Synthesis of single and few layer graphenes in flames

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Abstract
The results of the study of the formation of graphene layers in the flame in premixed flame propane and butane-oxygen mixture on a nickel substrate at atmospheric and low pressure is given. The influence of the ratio C/O and supply quantity of argon on the formation of graphene layers was researched. It is shown that in the flame of propane and butane on a nickel substrate is observed at atmospheric conditions the formation of predominantly 2-10 layers of graphene. It is shown that in the range of 40-100 Torr on a nickel substrate in butane-oxygen flame with the addition of benzene mainly formed 1-3 layers of graphene. It is established that in the pressure range 45-55 Torr observed formation on nickel substrate single layer graphene.
Keywords: graphene, propane, butane, flame, substrate

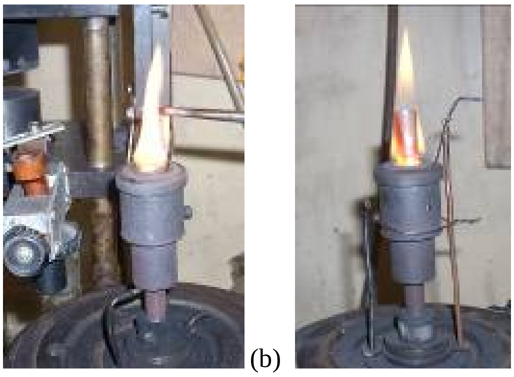
Introduction
Graphene has extremely useful properties: extremely high carrier mobility, high electrical and thermal conductivity, the dependence of electronic properties on the presence on the surface of graphene added radicals of different nature, and others [1, 2]. Application graphene due to its unusual properties may run as a basis for new nanomaterials with improved mechanical, electrical and thermal characteristics, as well as an element of nanoelectronic devices. Graphene layers prepared by different methods: mechanical splitting of the graphite layers, graphite bundle liquid phase oxidation of graphite etc. [1-3]. A promising method of producing graphene layers is the method of synthesis of graphene in flames. Bockhorn H. scheme has been proposed the formation of soot particles in the flame of which is logically possible formation of graphene as an intermediate step between soot and PAH [4, 5].

The studies [6, 7, 8] carried out under atmospheric conditions confirm that the process of obtaining graphene in the flame was not able to compete with other existing methods. The process of formation of graphene in a flame is a continuous, rapid, and inexpensive. The research synthesis of graphene in a flame at atmospheric pressure preferential formation on the catalyst substrate more than two layers of graphene was showed. Conditions for the synthesis of graphene single layer in a flame of interest. Currently available literature there is no information about research synthesis of graphene layers at low pressure, which may be of interest from the point of view of a single layer graphene formation. This paper presents the results on the synthesis of graphene layers in premixed hydrocarbon flames on a nickel catalyst substrate at atmospheric pressure and low pressure at various conditions.

2. Experimental methods of approach
The synthesis graphene layers were performed in the premixed flame-propane and butane-oxygen mixture at atmospheric pressure, with the addition of argon. Argon was fed in an amount of 150, 250, 350, 450 and 500 cm^3/min.

The substrate used a nickel plate of thickness of 0.2 mm, which was placed in the center of the burner flame. For more output graphene, the plate is rolled up into a cylinder. Between the edges of the plate, rolled into a cylinder, leaving the gap size of 2-3 mm, which create the conditions for the formation of gross graphene and on the inner surface of the cylinder. The photography general flames arranged there in a substrate catalyst are shown in Fig. 1.

The residence time in the flame of the plate was 5 minutes. Flame temperature depends largely on the amount of feed argon and the ratio C/O. Due to the fact that placing the substrate in its flame temperature is reduced to 30-50 °C due to the heat dissipation plate and the holder, the initial flame temperature exhibited within 950-970 °C.


(a) (b)

a - plate, b – cylinder

Fig. 1. The photo of flames with a catalyst substrate:

The flame temperature in the catalytic synthesis of graphene on a substrate maintained within 900-920 °C. Study of the formation of layered graphene layers performed at a constant flow rate of propane or butane - 219 cm^3/min. In order to obtain the desired ratios C/O unchanged oxygen consumption, the values of which are given in Table 1.

