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ITMO University

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Laser-Induced Breakdown Spectroscopy: an advanced method for analysis of nanocarbon materials chemical composition

V. F. Lebedev*, a M. K. Rabchinskii, b M. S. Kozlyakov, a D. N. Stepanov, a A. V. Shvidchenko, b N. V. Nikonorov a and A. Ya. Vul' a

Precise and express analysis of nanocarbon materials chemistry continues to be one of the key tasks in the field of studying and following application of these unique structures. Despite large variety of the analytical techniques have been commonly used for this purpose, development of new methods that will further expand the efficiency of the nanocarbon materials characterization is still needed. Hereby applicability of laser-induced breakdown spectroscopy (LIBS) for study of chemical composition of different types of nanocarbon structures was investigated. Graphene oxide, reduced graphene oxide (analogous of pristine graphene) and detonation nanodiamonds were chosen as the most attractive representatives of nanocarbon materials. The obtained results demonstrate that functionalization parameters, such as functionalization degree and predominant type of the functional groups can be effectively determined on the base of the analyzed plasma emission spectra. Furthermore, presence of various inorganic contaminants can be identified by the LIBS technique. In comparison to common approach with studying of samples in the form of thick pellets thin films of nanocarbon structures on various substrates were successfully analyzed. Several experimental features arise in this case, in particular possible ablation of wafer and formation of thermal emission background. To overcome these challenges and to obtain reliable informative spectra adjustment of the ablation parameters and additional spectra processing procedures were applied. As a result, LIBS method can be a valuable and simple tool for quality control and characterization of various nanocarbon structures.

1. Introduction

Despite the intensive research of nanocarbon materials for more than two decades these unique structures still remain at the forefront of nanotechnology, providing scientific and technological excitement for researches in various disciplines1-4. With their exceptional physico-chemical properties, these nanomaterials are seem to have applications in many fields, such as electronic, optoelectronic and energy devices, nanocomposites and biomedical engineering as well as being viewed as building blocks in upcoming nanotechnology applications5,6. One of the remarkable features intrinsic to nanocarbon materials is their versatility for chemical modification through either covalent or non-covalent attachment of various functional groups and inorganic species. This aspect provides an intriguing opportunity for tailoring their physico-chemical properties in a desired way7-11. For instance, surface functionalization of detonation nanodiamond can be used to change its wetting or adhesion characteristics enhancing the nanoparticle dispersion in matrices whereas covalent modification of graphene by fluorine, hydrogen or oxygen-containing groups appeared to be an effective way for altering its electronic and optical properties in a wide range12,13. On the other hand, various contaminants may also preserve after the synthesis process and additionally affect the materials physico-chemical properties in an undesirable way14-16. Thus, express and precise control of the nanocarbon materials chemical composition, as-synthesized or subsequently modified, becomes of a great importance and is a relevant task in the area of nanocarbon science. To meet this demand, facile analytical methods capable of accurate study of the materials chemical composition have to be developed.

Laser-induced breakdown spectroscopy (LIBS) is one of the spectral methods that is intensively evolving nowadays owing to its unique features, such as possibility of performing real-time and in situ analysis of various types of samples (gas, liquid, solid) and high sensitivity17-19. In particular, presence of various ions, atoms, molecules and even isotopes can be identified by detection of the corresponding emission lines that arise at different temperatures of the luminous plasma plume20. In comparison to other analytical techniques commonly used for characterizing materials chemistry, such as infra-red spectroscopy (IR spectroscopy), X-ray photoelectron spectroscopy (XPS), electron energy loss spectroscopy (EELS), etc. LIBS does not have limitations in the type of chemical elements that can be detected what makes analysis of the
sample full chemical composition possible by using only single method. Differentiation of distinct types of the functional groups, presented in the assayed sample, is a challenging task within LIBS method since produced plasmas contain emission of species both ablated directly from the irradiated target and produced by probable chemical reactions in gas phase.\textsuperscript{21,22} Nevertheless, dominant type of the functionalities presented in the sample still can be determined by comparison of the corresponding emission lines, giving an opportunity to identify the studied material\textsuperscript{23}. Thus, taking also into account versatility of the LIBS technique and absence of specific requirements to parameters of the studied sample, use of this method seems to be quite an effective approach for analysis of nanocarbon materials chemical composition.

Notwithstanding this, only a single precedent has reported on the use of LIBS for studying of nanocarbon materials, namely graphene\textsuperscript{24}. However, in this work, authors concerned mainly on the relationships between the optical emission from plasma plumes of different graphene-based materials and their structural properties, namely number of the layers and stacking sequence, rather than analysis of materials chemical composition, for instance presence of oxygen- and nitrogen-containing functional groups that is of a high interest in the case of graphene and graphene oxide (GO). At the same time, no studies of any nanocarbon structures using LIBS method beside the abovementioned study have been reported yet.

