatographic paper, silica gel spread on aluminum foil, filtration paper, pure cellulose and paper. Comparison of typical spectrums of carrier mediums with magnification of region of interests (Cd 508.58 nm and Te 276.67 nm) is presented in Figs. 1-5.

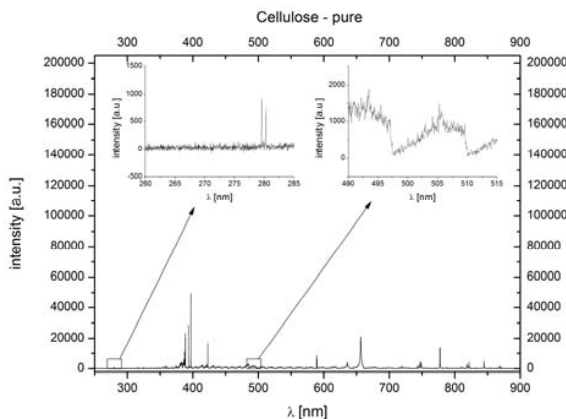


Fig. 1 LIBS spectrum of pure Cellulose

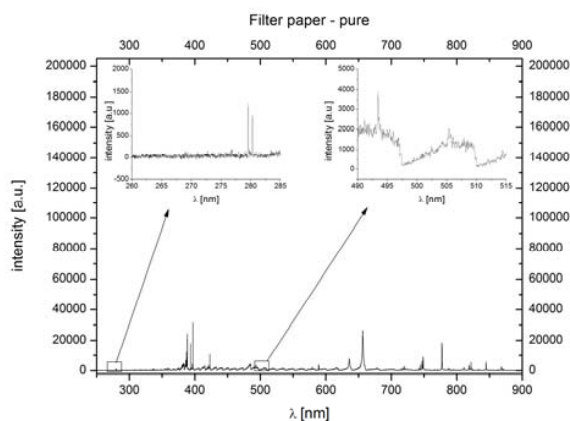


Fig. 2 LIBS spectrum of pure Filter paper

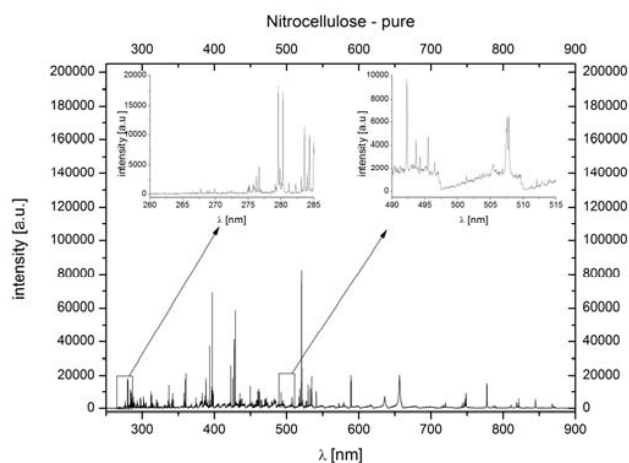


Fig. 4 LIBS spectrum of pure Nitrocellulose

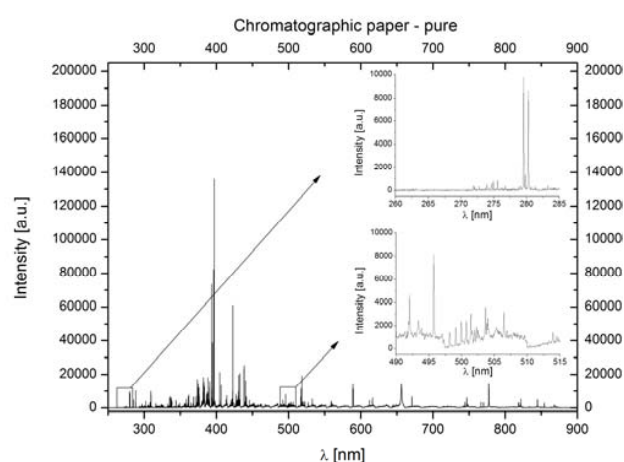


Fig. 3 LIBS spectrum of pure Chromatographic paper

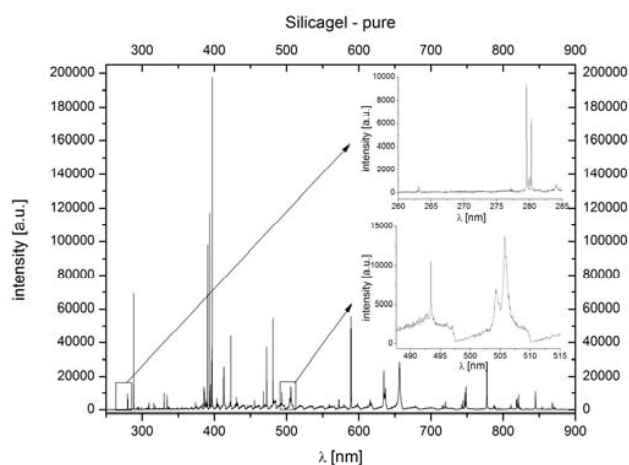


Fig. 5 LIBS spectrum of pure Silicagel

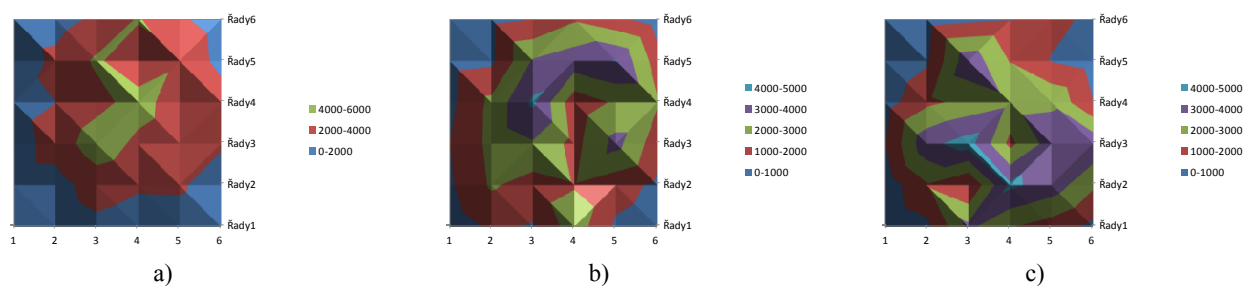


Fig. 6 Distribution of nanoparticles (CdS) on chromatographic paper (tracked spectral line was Cd I 508.58 nm) for volume a) 1 μl, b) 2 μl, c) 5 μl. Color scale exhibit the Cd I 508.58 nm line intensity in a.u

B. Application of Colloid QDs

To ensure reproducibility of the experiments, some basic conditions must be observed – the position of sample on the carrier medium must be well-defined, every single sample must have the same concentration in every position (uniform sample distribution on carrier medium) and the sample volume necessary to carry out the measurements should be as small as possible.

With respect to conditions mentioned above, vacuum sample application with Biorad system was chosen. This technique allows application of the sample to exactly defined raster of 12x8 spotsize. The sample application was tested for three different volumes - 5 μl , 2 μl and 1 μl .

Fig. 6 shows sample distribution for all sample volumes. The diameter of sample spot was 4 mm and the measured region was 6x6 mm with step 1 mm in both axes. It is clearly visible that with increasing volume the sample homogeneity is decreasing. For sample volume of 5 μl is the influence of diffusion most significant.

