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2D Graphene Structures for Safe Explosion Works Produced by Self-Propagation High Temperatures Synthesis

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Abstract: Carbonization of a biopolymer (lignin) in self-propagating high-temperature synthesis (SHS) led to the production of 2D graphene structures. With the help of modern analytical methods (Raman spectroscopy, X-ray diffraction) and electron microscopy, the resulting product was confirmed to have a few-layer 2D graphene structure. The predicted photovoltaic properties of the resulting few-layer graphene were implemented for laser ignition of a model pyrotechnic composition based on porous silicon. A phenomenological model of the formation mechanism of 2D graphene structures under the conditions of the SHS process is proposed.

Keywords: self-propagating high-temperature synthesis; few-layer graphene; laser initiation; pyrotechnic composition

1. Introduction

The high-energy pulsed impact of explosive decomposition products of energetic materials (EM) upon different environmental objects is the basis of many modern industrial technologies. In this regard, creating new technologies related to the controlled impact of pulsed action on materials is an important promising direction in mining, metallurgical engineering, oil-extracting industries, construction, and mechanical engineering. These methods can be used in the explosive cutting of reinforced concrete structures, crushing and loosening of rocks, special processing of slabs and non-metallic materials, cleaning surfaces, containers, and holes from ice and metal, and compacting hard-to-press powders [1].

It should be taken into consideration that in actual practice, the safe use of energetic materials (EMs) can only be partially guaranteed after some time. Thus, it is impossible to eliminate the risk of unpredictable explosive decomposition of EMs due to the influence of random external factors [2]. The transition from electrical means of initiation to laser ones is a promising solution to these problems. So, the use of laser detonators eliminates the necessity to connect electrical wires to the initiation means, making the laser detonators (LDs) immune to such threats as electrostatic discharge, stray currents, or lightning. The use of fiber optic communication lines between the laser source and the LDs also increases the safety of blasting compared in comparison with traditional electrical blasting methods [3,4]. Another significant advantage of LDs is the possibility of replacing toxic, highly sensitive to mechanical impacts primary explosives in the blasting means with less toxic and less sensitive EMs, for example, photosensitive pyrotechnic compositions [5]. Nowadays, it is clear that the best performance parameters are shown by LDs based not just on light-sensitive pyrotechnic compositions but also on their composites with nanocarbons [6]. At the same time, graphene is increasingly used as a nanocarbon component of the EMs [for example, work [7] and references therein]. The choice of graphene as a charge component is based on its inherent high electrical and

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thermal conductivity as a low-defect crystal. Currently, the choice of graphene is also associated with its ability to form a flow of electrons under the influence of an external photon stream [8]. Accordingly, the use of graphene as a component of the laser devices can provide a synergistic effect of the influence of the thermal energy flow and the laser photon stream of the EMs [9,10].

So, due to its unique properties, graphene has become the most studied allotropic form of nanocarbon in the last decade. However, it should be noted that although the first work publication devoted to the production of graphene 2D structures goes back to 1958 [11] - that is, long before the discovery of other allotropic forms of nanocarbon - graphene did not attract any significant attention to researchers—only the pioneer work of A. Geim and K. Novoselov awarded the Nobel Prize for the isolation and study of the properties of graphene1 obtained by mechanical exfoliation of graphite, which gave rise to numerous studies devoted to both the development of new synthetic methods and the search for areas of application of graphene [12–19]. The almost exponential annual growth of publications devoted to the search for new applications of graphene is mainly because, nowadays, the technique of mechanical splitting of graphite has been significantly improved [20]. Note that, according to the IUPAC definition, the term graphene refers to a single sheet of graphite one atom thick. Two or more layers of graphene are referred to as multilayer graphene (few-layer graphene, graphene nanoplatelets)

To expand laboratory experiments to practical investigation in blasting technologies, the possibility of its large-scale production should be found. Methods of liquid exfoliation [21], ion intercalation and exfoliation [22], chemical vapor deposition (CVD) [23], and water-chemical synthesis [24] of graphene have been developed. They are used in practice, making it possible to produce graphene in amounts sufficient for interlaboratory research. However, the performance of these methods is insufficient to meet the needs of real materials science that, for example, prevents the possibility of using graphene in such a promising area of its application as photovoltaics [25,26].

It should be noted that modern stringent environmental requirements are an important factor determining the prospects for scaling up both known and newly developed methods of graphene synthesis.

Choice of synthesis technique. When developing graphene synthesis methods, researchers have to choose between techniques producing classical graphene that are impossible to provide the required level of performance and more productive techniques that lead to graphene line-organized 2D structures, minding the requirements of a specific task. In particular, as in this work, the task of laser detonator creation.