Hereby we present for the first time experimental results on applying LIBS technique for studying of two classes of nanocarbon materials – detonation nanodiamonds (DND) and graphene oxide – that refer to sp\textsuperscript{2} and sp\textsuperscript{3} carbon nanoclusters, respectively. In particular, two types of detonation nanodiamond samples, DND with positive (denoted hereinafter as DND Z+) and negative (designated further as DND Z-) zeta potential, along with graphene oxide and thermally-reduced graphene oxide (rGO, analogous to graphene) samples that differ in type and relative concentration of the functional groups, presented in their structure, were studied.

Emission bands attributed to C\textsubscript{2} Swan system, CN, hydrogen and oxygen, originating from incorporated nitrogen and various hydrogen- and oxygen-containing species, were observed, providing information about the overall content and preeminent type of the functional groups presented in the assayed nanocarbon materials. Moreover, emission signals of several in-organic elements were also detected, demonstrating that presence of various contaminants can be also effectively identified by this method.

In comparison to millimeter-thick cylindrical pellets, used for studying of graphene samples by J.Serrano et al.\textsuperscript{25,26}, all samples were studied in the form of films with thickness of 100-300 nm on quartz and silicon wafers. This approach allows to significantly minimize the amount of material needed for an analysis and also demonstrates further applicability of this method for in-situ studying of the graphene and nanodiamond coatings on various substrates commonly used in formation of nanocarbon-based optoelectronic devices\textsuperscript{27,28}. In turn, study of the LIBS spectra of thin films additionally revealed strong influence of the sample thickness on the resulting plasma emission spectra. In particular, formation of an intensive broadband background signal can be observed in this case. As it was experimentally determined this background signal originates from thermal radiation of the sample. To solve the problem of presence of the thermal background along with temporal or spatial homogeneity in the expanding plasma and thus to obtain reliable data of the sample composition additional spectra processing procedures were applied.

Overall, the results obtained demonstrate that LIBS can be effectively used as an express and comprehensive method for identification of distinct types of nanocarbon materials and analysis of their chemical composition.

2. Experimental

2.1 LIBS setup and acquisition conditions

A scheme of the experimental set-up is shown in Fig. 1. A flash-lamp-pumped Nd\textsuperscript{3+}:YAG laser LQ-129 (SolarLS JSC) was used as an excitation source. The pulse generation was performed in an active Q-switching mode with a repetition rate of frequency 2 Hz, pulse duration and energy varied from 50 to 20 ns and 50 mJ to 210 mJ, respectively. The laser beam was focused onto the surface of the wafer with nanocarbon film via a lens with the focal length f=100 mm. The diameter of the laser spot on the sample surface was measured to be 125 μm. During the whole series of the experiments configuration of the optical elements and distance between the lens and surface of the samples preserved the same, thus resulting in absence of variation of the diameter of the laser spot. The laser jet radiation was collected by the collimation lens COL-UV/VIS (Avantes BV) and focused onto the end of the receiving optical fiber with the core diameter 600 μm connected with the spectrometer input. The plasma emission was recorded using a high-speed fiber spectrometer AvaSpec-ULS2048L-USB2 (Avantes BV) with the spectral range of 336-886 nm, determined by the diffraction grating that is used in our particular model. Spectral resolution of the used spectrophotometer is 1 nm. Detector array involves 2048 CCD detectors with the gate width of CCD 1.05 ms. Control of the spectrophotometer, launch of the laser with generation of the probe pulse and preliminary spectra processing was carried out using originally developed software on the base of NET Framework 4.5, with use of the dynamic library avaspec.dll. The studied samples were placed onto a manually moved linear translator with a flat surface rectangular to the laser beam direction. Measurements were performed both in the air ambient and in argon flow (buffer gas). In the latter case, the Ar flux with a flow rate of 0.7 l/min was directed to the sample surface adjusted to exclude the ambient air completely from the plasma plume. Image of the LIBS setup is shown in Fig. S1.

2.2 Samples

2.2.1 DND samples

Industrial DND material from FGUP kombinat Elektrokhimpribor (Russia) that is initially purified from non-
carbon impurities and non-diamond carbon using mixture of concentrated H$_2$SO$_4$ and CrO$_3$ was additionally treated by 40% solution of KOH, washed in solutions of strong acids, washed with deionized water and dried in hydrogen environment to get pristine DND powder. The DND Z- hydrosol was prepared by annealing of the obtained pristine DND powder in air at 410 °C during 6 hours and its subsequent dispersion in deionized water according the procedures, described by Alekseenkiy et al.\textsuperscript{26} Thereafter, 100 μL of the obtained DND Z- hydrosol 0.7 wt % in concentration was drop-casted on the quartz/silicon substrate and subsequently dried overnight at room temperature to form the studied film with thickness of about 300 nm. DND Z+ sample was prepared by annealing of the pristine DND powder in hydrogen atmosphere at 600 °C during 3 hours\textsuperscript{31} with the following procedures, as described for the DND Z- sample above.