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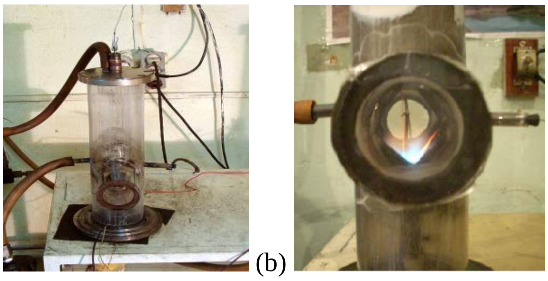
Table 1. The flow rate of oxygen depends on the type of fuel to obtain the desired ratio C/O

The value of C/O	0.75	0.85	0.95	1.05
Consumption of O_2 for C_3H_8, cm^3/min	438.0	386.0	346.0	313.0
Consumption of O_2 for C_4H_{10}, cm^3/min	584.0	515.0	461.0	417.0

The studies of the formation of layered graphene films were premixed flame in butan-argon-oxygen mixture with adding benzene at a pressure of 40-100 Torr. For this purpose, the burner as depicted in Fig. 1, was placed in a quartz tube in which an initial vacuum is created 5 Torr. The experiments were performed in the following conditions: flow of butane – 450 cm^3/min, the flow rate of oxygen – 740 cm^3/min, flow of benzene – 70 – 120 cm^3/min corresponding to the ratio C/O = 0,8-0,9. As the catalyst substrate applied plate made of nickel. The flame temperature in the experiments was in the range of 900-950 ^oC. The residence time in the flame plate was 3 minutes. Photo of the burner to carry out research on the synthesis of graphene layers in the flame at low pressure is shown in Fig. 2.

(a)  (b)

a – general view, b – with the substrate placed in a flame

Fig. 2. Photo of the burner for the synthesis of graphene layers in the flame at low pressure

At the expiration of this time, the substrate deduced from the flames. Then, the system switched off, the pressure was increased to atmospheric pressure, the substrate is removed for further study.

The study produced by the catalytic substrate particulate soot of structures was performed on Raman spectrometer NTEGRA Spectra at a wavelength λ = 473 nm. The presence of graphene layers was evaluated by the presence of three characteristic peaks have: a first peak D at 1351 cm^{-1}, G second peak at 1580 cm^{-1} and 2D third peak at 2700 cm^{-1}. The ratio between the intensity of the G peak (I_G) and 2D peak (I_{2D}) give an estimate of the number of layers (I_G/I_{2D}) [9]. For a mono-layer of graphene this ratio is less than unity. Raman spectroscopy has allowed to establish the presence of layered graphene films, as well as to evaluate the quality of the graphene layers.

3. Results and discussion

3.1 Formation of graphene layers in a flame at atmospheric pressure

The experimental results in the synthesis of the graphene layers of the premixed combustion of propane and butane-oxygen mixtures at various ratios of C/O are shown below. Argon consumption in all experiments constant and equal 250 cm^3/min. The Results obtained minimum ratio I_G/I_{2D}, characterizes the amount of graphene layers on the substrate depending on the fuel source and the ratio C/O, is given in Table 2.

Table 2. The minimum ratio I_G/I_{2D} depending on the ratio of C/O and type of fuel

The value of the ratio, C/O	0.75	0.85	0.95	1.05
Propane, I_G/I_{2D}	2.2	1.8	1.5	1.9
Butane, I_G/I_{2D}	1.5	2.0	1.3	1.6

Investigations on synthesis of graphene layers in hydrocarbon flame at low pressure have shown that the formation of graphene layers is occurred in sooting zone as well as at atmospheric pressure, as was shown in [8]. Fig. 3 shows the Raman spectra (a) that characterizing the carbon structures are formed on nickel plate in areas 0, 1, 2, 3 (b). In zones 0, 1 and 2 (Fig. 3, and b) the amorphous carbon structure is observed, but in zone 3 the graphene layers are synthesized. At that, an area of graphene formation at low pressure is more expanded than at atmospheric pressure. Above zone 3 there is soot structure is formed (Fig. 3b).

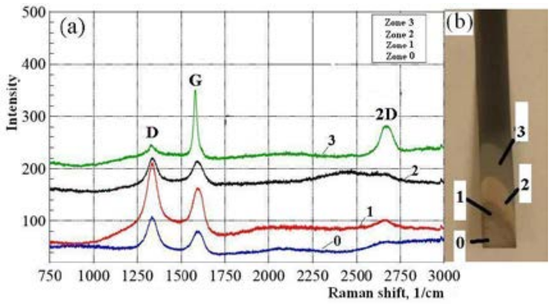
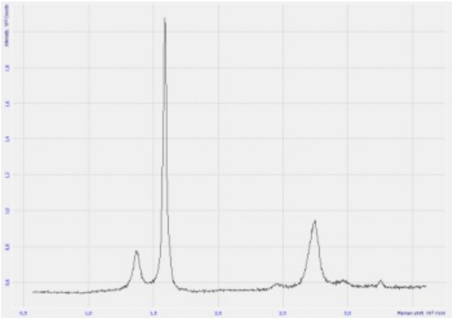


