One-step synthesis of N-doped graphene in a plasma jet reactor

M B Shavelkina, R Kh Amirov, S L Kanashenko, A V Naumkin, I R Vahitov, A I Gumarov, I V Yanilkin and L R Tagirov

1Joint Institute for High Temperatures of Russian Academy of Sciences, Izhorskaya Street 13/2, 125412 Moscow, Russia
2Research Institute of Biomedical Chemistry, Pogodinskaya Street 10/8, 119121, Moscow, Russia
3A.N.Nesmeyanov Institute of Organoelement Compounds of Russian Academy of Sciences, Vavilova Street 28, 119991, Moscow, Russia
4Institute of Physics of Kazan Federal University, Kremlyovskaya Street 16a, Kazan, Russia

E-mail: mshavelkina@gmail.com

Abstract. The possibility of doping graphene during its synthesis in a plasma jet of nitrogen has been studied. Direct current plasma torch with power of up to 40 kW was used as plasma jet generator. The source of carbon was propane-butane mixture, acetylene or methane. Synthesized materials are characterized by scanning electron microscopy, X-ray photoelectron spectroscopy and thermogravimetric analysis. It has been shown that XPS spectra of graphene flakes produced in nitrogen plasma differ in atomic nitrogen content. The maximum degree of nitrogen doping of graphene was obtained at decomposition of acetylene at 77 Torr.

1. Introduction
Graphene is a single graphite plane in which sp²-hybridized carbon atoms form a hexagonal lattice. For the use of graphene in the majority of the applications, a purposeful modification of its electronic structure is required. This has led to an active search for methods of graphene chemical modification by various atoms and functional groups. Obtaining functionalized single-layer and multilayer graphene using efficient cost-effective methods has opened up new possibilities in the production of multifunctional nanostructured carbon materials, dispersions and hybrids of carbon and polymers that find their use in machinery building, catalysis, energy engineering and biomedicine, production of protective coatings, intellectual materials and systems [1].

In this paper, the possibility of graphene materials doping with nitrogen directly in the course of synthesis in a plasma jet is investigated. In [2], the efficiency of graphene synthesis was demonstrated using helium and argon as plasma-forming gas. In contrast to [2], in the present work nitrogen is used as a plasma-forming gas.

2. Methods
To synthesize N-graphene, a plasma jet reactor was used on the basis of a powerful dc plasma torch with an expanding anode channel [2]. The precursor is introduced into the plasma torch
simultaneously with a plasma-forming gas. Hydrocarbon decomposes both in the arc discharge region and in the plasma jet to form a vapor-gas mixture, which, as it cools condenses in the form of flakes in the collector. Pressure in the reactor was 77-710 Torr and was maintained under dynamic pumping by a water pump. The arc current was kept constant and corresponded to 300-350 A. Power of the plasma torch reached 35 kW. Methane, mixture of propane-butane and acetylene were used as a source of carbon. Nitrogen was a plasma-forming gas. The rate of hydrocarbons and nitrogen varied independently of each other. The synthesis parameters are presented in table 1. For each experiment, the hydrocarbons were introduced after the temperatures in the collector would reach 350-400 °C. Monitoring the collector temperature was carried out using the chromel-alumel and chromel-copel thermocouples.

| Power (kW) | Current (A) | Voltage (V) | Gas pressure (Torr) | Nitrogen flow rate (g/s) | Hydrocarbons flow rate (g/s) |
|------------|-------------|-------------|---------------------|-------------------------|-----------------------------|
| 30-40      | 150-450     | 60-110      | 77-740              | 1.5-2.0                 | 0.05-0.4                   |

The synthesis products were examined by traditional methods for studying doped graphene [11]. To directly register the dimensional parameters and images of plasma torch pyrolysis products, a scanning electron microscope (SEM) - Hitachi S5500 with in-lens technology was used to obtain both ultra-high resolution and high sensitivity of EDS analysis. The survey was conducted on 3 detectors (SE-mode, BF-STEM (light-field mode), DF-STEM (dark-field mode).

To evaluate the efficiency of the synthesis, phase composition and thermal stability of carbon products, thermal analysis methods were used: DSC and TG (STA 449 F3 Jupiter platform from Netzsch) with linear heating in air at 10 K/min in temperature range of 20-1000 °C.

X-ray photoelectron spectroscopy (XPS) was used for quantitative study of the elemental composition and chemical state of atoms. XPS measurements were taken in an ultrahigh vacuum chamber (~ 5 × 10⁻¹⁰ mbar) equipped with an X-ray source (Mg Ka, 12.5 kV, 250 W) and a hemispherical energy analyzer Phoibos 150 SPECS Gmb Germany.

