Application of low-temperature plasma for the synthesis of hydrogenated graphene (graphane)

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Abstract. The possibility of a direct synthesis of hydrogenated graphene in decomposition of methane by means of low-temperature plasma was investigated. A DC plasma torch with an expanding channel-anode, a vortex gas supply and a self-setting arc length was used as a generator of low-temperature plasma. Argon was used as the plasma-forming gas. The temperatures of argon plasma and with methane addition to it were determined on the basis of spectral measurements. The synthesis products were characterized by electron microscopy and thermogravimetry. The effect of hydrogenated graphene as a nanomodifier on the properties of the cubic boron nitride based functional ceramics was investigated.

1. Introduction

Low-temperature plasma physics is a very active area of research located on the boundaries between physics, chemistry and materials science. Recent technological developments, e.g. in plasma etching or plasma deposition, have led to a revived interest in plasma physics and technology.

Plasma torches provide a stationary temperature at the level of several tens of thousands of degrees in a gas of arbitrary composition. This makes it possible to use them for synthesis of nanoscale particles with widely varying set of properties [1].

At present, low-temperature plasma is used not only for synthesis of carbon nanostructures, but also for their functionalization. In the work [2], with the help of a hydrogen plasma, the surface of carbon nanotubes was doped with hydrogen, for hydrogen doping of graphene obtained by micromechanical exfoliation the authors [3] applied hydrogen afterglow plasma.

The present work is devoted to the possibility of using a low-temperature plasma for direct synthesis of hydrogenated graphene (graphane).

2. Methods

To synthesize graphene we used a plasma jet reactor, which was used early for the synthesis of carbon nanotubes and graphene. A detailed description of the experimental setup was given in the studies [4, 5]. The key element of the installation is a direct current plasma torch with an expanding channel-anode and a self-setting arc length. The use of the expanding channel of the output electrode in the plasma torch allows to significantly increase the velocity of the cold gas at the inlet to the channel and to intensify the heat exchange between the arc and plasma-forming gas, which contributes to a decrease in arc length and more uniform distribution of heat fluxes to the electrode walls [6].

The experiment involved a simultaneous input of carbon precursor (methane) with a plasma forming gas (argon) into the plasma torch, wherein heating and decompositions occurred in the plasma
jet and in the region of the arc discharge, followed by condensation of the synthesis product on the metal surface of the target in a vacuum chamber. The rate of carbon precursor, plasma gas flow and the power of the plasma torch varied independently of each other. For the experimental conditions the electric power of plasma torch was set up to 35 kW.

Figure 1 shows the experimental setup.

![Figure 1. The experimental setup.](image)

The experimental conditions are presented in table 1.

| Power (kW) | Current (A) | Voltage (V) | Gas pressure (Torr) | Argon flow rate (g/s) | Methane flow rate (g/s) |
|------------|-------------|-------------|---------------------|-----------------------|------------------------|
| 22–35      | 300–350     | 60–90       | 150–740             | 3.0–3.75              | 0.05–0.37              |

The synthesis products formed in the volume of the plasma jet reactor were investigated by the standard methods for diagnostics of carbon nanomaterials structure. The method of electron microscopy (scanning electron microscope Hitachi S5500) was used in three modes: SE (displays the surface morphology), BF-STEM (provides a transmission mode), DF-STEM (displays regions that efficiently scatter electrons). To evaluate the efficiency of the synthesis, thermogravimetry was used - (STA 449 Netzsch) with linear sample heating in argon at the rate of 5 K/min at temperatures up to 1000 °C.

The spectra of argon plasma were taken on a three-channel fiber-optic spectrometer AvaSpec 2048 with spectral resolution of 0.1–0.4 nm and spectral range 200–1100 nm.

The electron temperature was found, using the method of relative intensities of the same lines of ionization particles (method of Boltzmann exhibitors).

Stark broadening of the hydrogen lines at 468 and 656 nm for a mixture of argon and methane was used to determine the electron concentration [8].

Volt-ampere characteristics of argon plasma generator were investigated at pressures in the planetary jet reactor of 350 and 710 Torr.
3. Results and discussions

It is known that the efficiency of technological processes increases significantly when using plasma torches with an increasing volt-ampere characteristic. Figure 2 presents the results of experimental studies of volt-ampere characteristics of argon plasma generator for argon flow rate of 3.0 g/s. They have clearly expressed growing character. Whereas, a larger inclination angle is observed at a pressure of 710 Torr. The increasing character of the volt-ampere characteristic is due to the peculiarity of the used plasma torch, in which the electric discharge burns completely in the expanding channel, and therefore the stability of arc combustion persists even in the transition from argon to a mixture of argon and methane.

Figure 3 demonstrates that when adding methane to argon, the arc voltage jump and, consequently, power jump occur, and afterwards the values do not change until the end of the experiment (duration of the experiments was 5–12 min).

