NANOSYSTEMS: PHYSICS, CHEMISTRY, MATHEMATICS, 2016, 7 (1), P. 60–64

Synthesis of high-purity multilayer graphene using plasma jet

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PACS 52.75.Hn, 81.05.ue **DOI 10.17586/2220-8054-2016-7-1-60-64**

A method to synthesize graphene materials using a DC high current divergent plasma torch has been developed. Carbon atoms were generated by the decomposition of propane-butane, methane and acetylene in a thermal plasma jet. The graphene materials were characterized by electron microscopy, thermogravimetry, Raman spectroscopy. The influence of the experimental conditions on the morphology and phase composition of the synthesis products was investigated. The optimal conditions for the synthesis of high-purity graphene flakes have been found.

Keywords: graphene materials, flakes, hydrocarbons, synthesis, plasma torch, plasma jet.

Received: 20 November 2015

1. Introduction

Graphene can be produced by variety of techniques, including mechanical exfoliation, growth on the basis of SiC substrates, high-pressure high-temperature growth, chemical exfoliation, and electrostatic deposition [1]. Depending on the synthetic method, graphene may be of three different types: single layer graphene (SLG), bi-layer graphene (BLG) and few-layer graphene ($n \leq 10$) [2]. The quantity and form of graphene required varies according to the application; some applications, such as transparent electrodes and sensors, require thin films of graphene, other applications, such as energy storage devices (such as batteries and supercapacitors) and polymer composites, require relatively large quantities of graphene nanosheets or platelets. Furthermore, the importance of using high quality graphene will vary with application type. For example, no noticeable improvement in electrochemical activity has been observed when going from few-layer- to monolayer-graphene, and defects in the material are thought to enhance both the electrochemical and hydrogen storage ability of graphene sheets [3].

Nevertheless, the issues of large-scale production and process control for graphene, remain essentially unresolved. Thermal plasma, which is produced by high-power discharges at or close to atmospheric pressure, has proven to be an effective tool for the fabrication of nanoparticles and nanostructured films and coatings [4]. Pure layered graphene was produced using a plasma jet reactor based on the DC plasma torch [5]. The number of layers of graphene sheets was controlled by adjusting the rate of ethanol injection.

The main aim of the present study is to obtain experimental data for the synthesis of graphene materials from carbon atoms generated by hydrocarbon decomposition (propane-butane, methane acetylene) in a thermal plasma jet by means of the direct current plasma torch with the extending channel of an output electrode.

2. Experimental setup and procedure

The synthesis of graphene has been investigated using a DC plasma torch with power of up to 40 kW with an expanding channel of the output electrode and the vortex stabilization of the arc [6, 7]. A detailed description of the experimental setup was given in the study [8]. The

TABLE 1. Technological conditions

Power	30 – 40
Current	350 – 400 A
Voltage	60 – 110 V
Plasma gas	0.5 – 3.75 g/s
Gas flow rate	0.05 – 0.37 g/s
Pressure	150 – 730 Torr
Duration of the experiment	10 – 20 min

experiment involved simultaneous input of hydrocarbons in a carrier gas (e.g. helium, argon) into the plasma torch, wherein heating and decomposition occurred in the plasma jet and in the region of the arc discharge, followed by condensation of the synthetic product on metallic surfaces. Consumption of carbon, plasma forming gas and plasma torch power were changed independently from one other. For the experimental conditions, the electric power of the plasma torch was set up to 40 kW. Helium and argon were used as plasma gases. The experimental conditions are presented in Table 1.

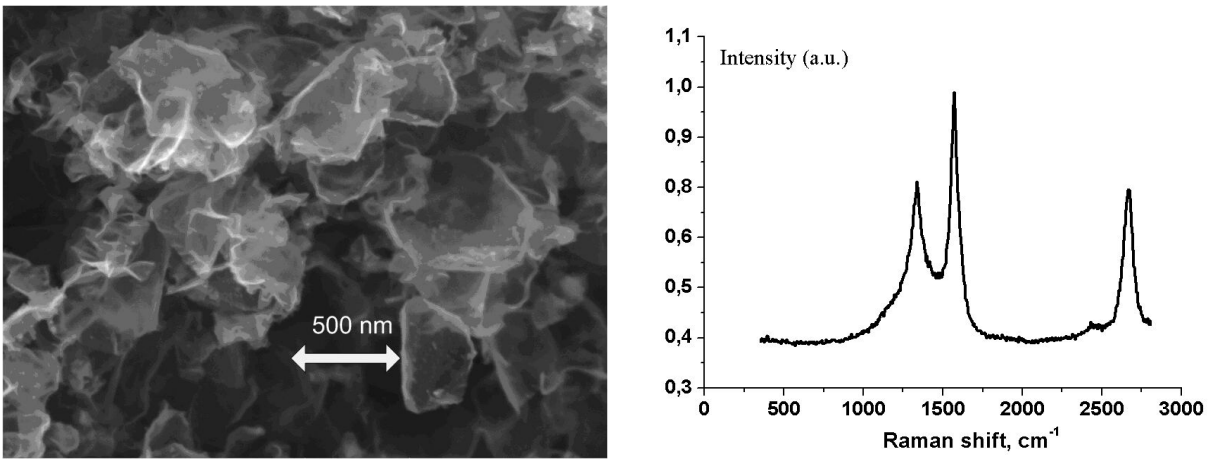
The main parameters were: varying the pressure and gas flow rate. The hydrocarbon flow rate ranged from 0.11 to 0.3 g/s for a propane-butane mixture; from 0.15 to 0.37 g/s for methane; and from 0.05 to 0.16 g/s for acetylene. Natural gases used as carbon source were: propane-butane in the ratio 30 : 70 %, technical methane and high purity methane (99.99 %). Upon completion of the synthesis, carbon materials samples were collected from the target surface and from the trap. Samples were not purified and were analyzed in the form in which they were synthesized in the reactor.

