Electrochemical behavior of the graphene materials synthesized using low temperature plasma

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Abstract. By means of DC plasma torch of up to 45 kW power, few-layered graphene sheets were obtained. Their properties and structure were characterized by using electron microscopy, thermal analysis, Raman and infrared (IR) spectroscopy. Boundary surface of samples have been investigated using the method of “limited evaporation” and BET method. Electrochemical examination of their properties was conducted. Due to the activity and stability of synthesized materials the conclusion was made regarding the possibility of the use of them as catalysts carriers for fuel cells electrodes, electric current sources, conducting additives for electrodes in non-aqueous electrolytes.

1. Introduction

The most of the existing methods of graphene production are related to the mechanical [1-3] or chemical [4-6] decomposition of graphite or epitaxial growth of graphene films [7]. In the first instance obtaining the high quality graphene layers is based exclusively on the fundamental research. In the second instance the chemical methods possess low cost and high productivity rate but do not completely separate graphite placed in the solution and flaked graphene in the solution does not preserve the sheet shape. There exists a method of graphite transformation into graphite oxide. It employs an approach named “oxidization - exfoliation - reduction” in which course basic graphite planes are coated with covalent-linked functional groups of oxygen. That oxidized graphite becomes hydrophilic and separates into individual graphene sheets in aqueous solution under the impact of ultrasound. However, the obtained graphene would possess electric conductivity by a few orders of magnitude lower compared with the conductivity of graphene produced by the Scotch-tape method from highly oriented pyrolitic graphite. That method does not provide for the possibility to free from oxygen completely and leads to the formation of graphene with high concentration of defects of hybridization.

The use of plasma is considered as one of the promising methods for graphene production. In the study [8] the gas discharge was ignited in the mixture of helium and carbon dioxide. The optimal conditions for synthesis of graphene with few numbers of layers were discovered whereas the number of defects was lower than in the graphene obtained by the chemical methods. However, because of the low speed of carbon evaporation the mass production of high quality carbon nanostructures cannot
be implemented. From the viewpoint of large scale production of graphene it is of interest to use a plasma jet.

Our approach is relatively simple and easy for the commercial-scale production for electrochemical applications compared with CVD or wet chemistry techniques. The essence of it is the synthesis of functional groups - free graphene materials with a large area in a plasma jet generated by DC plasma torch of up to 45 kW power.

2. Methods

The basis of the plasma jet synthesis method is the principle of simultaneous input of plasma forming gas with carbon containing precursor (soot, hydrocarbons, alcohols) and its evaporation in the discharge gap with formation of carbonic vapor and further condensation in the form of solid carbon. Figure 1 presents the schematic setup of the facility which main component is a plasma torch of the original design. The choice of plasma torch with the expanding channel of the outlet electrode is grounded by the ability of such design to ensure burning of the arc in the laminar flow at the sufficiently high speed of gas flow at the inlet [9]. Specifically the expanding channel is capable to provide for distribution of the electric current over the outlet electrode surface and, respectively, the magnetic field, which promote the increase of the positive column stability in the discharge gap.

![Figure 1. Schematic of the assembled plasma jet set up, used for the synthesis of graphene. (1) Plasma torch, (2) water cooling of plasma torch, (3) graphite tube, (4) water cooling of graphite tube, (5) vacuum chamber, (6) collector, (7) water cooling, (8) plasma forming gas with carbon precursors, (9) vacuum pump.](image)

Helium, argon (technical and high-purity) and nitrogen are used as plasma forming gases. Carbon sources are presented by hydrocarbons: propane-butane, methane and acetylene. Hydrocarbons flow rates were: propane-butane in the ratio 30:70 mass % - 0.11-0.30 g/s, methane - 0.15-0.37 g/s, acetylene - 0.05-0.16 g/s.

The optimal regime of functional groups - free graphene materials is achieved by widely ranged varying of pressure, energy input and flow rates proportion of plasma forming gas, initial substance and catalyst, formation of a flow with the using of the outlet electrode-anode expanding channel and by changing the geometric parameters. A detailed description of the experimental setup was given in the studies [10]. The synthesis parameters are presented in table 1.
For direct registration of the dimensional parameters and images the method of scanning electronic microscopy (SEM) was applied – microscope Hitachi S5500 with in-lens technique for obtaining a super-fine resolution as well as high sensitivity of EDS analysis.

Efficiency of the synthesis, phase composition and thermal stability of the carbon products were evaluated by the thermal methods: Differential Scanning Calorimetry (DSC) and TG (STA 449 platform F3 Jupiter (Netzsch)) with linear heating of sample in the air at the rate 10 K/min in the temperature range -- 20 -1000 °C.

The topology of formed graphene structure was estimated by Raman scattering (Ntegra Spectra). Excitation wavelength was 532 nm, output power was adjusted so as to prevent overheating of the material.

To determine the characteristics of the porous structure (pore volume, pore radius, surface area) we used a relatively new method of adsorption "Limited Evaporation" based on the analysis of the kinetics of evaporation of the adsorbate from the test material. To evaluate the specific surface area of materials the classic BET method was applied using a low-temperature nitrogen adsorption analyzer Quadrasorb SI.

IR spectroscopy (FT-IR spectrometer VERTEX 70 (Bruker, Germany) used in the mid-IR range (4000-400 cm⁻¹, or 2.5-25 μm) at a resolution of 2 cm⁻¹ to determine the structure of samples on the presence of the or other functional groups.