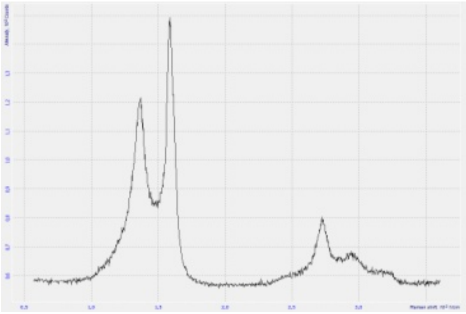
Fig. 3. The Raman-Spectra of carbon structures in accordance with (a) zones; and photo of nickel substrate (b) with an indication of formed carbon structure zones (P = 90 Torr, C/O = 0.8, T = 900 °C, t = 30 sec)

It is stated that preferably in the flame of propane and butane is observed under these conditions the formation of graphene layers in an amount of 5-10 layers. The results of Raman spectroscopic studies of soot samples are shown in Fig. 4 and 5.

It is found that the graphene layers are formed independently of the type of fuel in the studied range of ratios C/O with a pronounced peak of graphite G. The tendency for increasing the degree of disorder of the graphene layers with increasing ratio of C/O, hich is characterized by an increase in the peak intensity D. For propane-oxygen mixture degree of disorder is observed at a higher ratio of C/O than for butane-oxygen mixture. However, butane-oxygen mixture at a ratio of C/O = 0.95 was obtained the minimum number of graphene layers (three layers, I_G/I_{2D} = 1.3, Table 2).



a



b

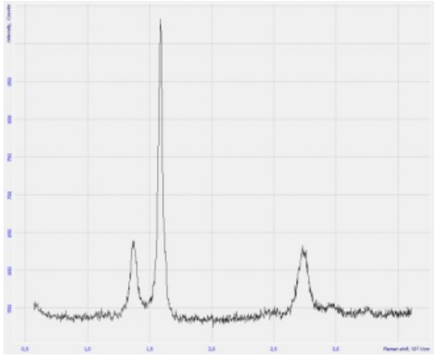
a – C/O = 0.75 (I_G/I_{2D} = 2.2); b – C/O = 1.05 (I_G/I_{2D} = 1.9)

Fig. 4. Raman spectra of graphene layers on a nickel substrate obtained in propane-oxygen-argon flame at values of C/O

It was studied the effect of argon flow on the synthesis of graphene layers in its submission to the propane or butane-oxygen flames. Feed argon flame affect its temperature. There is a process of lowering the temperature of the flame adjustment to the values of 950-970 °C, which is most favorable for the synthesis of graphene layers. It was necessary to determine the flow rate of argon, the most favorable for the synthesis of graphene at different combustion conditions.

It is found that when the ratio of C/O = 0.75 for propane-oxygen flame increase in argon from 150 cm^3/min to 500 cm^3/min not activate the process of the formation of graphene layers, and leads to the formation of predominantly amorphous soot structure. However, the argon flow rate 150 cm^3/min there is a clear graphitized structure that is characterized by the presence of three peaks characteristic of the graphene layers, Fig. 6.

The research for propane-oxygen flame at a ratio of C/O = 1.05 at different flow rates of argon showed the presence of layers of graphene, but with the presence of disorder, which is characterized by a peak of D greater intensity. When the ratio of C/O = 1.05 with filing 150 cm^3/min argon on nickel substrate in propane-oxygen flame is observed the formation of a minimum number of graphene layers (three layers - I_G/I_{2D} = 1.3).



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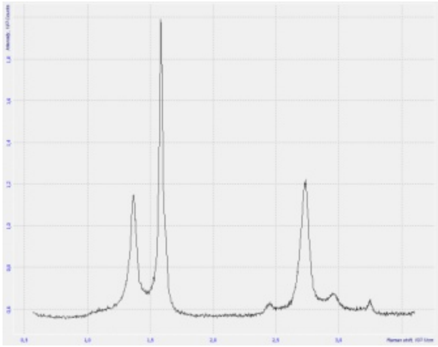


b

a – C/O = 0.75 (I_G/I_{2D} = 1.5); b – C/O = 1.05 (I_G/I_{2D} = 1.6)

Fig. 5. Raman spectra of graphene layers on a nickel substrate obtained in the butane-oxygen-argon flame at values of C/O

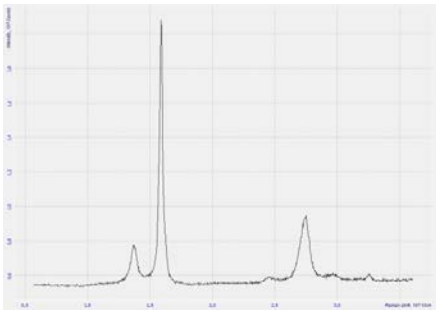


Fig. 6. Raman spectrum of graphene layers: Ni, $C_3H_8/O_2/Ar$, C/O = 0.75, the flow of argon 150 cm^3/min (I_G/I_{2D} = 2.2)