Therefore, many research groups are constantly looking for new possibilities for the synthesis of graphene-like structures, based both on different precursors and on new synthesis techniques.

Previously, we proposed the method for the synthesis of 2D graphene structures by carbonization of biopolymers under the conditions of the process of self-propagating high-temperature synthesis (SHS) that meets the given above requirements. The term SHS refers to moving a spin wave of a strong exothermic reaction through a mixture of reagents (oxidizing agent and reducing agent), where the heat release is located in the thin layer and is transferred from layer to layer by heat transfer. In the SHS process, branched-chain ignition, in contrast to thermal ignition, is caused by an avalanche multiplication of active intermediate products - free atoms, radicals, and excited particles - in their rapid reactions with the initial reagents and among themselves [18].

While choosing a carbonization technique, we took into consideration the fact that the advantage in comparison with the processes of pyrolysis and hydrothermal carbonization traditionally used for the carbonization of biopolymers [27] is the simplicity of the instrumentation of the SHS method. Other advantages of SHS methods are high synthesis rates, the possibility of carrying out the process without a constant supply of energy from external power sources, the possibility of synthesizing in any atmosphere or vacuum, and the absence of fundamental scale restrictions [28,29]. It should be noted that the synthesis of 2D nanocarbons under the conditions of the SHS process proceeds according to the "bottom-up" mechanism. The stages of the "bottom-up" mechanism include successive processes of thermolysis of the biopolymer to some primitives and the processes of their self-organization into 2D structures. However, the 2D nano carbons (G_{SVS}) obtained in the SHS process

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do not correspond in their morphometric parameters to the graphene samples obtained using known methods, and so does not allow us to recommend this method as an alternative in EM charges.

T The purpose of this work was to develop a new method of complete 2D graphene structure synthesis and demonstrate the possibility of its application as a component of initiating energetic compositions with low laser ignition thresholds.

2. Experimental Part

2.1. Materials

Precursor. Lignin, a complex, irregularly structured, resistant to decomposition, insoluble in water and organic solvents, high molecular weight polymer with branched macromolecules of a cyclic structure, was used as a precursor [30]. Lignin used in the experiments was obtained from long-term storage dumps under atmospheric conditions from the Arkhangelsk hydrolysis plant. The choice of lignin as a precursor of graphene-like material is explained by its reserves accumulated at storage sites in the amount of millions of tons and pose a severe environmental threat [31]. In this regard, the choice of lignin as a precursor to graphene structures was also due to the desire to develop a method for its utilization to have some benefit.

2.2. Synthesis of Few-Layer Graphene (FLG)

The synthesis of 2D graphene structures was carried out by carbonization of lignin under the process of self-propagating high-temperature synthesis (SHS) [11]. The method of obtaining FLG was carried out using a laboratory reactor, which is a quartz vessel (capacity 1 l) with a heating element in the lower part, which provides initial heating of the reaction zone to the temperature required to initiate the process (220 0C). The temperature in the reaction zone was controlled using a thermocouple. The preparation of the synthesis included a number of successive stages. The pre-dried lignin was transferred to a ball mill and grounded for 15 minutes. Next, a mechanical mixture of an oxidizing agent (ammonium nitrate NH4NO3, chemically pure, Sigma-Aldrich, St. Louis, USA) and a precursor (lignin) was prepared in a 1:1 weight ratio. The prepared mechanical mixture of oxidizer and precursor was placed in a "drunk barrel" type mixer and stirred for 15 minutes. Then, the resulting crushed mixture was transferred to a reactor preheated and purged with a current of dry argon. The start and end of the reaction were recorded by the start and end of the release of gaseous reaction products. The duration of the process was equal to 5-8 minutes. The yield of the carbonization product (based on the precursor) is 30-35% wt. The rest of the reaction mass passes into the gas phase and is captured in a trap cooled with liquid nitrogen.

2.3. Methods Used for Studying the Resulting Carbonized Structures

XRD diffraction. The phase composition of synthesized samples was studied using diffraction patterns recorded on an XRD-7000 diffractometer (CuKα radiation, λ = 0.154051 nm) (Shimadzu, Japan).

Raman spectroscopy. The quality of synthesized samples was estimated using Raman spectra recorded on a Horiba Jobin Yvon LabRam HR 800 spectrometer (532 nm laser; 1800 g/mm diffraction grating; micro-Raman system, microscopic objective, optical magnification ×20).

