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Laser-induced breakdown spectroscopy as an unconventional tool analysis for carbon allotropes

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Laser-induced breakdown spectroscopy (LIBS) is a new approach for determination and characterization of various nanomaterials structures. In this work, LIBS emission spectra of different species of nanocarbon nanomaterials (carbon allotropes) were described. Ablation was performed using an Nd: YAG laser at 1064 nm in ambient air at atmospheric pressure. Results are consistent with the atomic emission lines of carbon or molecular bands, C_2 being released directly from the target, and CN being formed later by the interaction of C_2 with nitrogen gas (N_2) in the atmospheric ambient of plasma. It was indicated that probably there is a relationship between C_2 emission from the plasma and the presence of aromatic rings (containing carbon-carbon double bonds) in the compounds.

KEYWORDS

Laser-induced breakdown spectroscopy; carbon allotropes; plasma plume; molecular emissions.

Introduction

Laser-induced breakdown spectroscopy (LIBS) is one of the powerful advanced instruments for analytical applications. It is a beneficial technique to determine the chemical and physical properties of different materials, and it is strongly evolving due to its unique features and advantages, such as qualitative and quantitative analysis. Determine the compositional elements of various types of samples (solid, liquid, gas, and nanoparticles) [1,2,3].

In addition to the elemental analysis, LIBS is successfully used for identifying the metals' quality, chemical analysis of explosive materials, characterization of soils, and detection of radioactivity [4]. Likewise, it has some capabilities as a rapid tool for pollution monitoring, forensics, biochemical applications, archeology, and space exploration [4,5].

In this technique, a pulsed laser is required to generate micro-plasma on the target surface [1,6]. When the laser pulse heats (ablation) the surface of the target, it does not only vaporize the material, but shatters all chemical bonds and ionizes the elements create a plasma plume. Plasma contains neutral atoms, electrons, ions, and the excited atoms [7] in which are excited in the hot plasma, then they relax to generated atomic and ionic spectrum at a characteristic wavelength that identifying the elemental composition of the target [8,9]. Each element has its unique emission lines as the "fingerprint". The wavelength of the emission lines is used to identify the elements [8].

Nanomaterials exhibit unique physical properties to be promising to improve optical signals [10]. The properties are changed upon the decrease of the nanoparticle size by which a greater proportion of atoms are found at the surface compared to that inside [10,11].

Among nanomaterials, nanocarbon materials (carbon allotropes) have attracted particular attention due to their unique structural and physical properties are revolutionizing several fields of fundamental science and nanotechnology [5].

To the best of our knowledge, little works have been done to examine the spectroscopic signal emitted from the plasmas of nanomaterials targets [11]. Nevertheless, the research studies on the analysis of particles using LIBS have shed light on the fundamental features and many potential applications [12].

This work focused on using LIBS as an express and comprehensive method for the identification of distinct types of carbon allotropes and analysis of their chemical descriptions.

Materials and methods

The instrumentation of LIBS set-up includes pulsed Nd: YAG laser, collector lenses, and a spectrograph with the detector.

The laser beam was directed to the sample surface. The microplasma which was created on the sample surface was collected by lenses placed at a distance of a few centimeters from the sample surface and coupled to optical fiber and transmitted to a spectrometer coupled to an ICCD camera.

All experiments were performed in the air atmosphere. The specimens were investigated in powder form. For easy and fast LIBS analysis each sample powder was poured and compressed into a suitable size plastic template to complete the experiment to achieve the aim of work. This study concentrated on the spectrum analysis by libs for carbon allotropes. The table below includes the specification of the samples which were used in this study.

TABLE 1 The specification of the specimens of carbon allotropes

Samples	Purity %	SSA m2/g	Specifications
Graphene	99.5%	120-150	Average particle diameter = 15 um
Nano-graphite	93%	540-650	APS= 3-4 nm
SWCNT	90%	400	OD= 1-4 nm , ID= 0.8 – 1.6 nm, length = 5-30 um
MWCNT	90%	200	OD= 10-30 nm, ID= 5-10 nm, length =10-30 um

Results and discussion

The LIBS usage seems to be quite an effective approach for the analysis of nanocarbon materials [2]. Different types of emission lines that are released from the tested samples by the LIBS technique depend on the characterizations of starting elements of the compound [13].