As a result, studies have found that as the ratio of C/O trend increase in the degree of disorder of graphene layers, which is characterized by an increase in the peak intensity D. For propane-oxygen mixture degree of disorder is observed at a higher ratio of C/O than for butane-oxygen mixture. It is shown that the formation of graphene layers, the optimal value is the ratio of C/O = 0.85-0.9 and the flow of argon in the amount of 150-250 cm^3/min, Fig.7.

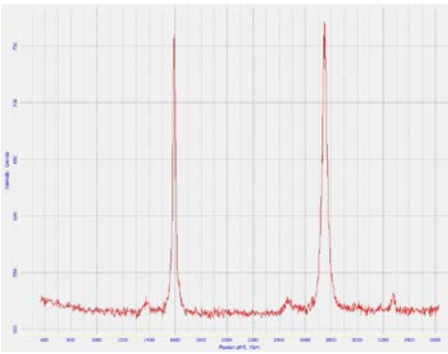
3.2 Formation of graphene layers in the flame at low pressure

Analysis of the results of synthesis of graphene layers in the flame at low pressure showed that in the pressure range of 40-100 Torr primarily on nickel substrate formed 1-3 layers of graphene, which is characterized by the intensity ratio $I_G/I_{2D} \leq 1.3$. The range of ratios I_G/I_{2D} Raman spectra of graphene samples, obtained at various pressures shown in Table 3.

Table 3. Range of ratios IG/I2D Raman spectra of graphene samples obtained at different pressures of flame $C_4H_{10}/O_2/C_6H_6$

Pressure value, Torr	45	55	60	65	90
Range of ratios, I_G/I_{2D}	0.99-1.27	0.58-1.25	1.1-1.25	1.2-1.35	1.27-1.33

It is found that with increasing pressure in the trend growth of the number of layers of graphene on a nickel substrate, which is associated with an increase in soot formation. At a system pressure of 45-55 Torr observed preferential formation of a single layer graphene, the characteristic Raman spectra are shown in Fig. 7.



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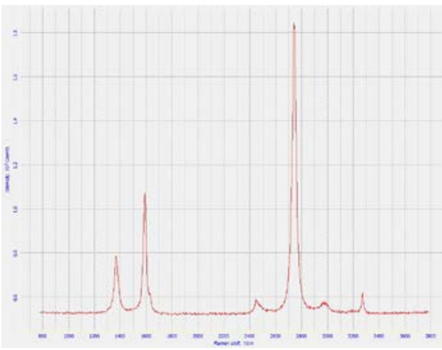

b

a – 45 Torr (I_G/I_{2D} =0.99), b – 55 Torr (I_G/I_{2D} =0.58)

Fig. 7. Raman spectra of single-layer graphene samples obtained with the addition of flame C_4H_{10}/O_2 benzene on a nickel substrate at a pressure

Obtained graphene layers were diluted in a acetone suspension to facilitate coating of the SSCs. To graphene layers were separated from the nickel substrate 70 % nitric acid was used. The raw graphene/graphite films were then immersed into a hydrogen peroxide solution (H_2O_2, 30 %) for over 24 h to remove the amorphous carbon impurities.

Conclusions

An analysis of the results of studies on the formation of layered graphene films in the flame, we can draw the following conclusions. It is established, that formation graphene layers occurs as in propane – oxygen and butane – oxygen flame in the range of the ratio C/O: 0.75, 0.85, 0.95, 1.05. It is shown that predominantly propane and butane flame formation is observed 3-10 layers of graphene. The increasing ratio of C/O observed trend of increasing the degree of disorder of the graphene layers, which is characterized by an increase in peak intensity D. The increasing ratio of C/O observed trend of increasing the degree of disorder of the graphene layers, which is characterized by an increase in peak intensity D. For propane-oxygen mixture degree of disorder is observed at a higher ratio of C/O than for butane-oxygen mixture. It is shown that the formation of graphene layers affects the flow rate of argon supplied to the flame. Found that for the formation of graphene layers at atmospheric pressure, the optimal values are the ratio C/O = 0.85-0.9 and argon consumption in an amount of 150-250 cm^3/min.

It is shown that in the range of 40-100 Torr on a nickel substrate in butane-oxygen flame with the addition of benzene mainly formed 1-3 layers of graphene. Found that at a system pressure of 45-55 Torr observed preferential formation of a single layer graphene.

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