SEM and TEM. The synthesized images were obtained by scanning electron microscopy on a TESCAN Mira-3M microscope with an Oxford Instruments X-max EDX accessory and by transmission electron microscopy on 828 a 50 kV FEI Tecnai G2 30 S-TWIN microscope. In the TEM study, the powder samples were placed in ethanol, sonicated for 5 min, and mounted on a carbon grid. The obtained ring XRD patterns were identified using the software implemented in the Rigaku Ultima-IV diffractometer. XRD diffraction. The phase composition of synthesized samples was studied using diffraction patterns recorded on an XRD-7000 diffractometer (CuKα radiation, λ = 0.154051 nm) (Shimadzu, Japan).

2.4. Specific Surface Area Determination

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The specific surface area of synthesized samples was determined by polymolecular adsorption (BET method) using an ASAP 2020 Accelerated Surface Area and Porosimeter analyzer (United States). Nitrogen was used as an adsorbate gas. Prior to measurement, heating in a vacuum at a temperature of 300°C for 3 h was used as a standard sample preparation method. The measurement error was no more than 3%.

The true density of FLG powder particles was determined by helium pycnometry using an Ultrapycnometer 1000 device (Quantachrome instruments, USA).

2.5. Production of Pyrotechnic Compositions

A promising composition based on porous silicon was used as the base pyrotechnic composition [32], according to the method described in the article [33]. Nanoporous silicon (por-Si) with a porosity of 70–80% and an average pore size of 12–15 nm was obtained. In this work, we used nanoporous silicon powder with a particle size in the range of 30 – 40 μm.

2.6. Samples of Charge of Pyrotechnic Composition (PC) Based on por-Si Powder and Calcium Perchlorate $Ca(ClO_4)_2$

Basic composition. 18 mg of por-Si powder was pressed into a metal cap of 4 mm high with an internal diameter of 4 mm and a hole in the bottom 3 mm in diameter under a pressure of 80 MPa. The pressed por-Si powder was impregnated with a solution of $Ca(ClO_4)_2$ in methanol so that after evaporation of methanol, the mass ratio between $Ca(ClO_4)_2$ and por-Si powder was equal to 1:1. The height of the charge in the cap was equal to 3 mm. Then, the caps were placed in a thermostat under the temperature of 80 ^{0}C and dried for 15 minutes until the complete evaporation of the remaining solvent. The process was checked by weighing control of the caps (their mass became constant).

Basic composition modified with graphene particles. Powders of por-Si and multilayer graphene sheets were mixed in a ball mill in a ratio (por-Si:FLG) of 1:0.5 or 1:1 for 1 hour until a total homogeneous mixture was obtained. T Then, from the resulting mixture, PC samples were prepared: 18 mg of the mixture was pressed into 4x4 mm metal caps under a pressure of 80 MPa. The pressed powder of the mixture was impregnated with a solution of $Ca(ClO_4)_2$ so that after the evaporation of methanol, the mass ratio between $Ca(ClO_4)_2$ and por-Si powder was at the level of 1:1. Thus, the following PC was produced. We obtained two PC with the resulting ratios between the components [por-Si: $Ca(ClO_4)_2$:FLG] 1:1:1 (PC-1) or 1:1:0.5 (PC-2).

Testing of pyrotechnic compositions. The susceptibility of PC to laser radiation was studied with the help of a semiconductor laser diode of the Focuslight ECSE01-08-976 type (USA) with a wavelength of 976 nm (infrared radiation) and an output power of up to 8 W. Under test conditions, charges of the PC were exposed to laser radiation with constant flux $q \approx 15$ MW/m^2. A Tektronix TDS 2014 oscilloscope was used to record the burning time of a pressed PC placed in metal caps. The first signal was detected by the oscilloscope at the moment the pulse was applied to the Focuslight FL-FCSE01-8-976 laser diode, and the second signal was fixed by the oscilloscope from the FD-256 photosensor at the moment the combustion front reached the free surface of the composition. The main camera of the Honor 10 smartphone (16 MP, aperture f/1.8), frame rate 720 fps (or 480 fps) recorded the process of PC burning after laser ignition.

3. Results and Their Discussion

The lignin carbonization product turned out to be a highly dispersed black powder. To confirm the stated model ideas for the carbonized product to have a graphene-like structure, a set of complementary research methods such as - electron microscopy, Raman spectroscopy, and X-ray diffraction was used.

Electron microscopy. Electron micrographs of carbonized lignin are presented in Figure 1. From Figure 1, it can be concluded that the resulting particles have a volumetric-planar “scaly” form. These particles are typical for 2D carbon structures see, for example, [34]. Attention should be paid to the electron microscopy method as the most visual way to determine the morphology of the resulting carbonized product.