![Fig.1 Schematic diagram of the experimental setup for LIBS spectra acquisition.](image)

### 2.2.2 GO, rGO and graphite samples

Graphene oxide suspension was synthesized by a modified Hummers method that includes use of concentrated H$_2$SO$_4$, NaNO$_3$ and KMnO$_4$. In the synthesis process, sonication was excluded to prevent damaging of graphene oxide flakes and obtain suspensions with the utmost size of GO flakes (with lateral size of up to 100 μm). To prepare GO films, 200 μL of GO suspension 0.03 wt % in concentration was drop-casted on a silicon/quartz wafer and dried overnight at room temperature, forming GO films with thickness ~100 nm. The reduction of graphene oxide and formation of rGO films was carried out by high-temperature annealing of the formed GO films at 800 °C for 1 h in the hydrogen environment\textsuperscript{31}. Additionally, two graphite samples – natural crystalline graphite (GSM-1) used for the abovementioned graphene oxide synthesis process and highly oriented pyrolytic graphite (HOPG) – were analyzed as control carbon systems with no nitrogen or oxygen-containing species in their structure.

### 2.3 Spectra normalization

To obtain reliable data of the studied nanocarbon material chemical composition from the obtained LIBS spectra in conditions of lack of temporal and spatial homogeneity in the expanding plasma due to nonuniformity of the film structure and laser pulse parameters modified processing procedure was established. In comparison to commonly used approach, where processed and normalized spectrum is usually obtained by averaging of an array of laser pulses\textsuperscript{32}, normalization of each of the spectra, from pulse to pulse, was applied. Such an approach leads to more accurate and precise determination of each emission line contribution\textsuperscript{30,31} into the whole spectrum due to consideration of the relationship between the integrated plasma emission and laser power. Following normalization procedure was based on division of intensity, registered by each detector from the whole array of 2048 detectors to total intensity of the emission:

$$I_{k}^\text{norm} = \frac{I_k}{\sum I_k} \quad (1)$$

where $I_k$ unnormalized intensity of emission, registered by the corresponding detector, $N$ – number of detectors (2048 in our case) and $\sum I_k$ total intensity of the plasma emission, registered by the spectrograph.

![Fig.2 Integral intensity of the C\textsubscript{2} emission line in LIBS spectrum of pyrolytic graphite as a function of (a) pulse energy and (b) delay time used in the experiment without (blue curves) and with (black curves) normalization procedure.](image)

Normalized in this way, LIBS spectra obtained with different delay times and laser pulse energies do have nearly equal contribution of emission lines into the whole spectra (Fig.S2), thus providing possibility of correct analysis and comparison of the plasma emission spectra of various nanocarbon samples that were assayed. Fig.2 represents an example of the C\textsubscript{2} emission line behavior before (absolute integral value) and after (relative integral value) the applied normalization procedure, clearly demonstrating effectiveness of the
approach used. Hereinafter all the obtained spectra are presented in the normalized form.

3. Results and discussion

3.1 Spectra features related to the film form of the sample

One of the key factors that determine efficiency of use of LIBS technique for analysis of nanocarbon materials chemical composition is the form of the studied samples. Preparation of cylindrical pellets with thickness of up to several millimetres by pressing powder of the analyzed sample, the technique that is commonly used in LIBS measurements, requires large amount of the studied material, making this approach rather inconvenient in the case of nanocarbon structures. At the same time, formation of thin films with thickness of 10-100 nm from graphene oxide, graphene or detonation nanodiamonds on various substrates is quite common procedure that requires only small amount of the corresponding nanocarbon material. Furthermore, most of the nanodiamond- and graphene-based optoelectronic devices that are designed nowadays are mainly based on coatings, obtained from the corresponding nanocarbon material, and determination of their chemical composition in-situ is of a high interest. Thus, LIBS study of nanocarbon materials in the form of films on a certain substrate instead of pellets appears to be the most appropriate approach. However, several challenges arise in this case as was observed, resulting in necessity of additional adjustment of energy parameters of the applied laser pulses and spectra processing to obtain informative and representative spectra.