Inorganic and organic carbon can be detected by LIBS through its atomic carbon lines, and molecular bands C_2 and CN. Typically nitrogen emission lines are related to this task [13,14]. The molecular emission CN is related to the interaction between the elements in plasma content and atmospheric nitrogen gas [14,15].

In the LIBS spectra of carbon compounds, there are emission lines of the other specific elements which may result from production technology. In addition, the detection of Ca and Na are no surprise as these are in ambient air [9].

Figures (1.a,b) displays libs analysis related to graphene specimens. The spectra demonstrate the atomic carbon emission lines recorded at 247.7 nm and 229.5 nm, respectively in addition to the emission lines of atomic nitrogen at 399.5 nm and nitrogen gas at 358.5 nm. The Ca and Na emission lines release near to 393 nm and 589 nm, respectively, as are predicted being in the air exists. The results pointed to the molecular emissions CN within the range (385-388.5 nm) and C_2 at 516 nm.

The LIBS spectrum gets especial performance when C_2 disappears, the

emission of CN get higher intensity, as illustrated in Figure (1. b).

Several studies concluded that CN emission arises from the recombination of C_2 molecules in the sample plasma with the atmospheric nitrogen [16,17,18].

It should be mentioned that it is generally, the emission rate of C_2 depends on the presence of double bonds C=C in carbonic compounds, atomic carbon emissions related to the C-C bond [2,17,18].

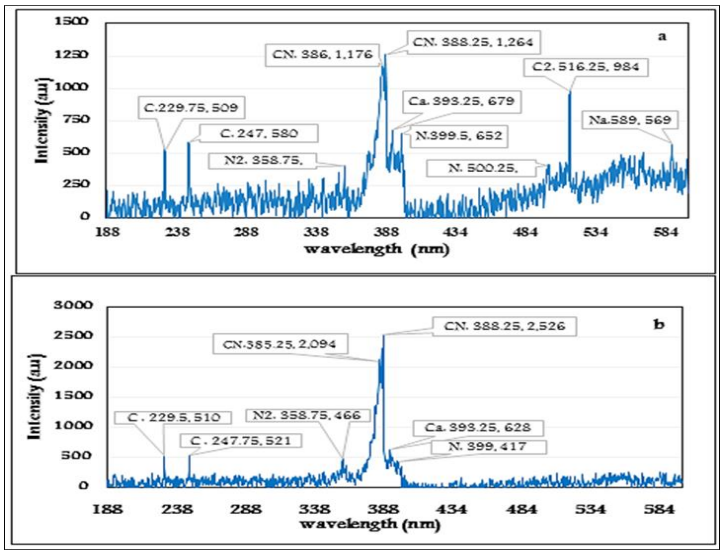

FIGURE 1 Spectral LIBS analysis of graphene

The same previously mentioned features were achieved in LIBS analysis of graphite. Figure (2.a,b) demonstrates the presence of atomic carbon emission lines and the molecular emission bands CN and C_2. It was indicated the presence of emission lines for N and Ca since they are necessarily existed in plasma plume.

The absence of C_2 emission indicating its recombination with the atmospheric nitrogen gas N_2 to enhancement the intensity of CN emission to being higher value as depicted in Figure (2.b).