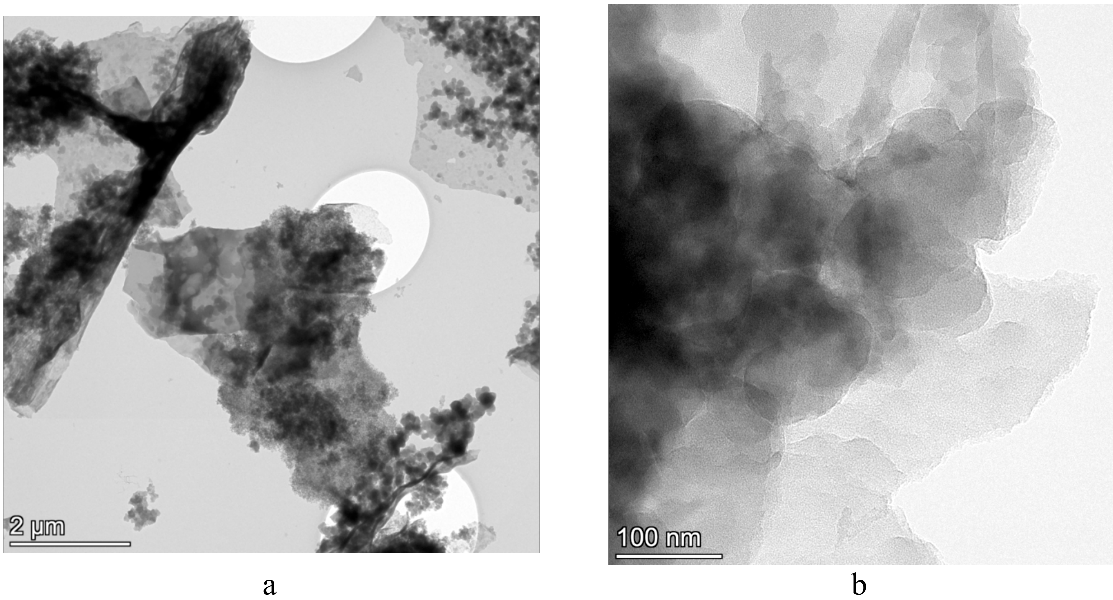

Figure 1. Electron micrographs of carbonized lignin: a – scanning electron microscopy (SEM); b – transmission electron microscopy (TEM) method**.**

Spectroscopic studies should confirm the fine structure of the product. To clarify the nature of the obtained product, spectroscopic studies were carried out.

X-ray. The diffraction pattern of the carbonized product is shown in Figure 2. A narrow, intense peak is observed in the diffraction patterns of graphite at 26.50. A weak, diffuse peak is typical for 2D carbon structures.

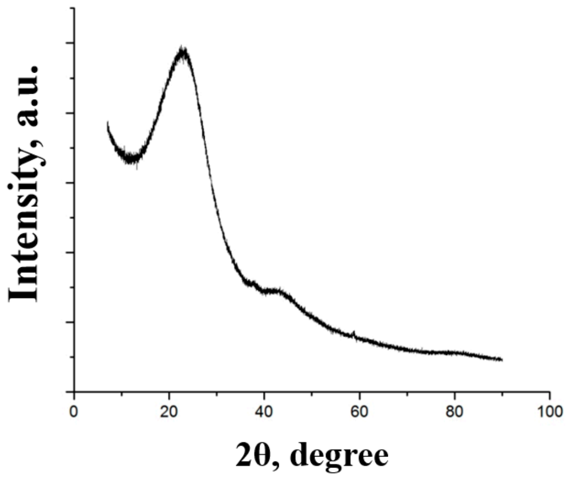

Figure 2. X-ray diffraction pattern of carbonized lignin obtained by self-propagating high-temperature synthesis.

The blurring of the XRD peak indicates that the particles are formed by a stack of several graphene sheets [35].

Raman spectroscopy. Raman spectroscopy is currently an effective way to determine the number of layers of 2D graphene structures without destroying their crystal lattice. In addition, the shape and position of the 2D peak allovers to clearly distinguish single-layer, bilayer, and multilayer graphene. Single-layer graphene usually exhibits a single and sharp 2D peak below 2700 cm-1, while bilayer graphene exhibits a broader and elevated 2D peak at 2700 cm-1. In the case of graphene sheets

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with more than five layers, we see broad 2D peaks that are shifted to positions 2700 + (20 ÷ 40) cm-1 and are similar to the 2D peaks of bulk graphite.