Figure 3 shows the emission spectrum of argon plasma and mixture of argon and methane. The spectra were recorded in the discharge region near anode on its axis at a pressure of 710 Torr. According to the processing of the emission spectra of argon plasma, the electron temperature was 11700 K, and in the mixture with methane – 11300 K. The electron concentration was $6.75 \times 10^{16} \text{ cm}^{-3}$.

**Figure 2.** Volt-ampere dependence for argon plasma. Argon flowrate is 3.0 g/s.

**Figure 3.** The change in current and voltage during the experiment. Argon flow rate is 3.0 g/s, methane flow rate is 0.3 g/s. Pressure of the medium is 710 Torr.

**Figure 4.** Emission spectra of plasma Ar and Ar-CH$_4$. 
Figures 5–6 present the morphology of graphene materials obtained by a plasma jet. The synthesis products are flakes, which are usually observed in the synthesis of graphene with the use of thermal plasma [8–10]. Inflation is noticeable on the surface of the cup-shaped graphene. Comparison of the two images obtained from different detectors gives the main result - the inflation is represented by gas-filled bubbles. These inflations in their morphology are the same as in [8], where graphite and graphene were treated with hydrogen-argon plasma. The authors associate the structural changes with surface doping by hydrogen.

![Figure 5. SEM image of graphane flakes.](image1)

![Figure 6. STEM image of graphane flakes.](image2)

The results of thermogravimetric analysis confirmed the presence of hydrogen in the synthesized samples. Figure 7 shows the mass loss curves when samples are heated, the rate of its change, and desorption of hydrogen. Emission of hydrogen is observed throughout the entire temperature increase region. The peak is observed near 300 °C as in [3].

![Figure 7. Thermogravimetry of graphane flakes.](image3)

The obtained hydrogenated graphene were introduced into the composition of ceramic bond of a high-strength material based on cubic boron nitride (its hardness is close to diamond) fabricated under hot pressing conditions. According to [11], in these conditions, the use of fine-dispersed highly active composite powders, which ensure the formation of a dense fine-grained matrix in the process of hot pressing, is especially promising. At 1450 °C and pressure of 5.5 GPa a modified ceramic composition with a content of up to 70 mass % of cubic boron nitride was obtained.

Microstructure of the obtained samples, average particle size, nature and value of the closed porosity were studied by scanning electron microscopy. Figure 6 shows the surface of a sample
destruction with a matrix containing from 0.05 to 1 mass % of graphane. Analysis of the ceramic samples fractures microstructure was carried out on a scanning electron microscope Nova NanoSem 650 using the standard procedure after testing the samples for bending. The study showed that the microstructures of fracture surfaces of these three samples, both in the locations of localization of nanofibers and in zones free from them were similar to each other in the basic features. On the bends, boron nitride grains with characteristic dimensions of ~1 to 2.5 μm and surrounding shells of bond composed of more dispersed formations based on Al and Ti are observed. Both - nanotube groups and individual nanotubes with a diameter of 20–40 nm are protruded from those shells, (i.e. formation of a framework in a ceramic matrix is seen). Thus, under the conditions of hot pressing due to the presence of hydrogen in graphene materials, graphene flakes are folded into filamentary nanostructures and self-reinforcement of the ceramic matrix takes place.

Figure 8. Microphotographs of fractures of ceramic samples based on cubic BN with addition of CNS in the ratio: a – 0.05 mass %, b – 0.5 mass %, c – 1 mass %. Separate formed zones of carbon nanotubes localization are marked by rectangles.

Physical and mechanical properties (apparent density, open porosity and average tensile strength) of the samples were studied. The obtained data are presented in table 2. Determination of the average density and open porosity of the items was carried out by kerosene saturation with preliminary weighing of dry samples and subsequent hydrostatic weighing of saturated samples on precision scales. Density of kerosene for the calculation was measured with a hydrometer. While at the graphene content of 0.05 and 1.0 mass % the values of the composite strength are practically equal, the composite with 0.5 mass % has the strength properties by 1.12 times higher. The other parameters are approximately similar.

Table 2. Physical and mechanical properties of ceramics samples.

| Content of carbon nanostructures (mass %) | Apparent density (g/cm³) | Open porosity (%) | Average tensile strength (MPa) |
|------------------------------------------|--------------------------|-------------------|-------------------------------|
| 0                                        | 3.47–3.50                | 0.5–1.5           | 750                           |
| 0.05                                     | 3.491                    | 0.631             | 730                           |
| 0.5                                      | 3.495                    | 0.892             | 820                           |
| 1.0                                      | 3.435                    | 1.535             | 730                           |

4. Conclusion
In this paper, the possibility of hydrogen doping of graphene structures during their synthesis with the use of low-temperature plasma was demonstrated. To generate plasma with stable characteristics, we used a constant-current plasma torch with an expanding channel-anode, a vortex gas supply and a self-setting arc length. Studies of the plasma torch characteristics have shown the stability of its operation.
when introducing hydrocarbon into the plasma jet. The synthesized samples are flakes with a lateral dimension of 50 to 700 nm. The use of synthesized hydrogenated graphene samples in the composition of a binder in high-temperature hot-pressed nitride ceramics has led to the increase of its average strength.

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