Considering small thickness of the assayed sample, along with fragmentation of the studied film ablation of the wafer under it may proceed as well. This will lead to modification of the obtained plasma emission spectra in an undesirable way due to contribution of the components, released from the substrate. To prevent this, several preliminary experiments were carried out to adjust energy of the applied laser pulses so it would be both over the plasma formation threshold for the studied film and less than ablation threshold for the used wafers, namely quartz and silicon. Reduction of the laser pulse energy to the minimum level also provides decrease in the 50% thickness of the layer of the sample that is ablated by single laser pulse to the values that are less than total thickness of the studied GO, rGO or DND film, additionally preventing ablation of the wafer during first pulses. For whole set of the studied films the minimal laser pulse energy, optimal for obtaining informative plasma emission spectra, was estimated as 69.4 mJ. Fig.3 demonstrates set of LIBS spectra from series of consecutive laser pulses with energy of 69.4 mJ acquired in the air ambient for the 300 nm DND Z+ film on quartz and silicon wafers. As seen, in the case of quartz substrate first three pulses lead to ablation of the DND Z+ film that can be indicated by presence of prominent C2 molecular emission lines, presented by series of bands at 453.8-474.4 nm, 494.6-517.5 nm, 525.9-563.8 nm and 593.2-620.7 nm. In turn, no signal from silicon of the substrate can be observed.

Moreover, no signal can be further observed both from the studied film and quartz wafer after two following pulses (4th and 5th pulses), clearly demonstrating absence of substrate ablation during the experiments with the determined energy of laser pulse. The same results were observed for GO and rGO films where no fragmentation of quartz wafer proceeded with its disruption only after series of 15 laser pulses pointed to one area resulted in its disruption (Fig.S4). On the other hand, in the case of silicon wafer discernible lines at 531.6 nm, 634.3 nm and 656.1 nm, corresponding to silicon, appear, indicating partial fragmentation of the substrate along with the studied film. Fragmentation of the silicon wafer even after the 1st pulse, when DND film is not completely ablated is most probably related to non-uniform structure of the film, when several areas of the wafer are not covered with the sample. Nevertheless, contribution of Si emission lines in the resulting plasma emission spectra at this level of ablation is relatively low, not impeding analysis of the obtained spectra.

Along with the problem of possible influence of substrate on the plasma emission spectra, obtained from the nanocarbon film, small thickness of the assayed sample also leads to formation of a broadband background signal as is seen from...
Fig.3 for DND Z+, which intensity reduces simultaneously with fragmentation of the film. Since the presented spectra were obtained with delay time of 1.4 μs it is unlikely that this background signal originate from the inverse bremsstrahlung radiation that dominates in the plasma emission spectra during first hundreds of nanoseconds after the plasma plume formation. At larger times, significant reduction in the overall intensity of the inverse bremsstrahlung radiation happens. Moreover, intensity of the observed background signal depends on the thickness of the studied sample what is demonstrated by comparison of LIBS spectra acquired for rGO film (thickness of 100 nm) and 1 mm pellet of HOPG (Fig.S5), where background signal cannot be observed for the latter one with its presence in rGO spectra. Considering that reduction in the film thickness results in simultaneous decrease of its thermal conductivity and taking in account shape of the background signal it was suggested that presence of broadband background in the as-obtained spectra does originate from thermal emission of the film and nanocarbon clusters, namely individual graphene or graphene oxide platelets and nanodiamond particles, directly ablated from the assayed film. This assumption is further supported by the fact that the observed background signal has several times higher intensity in the spectra of DND films that have lower thermal conductivity due to high number of interparticle interfaces in comparison to rGO films, where value of in-plane thermal conductivity is quite high.

To experimentally verify this suggestion optical emission spectra for DND Z+ film, obtained with laser operating in Q-switched and free-running modes, were compared (Fig.4). Irradiation of the sample by laser in free-running mode with length of the pulse of about 130 μs results only in the heating of the film without plasma formation. Emission lines that are clearly seen in this spectra originate from ionization of Na and O that have low values of the ionization threshold and thus can produce distinguishable emission lines even in the case of irradiation by laser pulses obtained with the laser operating in free-running mode. As is clearly seen from Fig.4,b spectrum of thermal emission of the DND film almost perfectly fit the background signal in the plasma emission spectra of the corresponding sample. Little discordance in the compared spectra in the ultraviolet spectral region is related to the fact that intensity of sample heating by radiation of laser operating in Q-switched mode and free-running mode are a little bit different what causes slight shift of the thermal spectrum maximum. Thus, the presented results do demonstrate that in comparison to bulk materials LIBS spectra of nanocarbon films are well dominated by additional broadband thermal emission band which intensity is significantly determined by the film thickness and its thermoconductivity. Apparently, this background signal might be observed not only during studying of the nanocarbon samples, but also in the case of various thin films and low conducting materials. In addition to the abovementioned comparison of the optical emission spectra, obtained with and without plasma formation, univocal identification of presence of the thermal emission background can be also based on comparison of plasma emission spectra obtained by laser pulses with different energies. Increase of the pulse energy also results in higher degree of heating of the sample what, in turn, leads to shift of the background signal maximum to lesser wavelength. This shift can experimentally be observed by comparison of several plasma emission spectra, obtained with different energies of the laser pulse. After thermal emission signal is identified, it can be simply excluded from the obtained plasma emission spectra. First approach is subtraction of the experimentally measured thermal emission band, normalized to the informative plasma emission spectra, as is demonstrated at Fig.4,b. However, thermal background signal can be also simply modelled by B-spline approximation with subsequent subtraction of the obtained spline from the experimental spectrum[30]. As a result, plasma emission spectra without background signal can be obtained after these procedures, providing possibility for their further correct analysis.