Raman spectroscopy data are shown in Figure 3. The Raman spectrum has two distinct peaks - at 1300 cm^{-1} and 1590 cm^{-1}. The first peak reflects defects in the sp^2 lattice (peak D), and the other - corresponds to hybridized carbon sp^2 (peak G). The relationship between D and G is the characteristics of each specific sample of graphene structures, determined both by the nature of the precursor and the method of the synthesis.

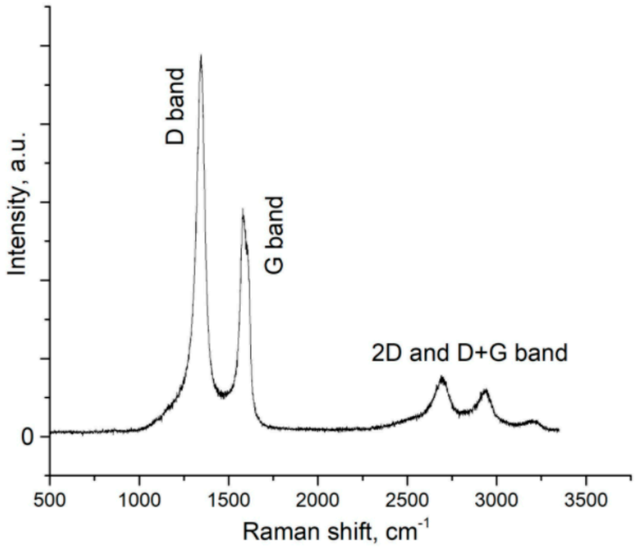

Figure 3. Raman scattering spectra for carbonized lignin particles (laser wavelength 532 nm).

The true particle density of the carbonated product. Additionally, such an important characteristic of the carbonated product as its true density was determined. The measured value of the true density of powder particles turned out to be equal to ϱ=1.98±0.02 g/cm^3 and satisfactorily coincided with the literature data for the true density of low-defect particles of few-layered graphene (ϱ=2.21 g/cm^3) [36].

Summarizing the data of complementary electron microscopy methods and spectrometric analysis methods, namely: the presence of a wide diffuse maximum around the value of 2θ = 26.5° in the diffraction pattern and the presence of three characteristic lines (peaks) in the Raman scattering spectrum of carbonized lignin samples, as well as data for the true density allows us to compare the obtained carbonized samples with samples few-layer graphene described in literature [37–39]. Taking into account of the method, we denote it as FLG_{SVS}.

4. Application of 2D Graphene Structures to Reduce the Ignition Threshold of Pyrotechnic Compositions

A pyrotechnic composition based on porous silicon and calcium perchlorate can be a likely replacement for traditional primary explosives (for example, lead azide) [40]. The advantage of this composition over traditional primary EMs is the absence of heavy and toxic metals in the composition. Previously, similar pyrotechnic compositions showed fairly high sensitivity to various electrophysical pulses (such as a high-current electron beam of nanosecond duration, a high-voltage discharge, an electrical explosion of a semiconductor bridge) [41,42], and thermal effects [43]. However, their susceptibility to coherent radiation remained unexplored.

We started the work by studying the fundamental possibility of using PS in laser means of ignition and initiation. At first, the susceptibility to radiation of a laser diode of a two-component pyrotechnic composition based on nanopore-Si powder and calcium perchlorate $Ca(ClO_4)_2$ was studied. During the experiment, five tests were carried out. In all cases, no ignition of charges was observed. It is known that graphene and its derivatives sensitize EM of various natures to coherent radiation. For example, when multilayer graphene was added, the threshold for ignition of a high-