Methods of electronic microscopy were used to investigate the structure of the synthesized products on a scanning electronic microscope of MIRA 3 TESCAN. Efficiency of synthesis, thermal stability and phase composition of carbon products were evaluated by thermogravimetry and differential scanning calorimetry on a synchronous thermal analyzer STA 409PC Luxx (NETZSCH) with linear heating sample in air at the rate of 10 K/min at temperatures up to 1000 °C. Nano Raman spectroscopy (NTEGRA) was used in the characterization of the graphene with an excitation wavelength of 532 nm under ambient conditions from 300 – 3000 cm^{-1}. The laser power was about 3 mW for a spot size of 1 μm.

3. Results of experiment

Experiments on the decomposition of a propane-butane mixture show that depending on the pressure and the value of plasma gas flow rate, nanostructures in the form of flakes with various geometries are formed. At lower He pressures (200 Torr), a large amount of amorphous carbon (37 %) and graphitized particles are produced. Increasing the pressure led to the formation of graphene flakes. At 350 Torr He, the transverse dimensions of these flakes were in the range of 600 nm. Additionally, the graphene content in the synthetic product increased, although some amorphous carbon was still present in small amounts (Fig. 1).

Further increase of the pressure decreased the content of this phase and reduced the size of the produced graphene flakes. When reaching a He pressure of 710 Torr, the synthetic samples contained 2 % amorphous carbon and 81 % graphene materials. The synthetic products from the propane-butane mixture obtained under argon have transverse dimensions not exceeding 100 nm. As in the case of He, with increased argon pressure, amorphous carbon is present together with graphene materials.



(a) (b)

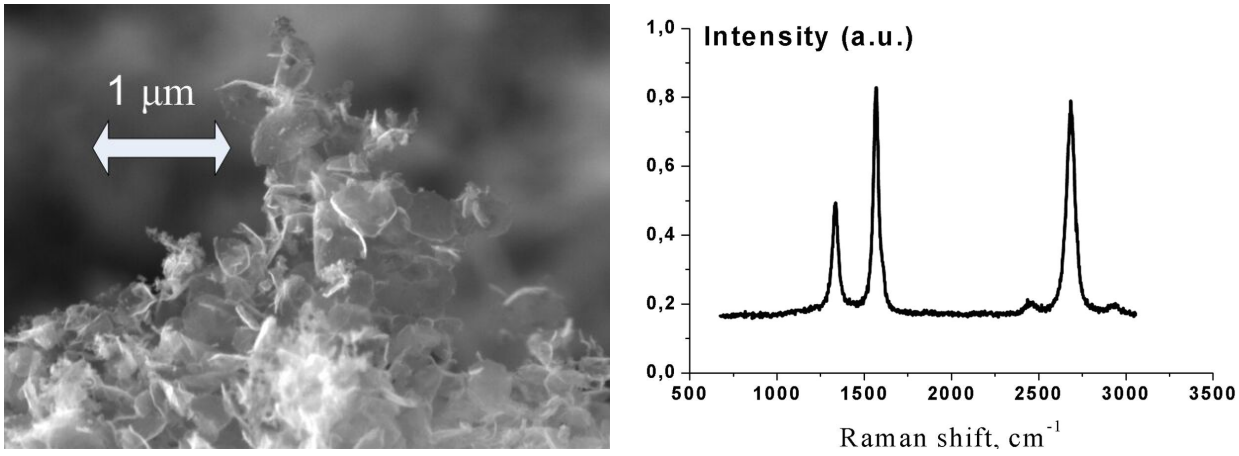
FIG. 1. The morphology (a) and the Raman spectrum (b) of the sample produced from the decomposition of propane-butane in helium plasma at a pressure of 350 Torr. Plasma forming gas is helium