Fig.4. Experimental modeling of thermal background in emission spectrum of studied films and its subsequent subtraction resulting in corrected form of the LIBS spectrum of the studied nanocarbon material. All spectra were obtained in the air with the energy of the pulse of 69.4 mJ.

3.2 Analysis of the functionalization parameters

Fig.5 demonstrates typical emission spectra of (a) GO – rGO and (b) DND Z+ – DND Z- films after processing, acquired in the argon atmosphere. As seen, along with presence of Ar emission lines in the near infra-red (NIR) spectral region, plasma emission spectra for all of the assayed nanocarbon
materials are well dominated by C$_2$ molecular emission. Two distinct origins for emergence of C$_2$ emission have been discussed in the literature, related to either formation of molecular bands due to a direct release of dimer molecules (C=\(\text{C}\)) from the parent compound$^{32,33}$ or from the recombinatin of the excited carbon ions, released during fragmentation of the nanocarbon material and disruption of its carbon network, by one of the following reactions$^{34,35}$:

\[
\begin{align*}
C + C + M & \rightarrow C_2 + M \quad (2) \\
C + CH & \rightarrow C_2 + H \quad (3) \\
CO + C & \rightarrow C_2 + O \quad (4)
\end{align*}
\]

Notably, on the base of LIBS studies of pristine graphene and graphene oxide in the air ambient Serrano et al.$^{24}$ proposed that the number of carbon-carbon double bonds (C=\(\text{C}\)) in the assayed sample play the primary role in formation of C$_2$ molecular emission bands and drastic reduction C$_2$ signal can be observed for GO because of alteration of the graphene basal plane sp$^2$-hybridized structure into a mixture of sp$^2$- and sp$^3$-hybridized C atoms and following reduction of amount of C=C bonds. Thus, preferential type of carbon atoms hybridization and, as a result, type of the assayed carbon sample crystalline structure can be determined on the base of analysis of C$_2$ emission lines intensity. However, in out experiments prominent C$_2$ emission can be observed in the spectrum, obtained for the GO film (Fig.5,a), with intensity of the corresponding emission lines only slightly less than in rGO that have restored sp$^2$-conjugated graphene network.

Furthermore, C$_2$ molecular emission can be also easily detected for both types of detonation nanodiamonds which structure is completely composed of carbon atoms in the sp$^2$-hybridization (Fig.5,b) with no double or triple carbon–carbon bonds. These results do suggest that the main route for emergence of C$_2$ emission is recombinatin of carbon atoms in the formed plasma rather than direct ablation of carbon dimers, although their content in the assayed sample also do contribute to the observation of C$_2$ signal, as it was demonstrated in series studies of various organic compounds using LIBS technique$^{32}$ and is seen from comparison of the plasma emission spectra of GO and rGO.

Primary role of the recombinatin mechanism in formation of C$_2$ molecular emission bands is further supported by comparison of the plasma emission spectra of GO film, acquired in air and argon ambient, presented at Fig.6. In the air atmosphere, interaction of plasma with surrounding ambient gas results in intensive recombinatin between released carbon and nitrogen and oxygen from the surrounding air, thus decreasing number of reactive carbon ions with following reduction of the C$_2$ emission intensity to the undistinguishable level. Evidently, this process is accompanied by discernible increase in CN signal due to formation of the corresponding species from the reaction$^{35,36}$ C + N$_2$ $\leftrightarrow$ CN + N or C$_2$ + N$_2$ $\leftrightarrow$ 2CN. At the same time, in the buffer gas abundance of nitrogen and oxygen atoms is relatively lower, determined only by the content of the corresponding elements in the treated sample. As a result, C$_2$/C=\(\text{C}\)=C formation becomes the preferential pathway resulting in higher emission intensity even in the case of graphene oxide. Moreover, in the buffer gas enhancement of plasma emission intensity occurs as a result of larger rates of the production of emitting species with higher electron concentration$^{37}$, leading to further increase in level of emission lines, including C$_2$ Swan system. All this makes determination of the hybridization type in the studied nanocarbon materials from the analysis of C$_2$ bands emission relatively complicated as it can be based only on comparison of integral intensities of the C$_2$ molecular emission lines. As seen, restoration of the sp$^2$-conjugated structure graphene oxide after its reduction results in increase of the C$_2$ emission by 1.6 times in comparison to the initial GO structure. Further comparison of the C$_2$ integral intensities in the rGO and DND plasma emission spectra reveals that C$_2$ emission is 2.2 times higher in the case of rGO. Arguably, these results indicate that one can determine predominant type of hybridization in the studied nanocarbon materials simply by comparison of the intensities of C$_2$ emission lines.