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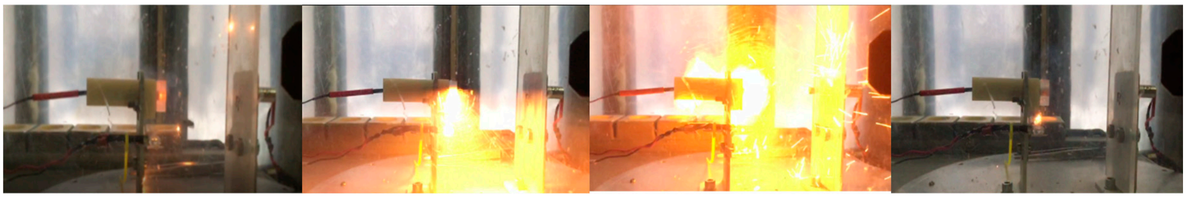
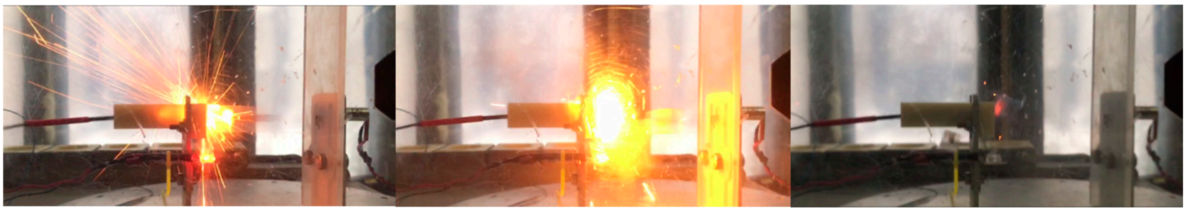
energy cobalt salt by a laser diode beam sharply decreased [44]. The work [45] proposed the use of graphene as a promising alloying component of solid rocket powders and primary and secondary explosives. The use of multilayer graphene as a promising alloying component of photosensitive PC based on fluorine rubber was demonstrated in [46]. Based on the presented data, we started to study the sensitivity of the PC por-Si+Ca(ClO4)2 sensitized with graphene FLGsvs to infrared radiation of laser diode.

Two types of charges were prepared (see experimental part). Three charges of each type were examined while testing the samples; in all six cases, an explosive transformation (ignition with a strong sound effect) was observed. This effect can be interpreted as explosive combustion. The sequence of processes of explosive transformation of charges PC-1 and PC-2 are shown in Figure 4 and Figure 5.



(a) **(b)** **(c)** **(d)**

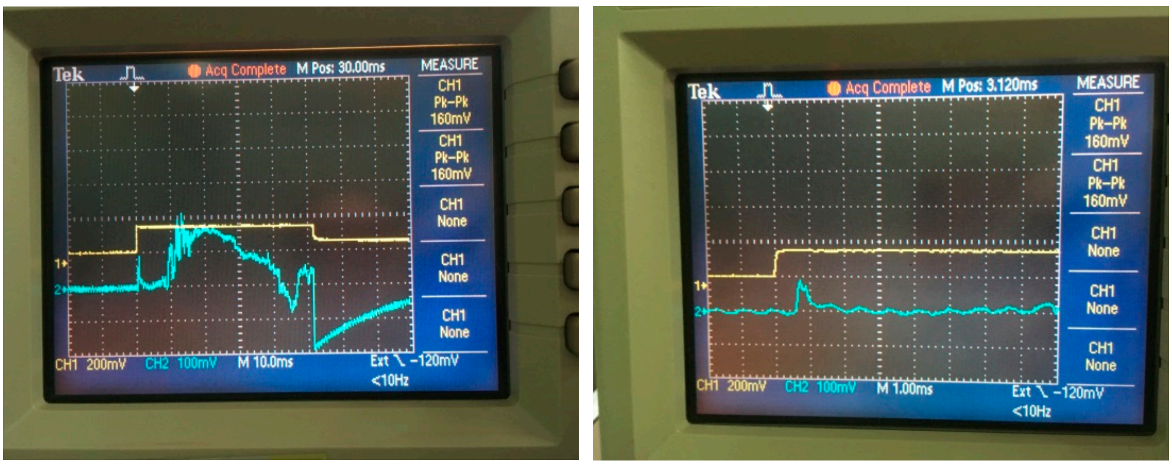
Figure 4. The process of explosive transformation of the PC-1 charge: a) the beginning of the combustion reaction; b, c) formation of a large combustion area; d) sample burnout**.**



(a) **(b)** **(c)**

Figure 5. The burning sequence of the PC-2 charge: a) formation of a large combustion area, c) burnout of the charge.

Oscillograms of the deflagration of compositions PC-1 and PC-2 showed that their combustion rates differ. So, under experimental conditions, the PC-1 composition burns out in ~ 10 ms (Figure 6a), and the PC-2 composition burns faster in ~ 750 µs (Figure 6b).



a b

Figure 6. Oscillograms of tests on the burning rate of charges PC-1 (a) and PC-2 (b)**.**

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Thus, the addition of graphene-like material powder to pressed samples of PC-1 and PC-2 increases the likelihood of their ignition by laser diode (infrared) radiation in comparison with the original PC. Consequently, the addition of graphene-like powder FLG_{svs} increases the ignition ability of PC based on nanoporous silicon to laser diode (infrared) radiation. Moreover, if in the case of classical explosive compositions initiated with a laser beam, the share of the absorbing additive does not exceed (3 – 5)% (mass) (the amount of the sensitizing additive over 5% (mass) leads to failures during laser excitation), in the case of PC the share of the sensitizing additive of FLG_{svs} can be (20 – 33)% (mass.).