Figure 1(b) shows the Raman spectra of the graphene materials formed from the decomposition of propane-butane in He plasma at 350 Torr. Raman spectra show common features in the 300 – 2800 cm^{-1} region: the G and D peaks, which lie at around 1560 and 1360 cm^{-1}, respectively, and 2D (2690 cm^{-1}). The number of layers can be derived from the ratio of peak intensities, I_{2D}/I_G, as well as the position and shape of these peaks. Our few-layered graphene materials show a single Lorentzian profile. However, we believe that this measurement was a mixture of graphene flakes with a different number of layers, from 1 to 10.

The best conditions for the synthesis of graphene materials obtained from decomposition of methane differ mainly in higher precursor consumption: pure methane, a pressure of 350 Torr, helium or argon, CH_4 flow rate of 0.75 or 3.5 g/s. Up to 77 % graphene flakes were formed with a transverse dimension of 400 – 600 nm. In helium, the yield of graphene materials was 91 %. The maximum yield of 82 – 88 % of graphene materials with crumpling sheets was observed in argon at 650 – 670 Torr and a high methane flow rate of 0.368 g/s.

Figures 2(a) and 2(b) show the characteristics of the plasma jet-grown multilayer graphene flakes and Raman spectra images under optimized conditions. Fig. 2(a) shows flakes. We believe that the sample used for this measurement may have consisted of a mixture of graphene flakes with differing numbers of layers (from 1 to 10 of graphitic layers formed with various thicknesses). Moreover, the Raman spectra of the image shown in Fig. 2(b) indicates that the graphitic layers observed are similar to the Raman spectra image of the few-layer graphene of [5], whose G and 2D peak intensities lie at 1580 and 2700 cm^{-1}.

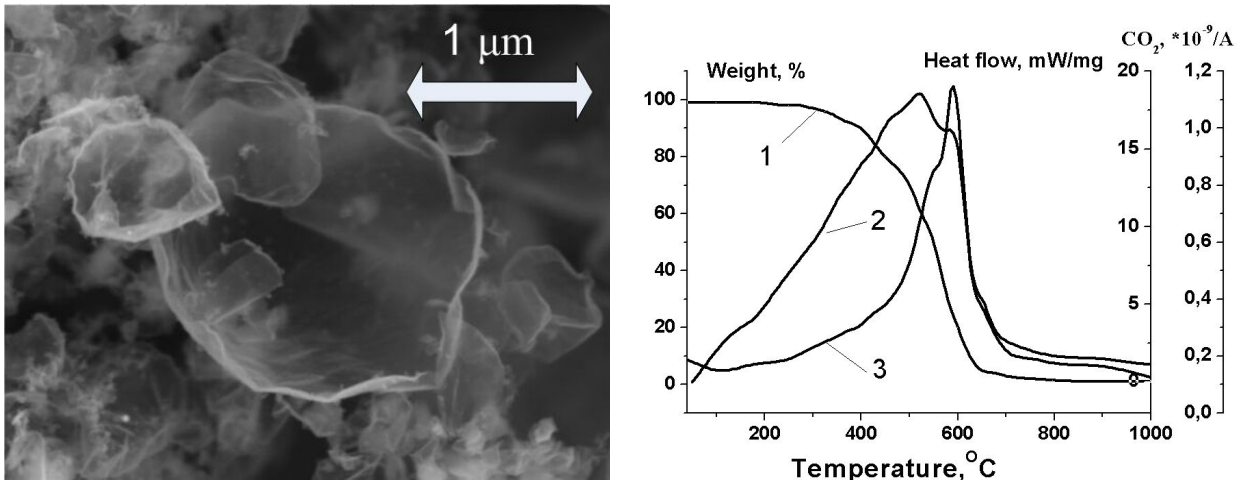
It can also be noticed from the image that the shape of the 2D band, particularly the absence of the graphite shoulder, shows a hallmark feature of few-layer graphene. Under our conditions, the samples have less than 10 layers, with the largest shift D line observed for a smaller number of layers. The majority of our samples had 2 – 5 graphene layers. The I_G/I_{2D} ratio of our product is ~ 1.03, which is comparable to the value for three layers of CVD-grown graphene ($I_G/I_{2D} \sim 1.3$).In our study, we used the well-known approach to make conclusions about the presence of graphene materials and the number of layers in those graphene structures in accordance with previous studies [9].