![Fig.5. LIBS broadband spectra of (a) GO – rGO and (b) DND Z– – DND Z+ acquired in the argon atmosphere with a delay time of 1.4 µs and pulse energy of 69.4 mJ. For clarity, rGO and DND Z+ spectra vertically offset from the GO and Z– respectively.](image-url)
However, parameters of ablation of various types of the nanocarbon materials are significantly distinct and the observed difference in C2 signals for the rGO and DND can also arise due to this factor. Thus, additional information about the ablation of the specific types of the assayed nanocarbon materials is needed for evident differentiation of the nanocarbon structures with distinct types of hybridization. Alternatively, one of the other approaches can be based on the analysis of plasma emission spectra in the air or another chemically reactive atmosphere. In this case formation of C2 signal due to recombination of carbon ions will be suppressed and the observed C2 emission lines will originate only from C=C bonds that is a characteristic sign of sp2 type of conjugation. However, further study is needed to verify this assertion, although it coincides with results of J.Serrano et al.12

Along with presence of series of C2 emission lines, plasma emission spectrum of the GO film is well dominated by hydrogen and oxygen emission bands (Fig.7.a): the hydrogen-alpha and hydrogen-beta lines (Hα and Hβ) at 656.1 and 485.8 nm respectively, the oxygen fine-structure triplet at 777.2, 777.4, and 777.5 nm that appears unresolved due to the spectrograph resolution and atomic oxygen line at 844.3 nm.

Considering absence of interaction between the plasma plume and ambient air by the argon flow, confirmed by the fact that there is no CN molecular bands as well as O and N atomic emission lines in the spectrum of the reference graphite sample (Fig.S3), origin of these prominent emission bands can be related only to dissociation of various hydrogen and oxygen functionalities, therefore indicating relatively large concentration of such species in the structure of the assayed GO film. This observation is consistent with the known fact of high functionalization degree of graphene oxide, in which basal plane and edges of graphene net are covered with large number of hydrogen- and oxygen-containing functional groups, mainly epoxides (-O-), hydroxyls (-OH), carbonyls (=O) and carboxyls (-COOH), resulting in C/O ratio of about 0.9-1.1.12

Hence, drastic decrease of the O and H emission lines must be observed in the case of rGO film and indeed, as it is evident from the presented spectrum (Fig.7.a), almost no signal for both oxygen and hydrogen can be detected for the obtained rGO sample. Comparison of the integral intensity of O emission lines in the GO and rGO spectra suggests that concentration of oxygen decreased by the factor of 8 during the reduction process what is in good coincidence with the value, obtained for this samples using X-ray photoelectron spectroscopy.11 Presence of O and H emission bands can be also indicated in the plasma emission spectra of detonation nanodiamonds, represented at Fig.7.b. However, here oxygen emission bands are significantly less prominent, being hardly distinguishable, and noticeably low intensity of the O emission line in the DND Z- emission spectrum is argued with the known data for chemical composition of such type of detonation nanodiamond, which indicates presence of carboxyl and other carbonyl-containing groups on the DND surface. Absence of atomic oxygen emission bands in the case of detonation nanodiamonds can arise from two possible reasons. The first one is related to rapid consumption of atomic oxygen by its recombination with carbon atoms, released through disruption of nanodiamond core, with formation of CO and CO2 molecules that can be described by one of the following reactions:40,41

\[ C_2O + C \rightarrow CO + C \]  
\[ C + O \rightarrow CO \]  
\[ C + 2O \rightarrow CO_2 \]