5. Model Representations of the Mechanism of Formation of 2D Graphene Structures under the Conditions of the SHS Process

Analyzing the experimental results, we tried to provide some considerations on the mechanism of carbonization of organic compounds with the formation of all nootropic forms of nanocarbon. As comes from the analysis of the literature, the first real example of obtaining an allotropic form of nanocarbon by carbonization of organic molecules is the synthesis of 3D nanocarbon (detonation nanodiamonds, DND) as the result of the explosive decomposition of the mixture of two organic molecules – trinitrotoluene and cyclotrimethylenetrinitramine (RDX) [47]. The simplest idea of the mechanism of carbonization of organic compounds in the process of detonation synthesis is the idea of the mechanism of their carbonization through breaking the covalent bonds of the atoms of the original molecules up to their complete atomization [48]. However, the activation energy of such reactions is very high and cannot be provided under the conditions of the detonation synthesis process [49]. Consequently, even under conditions of high pressure and temperature during the explosive decomposition of trinitrotoluene and cyclotrimethylenetrinitramine, the destruction of their molecules goes up only some primitives - carbon structures, which in subsequent self-organization processes form 3D nanocarbon particles (DND). Several studies have shown that the specific morphometric parameters of DND particles depend not only on the conditions of detonation synthesis but also on the nature of the precursor (original explosive) [50]. It should be noted that, despite the large number of works, the reliable structure of the resulting primitives is unknown and, until now, has been based only on phenomenological models.

Creating a model for the formation of allotropic forms of nanocarbon within the framework of the carbonization mechanism of organic molecules, we should proceed from the model developed by N.N. Semenov [51]. According to this theory, the probable mechanism of destruction of materials is the mechanism associated with the formation of chemical radicals that, in turn, include multiple successive shear movements of atoms. Thus, covalent bond breaking is not a result but a consequence of the synergistic effect of elementary acts with lower activation energy. As a result, the energy of covalent bonds breaking is reduced, leading to their breaking. Minding such a model of material destruction, it can be assumed that the amount of energy supplied to the system plays a key role in determining the structure of final nanocarbons during the carbonization of organic substances.

To test the proposed model, we carried out detonation synthesis under conditions corresponding to the production of DND [52] but excluding hexogen from the charge composition, using only trinitrotoluene as a nanocarbon precursor. The exclusion of hexogen from the composition of the charge results in a reduction in the energy of its explosive decomposition [53]. To characterize the carbonized product synthesized under conditions of energy-deficient detonation synthesis, we used a set of complementary research methods already used in the work.

A comparison of the data in Figure 1 and Figure 3 with the data in Figures 7 and 8 allows us to conclude that energy-deficient detonation synthesis does not lead to the formation of 3D nanocarbon but results in the formation of 2D graphene structures. It should be noted that although both SHS synthesis and energy-deficient detonation synthesis lead to the formation of 2D graphene structures, the particles of synthesized nanocarbons differ in their morphometric parameters. A rigorous comparison of morphometric parameters of synthesized particles with the help of different methods from various precursors of 2D graphene structures lies beyond the scope of this work and will be analyzed in future publications.

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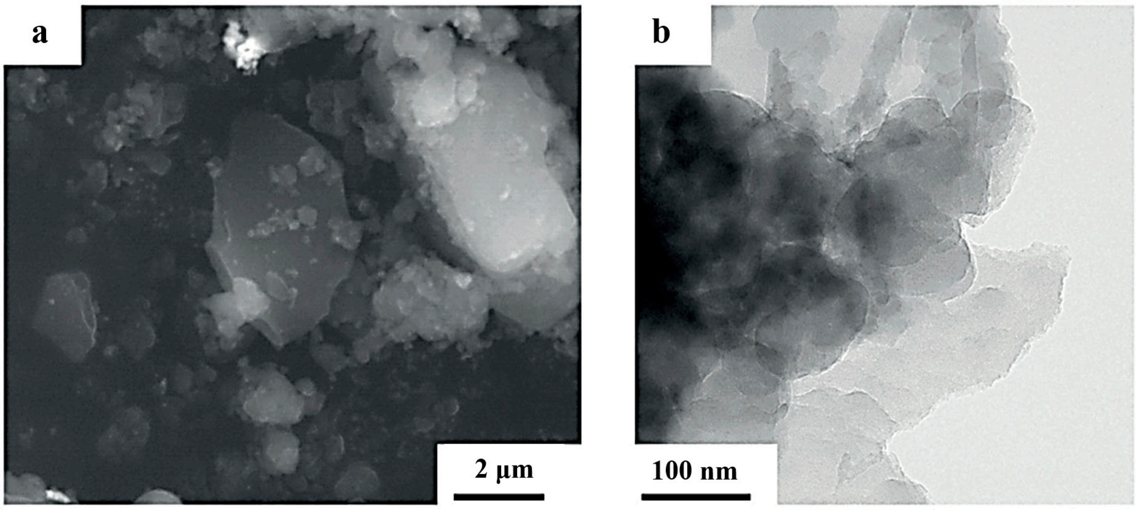