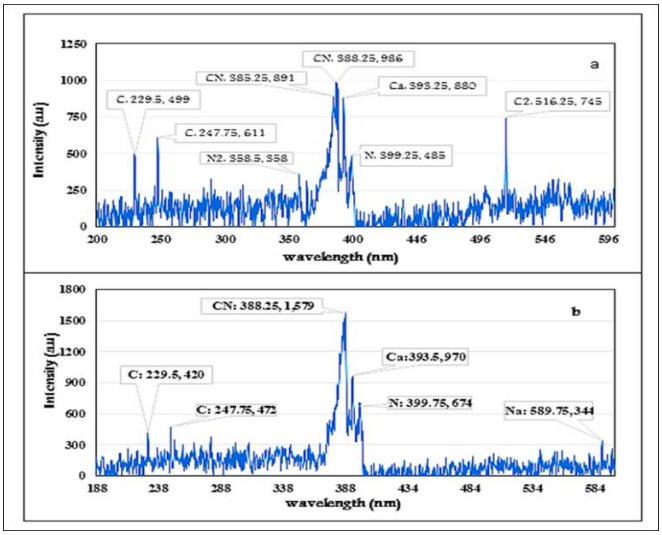

FIGURE 2 Spectral LIBS analysis of graphite

Carbon nanotube was investigated by LIBS for both types of single-walled carbon nanotube (SWCNT) and multi-walled carbon nanotube (MWCNT). As SWCNT is rolled single graphene layer, their spectral performance of LIBS illustrates the atomic emission lines of carbon, the C_2 molecular band is revealed as it related to the C=C double

bond in the rolled single graphene layer, and CN emission is related to the interaction of specimen with the atmospheric nitrogen, as presented in Figure (3.a). With the same knowledgeable strategy, CN be higher if C_2 is disappeared as is clarified in Figure (3.b).

Also, Al and Fe emission lines appear for the case of CNT which may result from the remains of production technology. Corresponding spectral lines of Al emit at (396.7 and 281.5 nm) and Fe at (237 and 279.5 nm).

A low concentration of both Al and Fe explains the non-simultaneous detection of these two elements; expect that not all the emissions are facilely noted only observed under convenient experimental conditions [3].

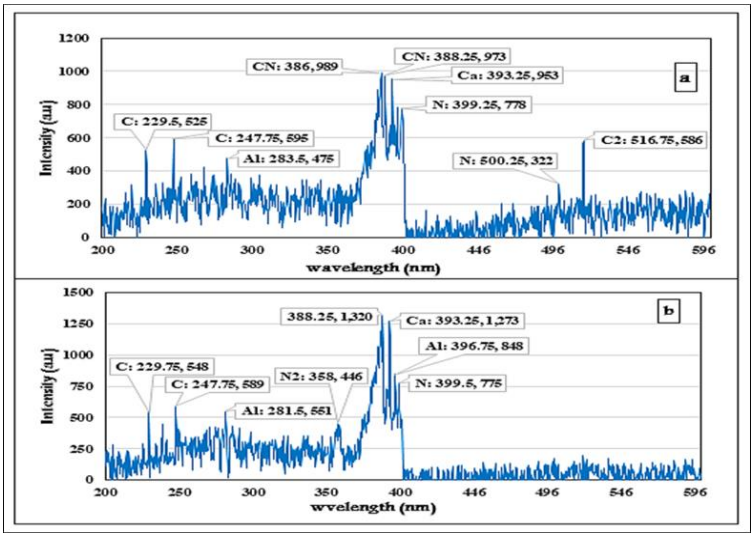

FIGURE 3 Spectral LIBS analysis of SWCNT

For case of MWCNT, LIBS analysis depend the same concept which lead to production spectral LIBS behavior for SWCNT. Nevertheless, there is special distinction that CN emission of MWCNT spectra were relatively higher for all status as its apparent in Figure (4. a,b).