Fig. 7 shows the comparison of LIBS spectrum for sample volume 2 μl and 1 μl .

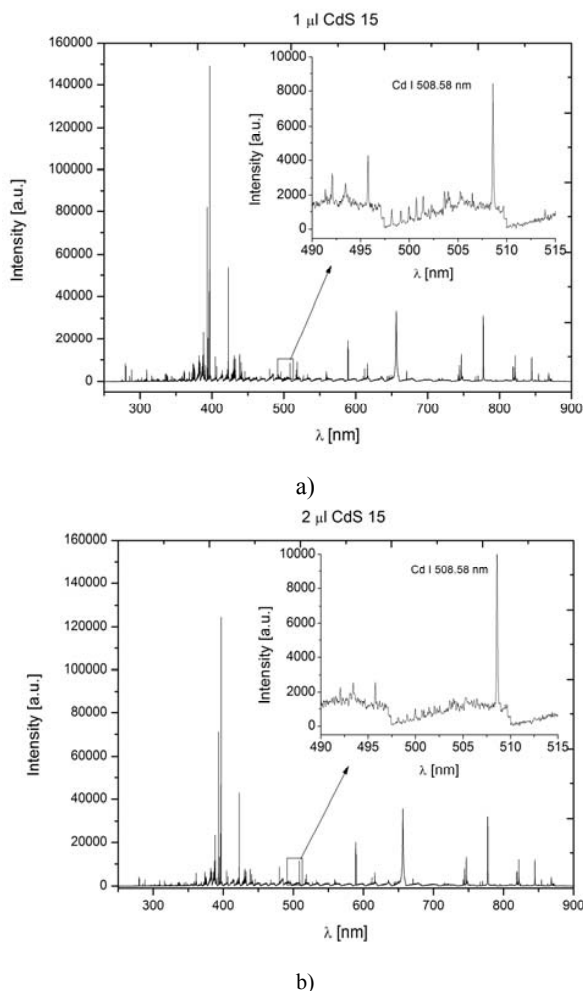


Fig. 7 Comparison of LIBS spectrum for QDs sample of 1 μl and 2 μl volume. Adopted from [4]

In the spectra it is visible that for 2 μl volume of the sample the increase of signal to noise ratio is only approximately 20% with respect to the 1 μl volume. Because of the sufficient signal to noise ratio and in order to minimize the sample consumption, in the following experiments the volume of 1 μl was chosen.

C. QDs analysis

The spectral lines of elements of interests (Cd, Te) were in the first step found in National Institute of Standards and Technology (NIST). The final selection was made by measuring the standards.

In the frame of ongoing work the limit of detection (LOD) for CdS QDs and CdTeQDs will be established.

IV. CONCLUSION

It has been demonstrated that colloid QDs can be detected using LIBS and that we can advantageously use chromatographic paper as a carrier medium. The optimal spectral lines were established and confirmed by a set of measurements.

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REFERENCES

- [1] J. Drbohlavova, *et al.* Quantum Dots - Characterization, Preparation and Usage in Biological Systems. *Int. J. Mol. Sci.* 10 (2009) 656-673.
- [2] D.W. Hahn, N. Omenetto, Laser-induced breakdown spectroscopy (LIBS), part I: review of basic diagnostics and plasma-particle interactions: still-challenging issues within the analytical plasma community. *Appl. Spectrosc.* 64(2010) 335-66.
- [3] W.B. Lee, J.Y. Wu, Y.I. Lee, J. Sneddon, Recent applications of laser-induced breakdown spectrometry: a review of material approaches, *Appl. Spectrosc. Rev.* 39 (2004) 27–97.
- [4] M. Ryvolova, *et al.* Modern Micro and Nanoparticle-Based Imaging Techniques. *Sensors* 12 (2012) 14792-14820.