Figure 7. Microphotographs of SEM (a) and TEM (b) synthesized under conditions of energy-deficient detonation synthesis of a carbonized product.

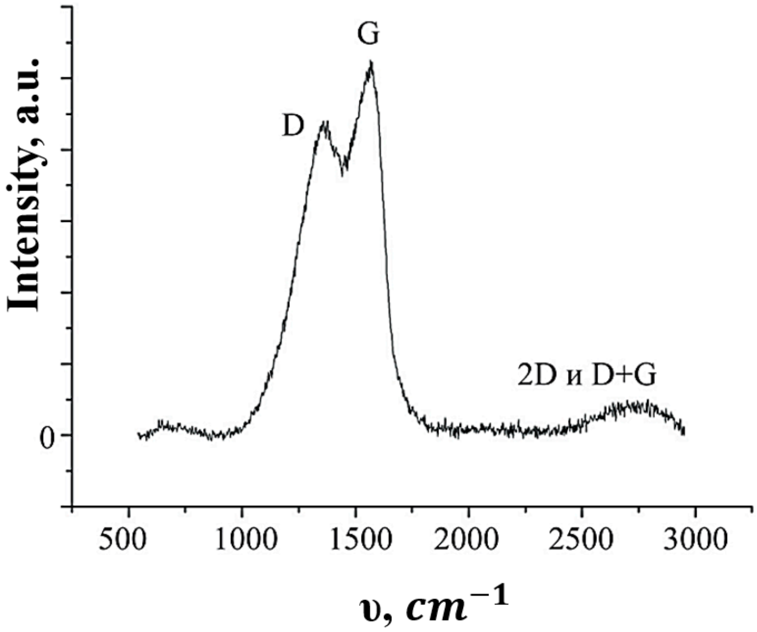

Figure 8. Raman spectrum synthesized under conditions of energy-deficient detonation synthesis of a carbonized product.

But based on our experimental results, we are able to make some following conclusions. Mechanisms of detonation and SHS syntheses have much in common, and the formation of nanoparticles, in the general case, is the combination of a high rate formation of initial primitives with their low rate of growth. The formation of nanocarbon particles is determined by the rate of diffusion of quantum primitives to the embryo of nanoparticles through their movement over a considerably t large distance. The size of a growing particle is proportional to the square root of the particle growth time [11]. The growth of particles is limited by interfacial turbulence, being the result of unequal media density, a gradient of concentrations, and temperatures.

The difference in the mechanisms of detonation synthesis of 3D nanocarbons (DND) and SHS synthesis of 2D graphene structures, in the most general case, is the result of different amounts of supplied energy.

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6. Conclusions

Using the lignin carbonation method under the conditions of a self-propagating high-temperature synthesis process, 2D nanocarbon corresponding to FLG in its morphometric parameters was obtained.

The resulting FLG was used as a component of a pyrotechnic composition based on porous silicon.

The addition of FLG powder to pressed samples of PC-1 [*por-Si: $Ca(ClO_4)_2$:FLG) 1:1:1*] and PC-2 [*por-Si: $Ca(ClO_4)_2$:FLG) 1:1:0.5*] increases the likelihood of their ignition with laser diode (infrared) radiation compared to the original PC [*por-Si + $Ca(ClO_4)_2$*].

The addition of 20–33% (mass.) graphene-like powder material FLG_{svs} to the PC leads to a sharp increase in sensitivity to infrared laser radiation and the excitation of explosive transformations in the PC.

A phenomenological model of organic compound carbonization with the formation of allotropic forms of carbon under the conditions of comparable carbonization mechanisms (SHS and detonation synthesis) is proposed.

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Conflicts of Interest: The authors declare that there are no conflicts of interest requiring disclosure in this article.

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