(a) (b)

FIG. 2. The morphology (a) and the Raman spectrum (b) of the sample produced from the decomposition of methane at the pressure of 350 Torr. Plasma forming gas is helium

Graphene materials produced from decomposition of acetylene under optimal conditions are less stable at high temperatures than the synthetic products generated using propane-butane. Upon decomposition of acetylene using argon and helium plasma, crumpled graphene structures were produced at pressures ranging from 150 to 350 Torr. In helium, the yield of graphene materials was 81 %. Fig. 3 shows the results of electronic microscopy and thermogravimetric analysis of graphene products. Decreasing the gas pressure to 150 Torr increased the amount of graphite and amorphous carbon phase. Fig. 4 shows a typical Raman spectrum for our product. The three intense features are the D band at 1334 cm^{-1}, the G band at 1577 cm^{-1} and the 2D band at 2662 cm^{-1}. The samples have fewer than 10 layers.



(a) (b)

FIG. 3. The morphology (a) and thermogravimetry (b) graphene materials produced from decomposition of acetylene at a pressure of 350 Torr. Plasma forming gas is helium. (1) Loss of weight, (2) heat flow and (3) rate of generation of CO_2

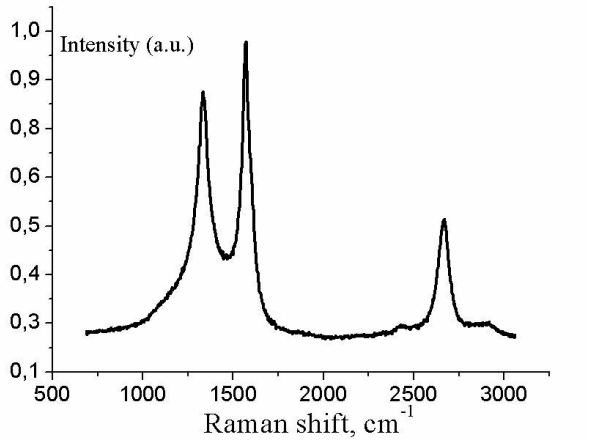


FIG. 4. The Raman spectrum of the sample produced from the decomposition of acetylene at a pressure of 150 Torr. Plasma forming gas is helium

4. Conclusions

Based on the Raman spectra and thermogravimetry for the samples, high-purity multi-layer graphene materials were successfully synthesized using a plasma jet. It has been shown that the selection of hydrocarbon source and their flow rate influenced the quality of the graphene produced. Depending on the synthetic parameters, the geometry of the graphene materials (from curved petals to disk diameter of 100 nm – 1 μm) and the graphene content in synthesis products (from 58 to 95 %) varied.

In general, the experimental data allowed stepwise scaling of the synthesis so that graphene having the desirable morphology could be obtained.

Acknowledgements

The authors gratefully acknowledge Russian Foundation for Basic Research for the support by grant No. 15-08-00165 and by State Assignments No. 2560 and No. 16.1103.2014/K.

References

[1] Calizo I., Bejenari I., et al. Ultraviolet Raman microscopy of single and multilayer graphene. *J. Appl. Phys.*, 2009, **106** (4), 043509 (5 p).
[2] Rao C.N., Sood A.K., Subrahmanyam K.S., Govindaraj A. Graphene: the new two-dimensional nanomaterial. *Angew. Chem. Int. Engl.*, 2009, **48** (42), P. 7752–7777.
[3] Edwards R.S., Coleman K.S. Graphene synthesis: Relationship to applications. *Nanoscale*, 2013, **5**, P. 38–51.
[4] Shigeta M., Murphy A.B. Thermal plasmas for nanofabrication. *J. Phys. D: Appl. Phys.*, 2011, **44**, 174025 (16 p).
[5] Kim J., Heo S., Gu G. Suh J. Fabrication of graphene flakes composed of multi-layer graphene sheets using a thermal plasma jet system. *Nanotechnology*, 2010, **21**, 095601(6 p).
[6] Isakaev E. Kh., Sinkevich O.A., Tyuftyaev A.S., Chinnov V.F. Thermal fluxes in a generator of low temperature plasma with a divergent channel of the outlet electrode. *High Temperature*, 2010, **48** (1), P. 97–125.
[7] Isakaev E. Kh., Sinkevich O.A., et al. Study of a Low Temperature Plasma Generator with a Divergent Output Electrode Channel. *High Temperature*, 2010, **48** (6), P. 777–788.
[8] Amirov R., Isakaev E., Shavelkina M., Shatalova T. Synthesis of Carbon Nanotubes by High Current Divergent Anode-Channel Plasma Torch. *J. Phys.: Conf. Ser.*, 2014, **550**, 012023 (7 p).
[9] Gupta A. Raman Scattering from High-Frequency Phonons in Supported n-Graphene Laer Films. *Nano Lett.*, 2006, **6** (12), P. 2667–2673.