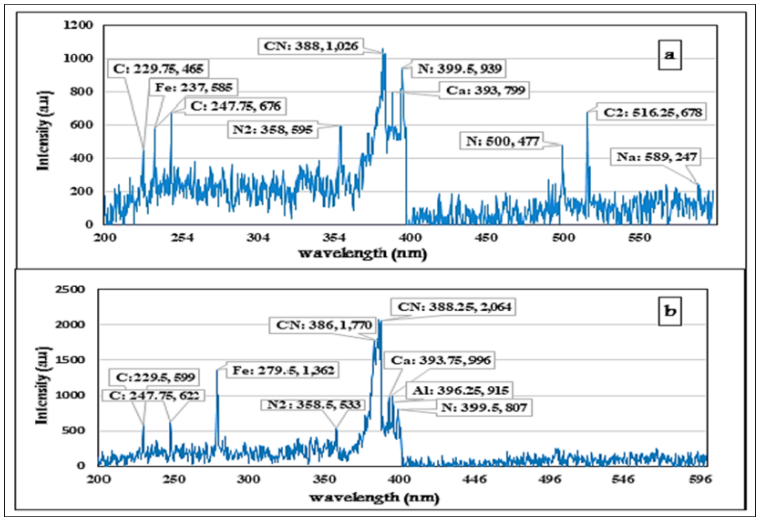

FIGURE 4 spectral LIBS analysis of MWCNT

It might be related to the increased number of rolled graphene layers to produce MWCNT, as it known C_2 and atomic carbon lines imputed to C=C and C-C bonds, respectively. Therefore, as the number of layers and diameter is increased in the case of MWCNT, it is expected that carbonic bonds will increase. This will affect the proportion of emissions of

C and C_2 which will lead to an increase in emissions of CN.

During many experiments on species of carbon allotropes, it was noticed that grapheme indicated the exceptional behavior as the CN emission bands intensity increased to very high values, as demonstrated in Figure (5. a,b). This obtained result included the disappearance of all other emissions represented by atomic emission lines of carbon and nitrogen, as well as the molecular emission band of C_2. It should be noted that the nitrogen gas, Ca and Na emission lines appear was no abruptness as these are existed in the atmospheric ambient of the obtained plasma plume.

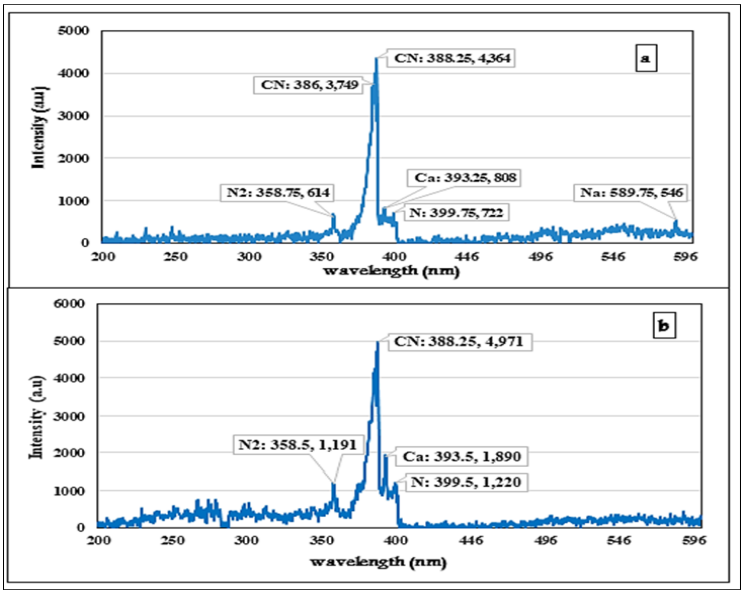

FIGURE 5 LIBS spectra analysis of graphene specimens when the CN emission demonstrated the highest intensity

Conclusion

The obtained results demonstrate that the LIBS technique can be efficiently applied for the characterization of various nanocarbon structures namely graphene, graphite, and CNT.

The spectra of LIBS included the atomic carbon emission lines in addition to the emission lines of atomic nitrogen, nitrogen gas, Ca and Na emissions as all are predicted being existed in the atmosphere ambient of created plasma.

The results pointed to the molecular emissions CN within the range (385-388.5 nm) and C_2 at 516 nm. All the atomic and molecular emission lines of specimens appear at the same wavelength bands, due to graphene is the basis in the production of all carbon nanomaterials.

The investigation was conducted to examine the influence of molecular structure on CN and C2 molecular emissions for different adopted specimens.

The relation between C_2 emission intensities and the number of aromatic rings represented by the (C–C) and (C=C) bonds present in the structure of the sample indicates evidence that C_2 is released directly from the specimen.

Experiments analysis shows CN emission arises from the recombination of C_2 molecules in the sample plasma with the atmospheric nitrogen. The LIBS spectrum gets the exceptional behavior that when C_2 disappears; the emission of CN gets the highest intensity.

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