Nitrogen plasma spectra were taken at a distance of 2 mm from the cathode on a three-channel AvaSpec2048 optical fiber spectrometer with a spectral resolution of 0.2 nm in the spectral range of 200 ÷ 1100 nm. Using a quartz condenser f = 150 mm, a sharp image of the plasma pinch was formed on a scale of 1.0 : 1.0. The input end of AvaSpec 2048 light guide perpendicular to the plane of this image could move in this plane, cutting out the necessary glow zone with a 1 mm diameter collimator aperture.

To determine the electron temperature, we used the relative intensities approach to the lines of particles with an equal multiplicity of ionization (method of Boltzmann exhibitors).

3. Results and discussions
The design feature of the plasma torch is the expanding anode channel, it provides an increasing volt-ampere characteristic (VAC) of the discharge in the region of high currents. Figure 1 shows the VAC at two pressures - 350 and 710 Torr. As it is seen from the figure, at a pressure of 710 Torr the dependence has a descending character in the region of small currents, while at currents exceeding 350 A the VAC is increasing. At a pressure of 350 Torr, the increasing character of VAC is observed starting from 200 A. The increasing character of VAC provides for a stable operation of the plasma torch. The use of the expanding channel of the output electrode in the plasma torch makes it possible to substantially increase the velocity of the cold gas at the inlet to the channel and intensify the heat exchange between the arc and the plasma-forming gas, which contributes to a decrease in the arc length, more even distribution of the heat fluxes into the electrode walls, and, in general, ensures the
stability of the arc burning. Figure 2 illustrates the stability of the electrical parameters of the plasma torch. Voltage fluctuations do not exceed 5%.

Figure 3 shows an example of the emission spectrum of nitrogen plasma and plasma with addition of methane. Lines H are clearly visible in the spectrum, and when the carbon precursor is added, the lines CN (380 nm) and C appear.

Based on the recorded spectra, the plasma temperatures and electron concentrations were determined. For nitrogen plasma without addition of the hydrocarbons, the electron temperature was 12,000 K (pressure 740 Torr). Electron concentration was $1.5 \times 10^{17}$ cm$^{-3}$. When methane was added at a rate of 0.3 g/s, the temperature dropped to 9500 K, and the electron concentration was $5.8 \times 10^{16}$ cm$^{-3}$.

Figure 4 presents the morphology of the carbon deposit collected on the collector. It is seen that the precipitate produced at propane-butane decomposition at 350 Torr is presented by flakes with the size of 200 to 500 nm. The observed morphology is typical for the synthesis of graphene using plasma jets. This confirms the possibility of plasma-jet synthesis without the use of catalysts and which does not require an additional purification stage.

**Figure 1.** Dependence of the arc burning voltage on the current at pressure change and constant flow rate of nitrogen (2 g/s).

**Figure 2.** Time dependence of the current intensity and the arc burning voltage at a pressure of 710 Torr.

**Figure 3.** The emission spectrum of nitrogen plasma with addition of methane (740 Torr, 300A, 0.3 g/s).

**Figure 4.** STEM image of graphene sheets produced at propane-butane decomposition at 350 Torr.
Figures 5-6 present photoelectron C 1s spectra and LVV Auger spectra of samples synthesized by decomposition of propane-butane mixture and acetylene at 77-710 Torr (table 2) and highly oriented pyrolytic graphite (HOPG). The C1s spectra of HOPG were used to determine the fraction of sp$^2$ hybridization and compensation for surface charging. The Auger spectra were used to determine the interaction between graphene layers.

**Table 2.** The proportion of the sp$^2$-state and relative atomic concentrations of the elements.

| Sample number | Synthesis condition | sp$^2$, rel. unit | C% | O% | N% | Cu% | Si% |
|---------------|---------------------|------------------|----|----|----|-----|-----|
| 1             | 77 Torr, C$_2$H$_2$ | 0.79             | 85.3 | 5.6 | 8.0 | 1.1 |
| 2             | 150 Torr, C$_2$H$_2$ | 0.83             | 75.9 | 11.2 | 3.8 | 9.1 |
| 3             | 350 Torr, C$_5$H$_6$-C$_4$H$_8$ | 0.79 | 87.4 | 7.2 | 3.6 | 1.8 |

The sp$^2$ hybridization degree for samples 1, 2 and 3 was 0.79, 0.83 and 0.79, respectively (table 2). The differences in the C 1s spectra are due to the difference in the relative concentrations of carbon groups containing oxygen (figure 5). Figure 6 shows fitting the C 1s spectra of sample 3 into components that correspond to the C-N, C-O/C=O, O-C=O/C=O and C(O)O groups [3]. The presence of oxygen relates to the leakage of air during dynamic evacuation.