Formation of CO and CO2 moieties in the case of DND is suggested to be relatively preferable since relation between number of O and C atoms in its structure is of about 1:50, leading to high probability of multiple interactions of each oxygen atom with carbon atoms. Moreover, OH and NO species can be formed as well, as was discussed in the literature, resulting in formation of observable molecular emission band systems. However, all these molecular emission bands lie at \textasciitilde270-336 nm that is out of range of the applied spectrograph, and thus were not analyzed in this work. The second reason is that direct ablation of C=O and COOH functionalities, without their dissociation, may proceed during the ablation process, thus additionally reducing amount of the observed atomic oxygen. On contrary, in graphene oxide amount of oxygen atoms is almost equal to the carbon ones and oxygen is mainly presented in the form of hydroxyl and epoxide groups that dissociate easily. Hence, relative concentration of atomic oxygen, presented in the produced plasma, is significantly higher, resulting in high intensity of O atomic emission bands as it is observed in the presented spectra. However, even in this case, total intensity of the O emission bands is less than intensity of the hydrogen emission bands, although concentration of oxygen in the GO structure is known to be several times higher than concentration of hydrogen, suggesting that similar processes that lead to reduction of the O emission signal do proceed. Nevertheless, it is worth mentioning that except reviewed O emission lines at 777.2-777.5 nm and 844.3 nm ionization of oxygen-containing...
species also should result in formation of series of O atomic emission lines in the deep UV and NIR spectral regions, in particular at 241.7-241.8 nm, 261.7-262.3 nm, 332.0-327.9 nm and 926.1-926.8 nm, 948.1-948.7 nm, 950.6-952.8 nm that cannot be detected in this work. Thus, total integral intensity of the O atomic lines is actually higher what additionally explains the observed discordance in O/H ratio in DND and GO samples. Although examination of barely oxygen emission bands cannot be effectively used to determine functionalization features of the DND samples, additional analysis of H emission lines still does provide sufficient information about the functionalization type of the studied detonation nanodiamond. In comparison to DND Z-, where dominant functional groups are carboxyls and lactones as was mentioned above, DND Z+ is functionalized mainly by hydrocarbon functionalities, such as CH and CH₂.

In the presence of electrons in the plasma electron-impact dissociation of these hydrocarbon groups does occur with formation of C and H along with CH₅ radicals (reaction (8) with their further possible interaction and release of hydrogen (9)):

\[
\text{CH}_n \leftrightarrow \text{CH}_{n-1} + \text{H} \quad (8)
\]

Consequently, predominant functionalization of DND by hydrocarbon groups can be clearly indicated by higher intensity of both H₂ and Hα emission lines in the corresponding plasma emission spectrum of DND Z+ in comparison to DND Z-, as seen in Fig.7, b.

Further analysis of the ultra-violet spectral region in the GO-rGO and DND spectra (Fig.8) also demonstrates presence of distinguishable CN molecular bands at 352.7-360.4 nm and 380.5-388.7 nm for both types of nanocarbon materials. In the case of detonation nanodiamonds, observation of CN molecular bands indicates detection of the nitrogen, incorporated into the core of detonation nanodiamonds during the synthesis process, in particular in the form of nitrogen–vacancy (NV) centers – a nitrogen atom next to a vacancy – with the total concentration of the nitrogen, presented in DND, of about 3-3.5%\(^{42}\). At the same time, origin of CN emission lines in GO and rGO plasma emission spectra is less evident since it is considered that pristine graphene oxide does not contain plentiful amount of nitrogen species and only the only possible external source for nitrogen in the case of GO is sodium nitrate residuals, remained after the synthesis and purification processes but concentration of such species is exiguous small to give rise for discernible emission lines. Furthermore, signal for CN molecular bonds also remains almost unchanged in rGO plasma emission spectrum, indicating stability of the corresponding nitrogen-containing species even under annealing at high temperatures (800 °C) when all residuals are eliminated from the sample. At the same time, it was demonstrated in several recent studies, in particular by Schultz et al.\(^{10}\), that nitrogen-containing groups in GO do remain during the high-temperature treatment with temperatures up to 1000 °C with almost no loss in their concentration. Thus, the most probable origin of the observed CN emission bands is ablation of the intrinsic nitrogen functionalities, namely nitrate, pyridinic or pyrrolic groups, indicating their probable formation during the synthesis of GO from interaction between nitrate ions and partially oxidized graphite, although question of nitrogen-containing groups formation during the oxidation process remains open.\(^{45}\).

Fig.7. Detailed LIBS spectra (630-875 nm spectral range) of (a) GO, rGO and (b) DND Z+,
DND Z- in the argon atmosphere. Acquisition conditions as in Fig. 5.