According to the C 1s spectra, the atomic percentage of nitrogen in N-graphene consists of 8%.

---

**Figure 5.** Photoelectron C1s spectra of synthesized samples: 1- sample 1; 2 - sample 2; 3 - sample 3; 4 – pure HOPG.

**Figure 6.** KVV Auger spectra: 1- sample 1; 2 - sample 2; 3 - sample 3; 4 – HOPG, 21.875°; 5 – HOPG, 78.125°.

**Figure 7.** The C 1s spectrum decomposition into components: 1 - sample 3, 2 – sp$^2$-state, 3 - C-N, 4 - C-O/C/OH, 5 - O-C=O/C=O, 6 – C(O)O.

**Figure 8.** The N 1s spectrum decomposition into components: 1 - sample 3, 2 – pyridinic, 3 – C-NH, 4 – graphitic.
As we have seen from figure 6 the C KVV Auger spectra of the investigated samples are close to that of HOPG, measured at an angle of 21.875° corresponding to the information depth close to one layer of graphite; it indicates a weak interaction of π-systems of layers of the investigated samples. This interaction, on one hand, can be caused by a small number of graphene layers in packages and/or, on the other hand, by the presence of oxygen and nitrogen, which interfere with their interaction. For samples 2 and 3, the binding energies of the C 1s spectrum of HOPG inscribed in the original photoelectron spectra at the best coincidence of the low-energy edges and the satellite-normalized intensity are 284.40 and 284.37 eV, respectively, which indicate their good electrical conductivity. For sample 1, the corresponding value is 284.57 eV. According to [3], the shift of the peaks toward higher binding energies indicates a decrease in the conductivity of the samples under the action of photons and secondary electrons.

It should be noted that, despite the same relative concentrations of the state with sp\(^2\) hybridization in the spectra of C 1s of samples 1 and 3, they differ in relative concentrations of oxygen- and nitrogen-containing carbon groups, which follows from the results of the decomposition of spectra C 1s into components. When analyzing the XPS spectra of N 1s (figure 8), several states were identified. Peaks located at 398.2, 399.5 and 400.8 eV refer to pyridinic, amino and graphitic nitrogen, respectively. The binding energies are in accordance with the published values [4 - 6].

4. Conclusion
The research study for direct synthesis of N-graphene during decomposition of hydrocarbons in a plasma jet reactor based on a dc plasma torch with an expanding anode channel with power of up to 40 kW was carried out. The electric characteristics of the plasma torch were studied depending on the current, pressure, nitrogen flow rate and carbon source (ethanol, propane-butane, methane, acetylene). Spectral measurements of plasma arc radiation in the plasma torch in the visible spectral range were performed depending on the carbon source (ethanol, methane). The resulting deposit in the plasma jet was presented by flakes containing from 2 to 5 layers of graphite. Study of the thermal stability of N-graphene system shows that the nitrogen impurity significantly increases the temperature stability limit compare to that of pure graphene. Photoelectron spectroscopy has shown that in the synthesized N-graphene, pyridine nitrogen, which is not an electron donor, predominates. The dependence of the synthesis parameters on the electronic characteristics of the obtained N-graphene has been established.

5. Acknowledgements
The authors gratefully acknowledge Russian Foundation for Basic Research for the support by grants No 15-08-00165, No 16-08-00145.

6. References
[1] Wang H, Yuan X, Wu Y, Huang H, Peng X, Zeng G, Zhong H, Liang J and Ren M M 2013 Adv. Colloid Interfac. 195–196 19
[2] Amirov R, Isakaev E, Shavelkina M and Shatalova T 2014 J. of Phys.: Conf. Ser. 550 0120
[3] Wei D C, Liu Y Q, Wang Y, Zhang H L, Huang L P and Yu G 2009 Nano Lett. 9 1752.
[4] Li X L, Wang H L, Robinson J T, Sanchez H, Diankov G and Dai H J 2009 J. Am. Chem. Soc. 131 15939
[5] Zhang, L S, Liang X Q, Song W G and Wu Z Y 2010 Physical Chemistry Chemical Physics 12 12055
[6] Artyushkova K, Kiefer B, Halevi B, Knop-Gericke A, Schlogl R and Atanassov P 2013 Chemical Communications 49 2539