3.23.3 Identification of contaminants in the nanocarbon materials

In addition to emission bands that correspond to the functionalities, intrinsic to graphene oxide and detonation nanodiamonds, series of signals in the UV and NIR spectral regions, attributed to several inorganic elements, can be also detected. Two groups of emission lines, namely triplet at 424.9-431.9 nm and set of bands at 519.2-543.6 nm, can be observed in the DND Z+ spectrum, indicating presence of chromium (Cr) in the studied DND film, most probably due to preservation of chromium trioxide (CrO₃) that is used on one of the purification steps during synthesis by its non-covalent bonding to the surface of DND particles. In turn, no emission bands, corresponding to Cr, are observed in the case of DND Z-. Furthermore, in the GO and rGO plasma emission spectra emission bands at 403.1-407.8 nm and 476.1-482.1 nm that can be attributed to manganese, doublet of emission lines at
766.2 and 769.6 nm, corresponding to potassium, and two prominent bands at 393.1 and 396.6 nm, related to calcium, does appear. Emission lines of Ca can be also detected in the spectrum of graphite, used for GO synthesis (Fig. S3), suggesting that presence of calcium in GO is a result of its preservation during the oxidation procedure whereas presence of manganese and potassium originate from residuals of potassium permanganate or products of its decomposition, remained in the GO suspensions even after several purification steps and, as a result, in subsequently formed films.

Moreover, strong emission line at 588.7 nm that correspond to Na can be also observed in the LIBS spectra of graphene oxide, most probably originating from residuals of sodium nitrate. Interestingly, that intensive Na emission line also appears in the DND Z+ spectra although no sodium-containing species are applied during the synthesis process. Origin of this line is related to progressive hydrolysis of glass flask in which DND Z+ hydrosol was stored with following modification of the DND particles surface by Na ions. High-temperature annealing of GO leads to significant reduction of amount of contaminants as seen from decrease of the corresponding lines intensity in rGO plasma emission spectrum, although discernible doublets of K, Na and Ca emission lines still remain. It is worth mentioning that in comparison to results of LIBS study, no signals corresponding to K, Na, Ca or Mn were observed in the same GO-rGO samples, studied using XPS technique, implying that concentration of these elements in the obtained films is below 1%. As a result, even small fractions of contaminants, presented in the studied nanocarbon materials, can be identified by the LIBS method.

Conclusions

Overall, the obtained results demonstrate that LIBS technique can be effectively applied for quality control and characterization of various nanocarbon structures. Despite identification of specific functional groups does not appear sustainable by this method, such important parameters for characterization of nanocarbon materials as overall degree and predominant type of functionalization can be well determined by this method. Analysis of the plasma emission spectra, obtained for DND Z- and DND Z+ samples showed that type of the detonation nanodiamond can be easily established simply by comparison of the intensities of $H_\beta$ and $H_\alpha$ emission lines. Analogously, GO and rGO films can be differentiated by the presence of distinguishable O and H emission lines in the plasma emission of the former one. Moreover, quantitative information about changes in degree of GO oxidation after reduction process can be also evaluated from the comparison of the integral intensity of O emission lines in the GO and rGO films. Apart of oxygen and hydrogen, presence of nitrogen species and impurities can be identified as well that is of a high interest for the nanocarbon materials, especially for detonation nanodiamonds.

Efficiency of the use of LIBS technique for analysis of nanocarbon structures is further expanded by the fact that presence of large variety of inorganic elements can be identified within this method as well. Presence of Na, Mn and K in the graphene oxide films as well as Cr and K in DND due to preservation of these elements after the synthesis process was successfully indicated from the obtained spectra, although concentration of these elements was of about 1 at%.

At the same time, study of C2 molecular bands revealed that type of hybridization of the assayed nanocarbon material cannot be univocally determined from analysis of these emission lines cannot provide univocal information about. This is related to the fact that origin of these emission lines is relatively complicated, depending on interaction between plasma and surrounding ambient, recombination of excited partials and direct release of carbon. However, comparison of the intensity of the C2 emission with consideration of parameters of the studied film ablation as well as analysis of C2 emission in the plasma plume, obtained in the chemically reactive ambient seems to be possible ways to solve this problem.

Study of nanocarbon structures in the form of films also revealed that formation of thermal background signal should be considered for the samples with small thickness and low thermal conductivity. Nevertheless, simple approaches can be used to identify and further exclude this background signal from the obtained plasma emission spectra. Furthermore, use
of the modified normalization procedure that neglects
temporal and spatial non-uniformity of the laser pulses
provides additional possibility to obtain reliable data from
series of sample areas.
As a net result, although further studies are needed in the field
of the recombination mechanisms in the formed plasma and
ablation parameters for various nanocarbon materials LIBS
technique appears to be simple and effective, versatile
method for express analysis of the nanocarbon materials
chemical composition and characterization of their quality.

Conflict of interest
There are no conflicts to declare

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