Electrochemical investigation was conducted in a universal laboratory cell of filter-press structure [10], with counter-electrode made of high capacitance activated carbon (CH-900 produced in Japan) which mass exceeded the mass of the working electrode by more than 100 times. The electrolyte was 0.5 M sulfuric acid solution. The graphs and the text indicate the potentials relatively to the stationary potential of activated carbon in the given electrolyte (around 700 mV RHE). Cyclic voltammetry was measured by potentiostat Elins P-30J(M).

### Table 1. Technological conditions.

| Power (kW) | Current (A) | Voltage (V) | Gas pressure (Torr) | Helium flow rate (g/s) | Nitrogen flow rate (g/s) | Argon flow rate (g/s) | Carbon flow rate (g/s) | Times of work (min) |
|------------|-------------|-------------|---------------------|------------------------|-------------------------|-----------------------|-----------------------|---------------------|
| 30-45      | 150-400     | 35-110      | 77-740              | 0.5-0.9                | 1.5-2.5                 | 3.0-3.75              | 0.047-0.276           | 6-10                |

3. Results and discussions

The structures which morphologies are presented on figure 2 were obtained by plasma jet decomposition of propane-butane, acetylene and methane at varying the vacuum chamber volume parameters by shifting target perpendicularly to vapor-gas flow. The 2D particle structures are labeled as flakes and showed a stacking averaging around 2 graphene layers (range 5 atomic layers, up to 2 nm thickness) and in plane dimensions between 50 and 1.5 μm.

Raman spectroscopy is established as the most accurate and easy tool to characterize graphene [1], the number of layers and the presence of defects (quality) especially when the number of layers is less than 5 [12]. Figure 3 demonstrates a typical Raman spectrum of graphene materials produced by the decomposition of acetylene when argon plasma was used at pressure of 350 Torr. There are characteristic of single-layer graphene materials [1] - G mode (1587 cm⁻¹), 2D strip (G') - (2669 cm⁻¹) and the D breathing mode (1355 cm⁻¹) on the spectrum. These are identified as the Raman fingerprints of graphene, namely of D, G and 2D peaks. Oxidation of these samples in the air shows that pure carbon phase amounts to 78-86 mass%.

Electrochemical studies of graphene synthesized in the plasma jet show high hydrophobicity and resistance to oxidation. Their hydrophobic properties are preserved for a long time even in intense
(greater than 1 V) cathode-anode polarization in sulfuric acid solution and in durable keeping in concentrated sulfuric acid in the absence of anode polarization.

Figure 2. SEM images: (a) products synthesized by the decomposition of propane-butane, (b) products synthesized by the decomposition of acetylene, (c) products synthesized by the decomposition of methane at 710 Torr under a helium atmosphere.

Figure 3. Raman spectra of synthesis products by the decomposition of acetylene using argon at a pressure of 350 Torr.

Figure 4. Specific surface area as a function of the pore radius for the samples synthesized by the decomposition of acetylene using helium (1) and argon (2) at a pressure of 350 Torr.

Figure 5. Cyclic voltammogram of graphene materials obtained by decomposition of acetylene at argon plasma at 500 Torr in 1M KOH at 50 mV/s.

Figure 6. The VF curves of graphene materials in 0.5 M H₂SO₄ solution at 20 mV/s. (1) Initial graphene, (2) oxidized graphene.

Despite the large value of specific surface area (from 280 to 500 m²/g) the samples demonstrate very low capacitance in aqueous electrolytes (around 0.1 F/g). Oxidation of graphene materials at potentials 1.6-1.7 V (versus RHE) leads to the capacitance growth by 2-3 orders of magnitude. Figure 4 presents the change of the value of specific surface area when different carbon precursors were used.
Figure 5 shows the typical cyclic voltammetry data for graphene materials in 1 M solution of potassium hydroxide (60 °C) at 50 mV/s. Extremely low capacitance of samples is reasoned by low wettability (hydrophobicity) of these materials. Figure 6 demonstrates the change of capacity of materials after oxidation in 0.5 M sulfuric acid solution. Analysis of the capacitance curves shape after oxidation shows that the capacitance of oxidized graphene materials is determined mainly by pseudo-capacitance of the surface functional groups formed in the result of electrochemical oxidation. According to the IR spectrum of the initial graphene materials obtained by the decomposition of hydrocarbons in a helium plasma do not contain functional groups. Capacitance of the double-electric layer does not exceed 10 F/g which may be related to the low electron-hole conductivity of the said materials.

Fuel cells consist of three key parts: cathode, anode and separation membrane. Among them, cathode materials are pivotal elements for the commercialization. Currently, expensive noble metals such as platinum, gold, ruthenium, and their alloys are best known cathode materials for oxygen reduction reaction. One is to minimize the use of expensive catalysts by increasing surface area via nanoparticle approach [13]. Due to the high specific surface area, good chemical stability and universal electrical properties the plasma jet graphene can be used as catalysts carriers for gas diffusion electrodes of fuel cells and air-metallic current sources. In addition, the low defectiveness and high electrical conductivity allow considering them as the promising conductive additives in a matrix of the composite electrode materials in non-aqueous electrolytes.

4. Conclusion
The present study has shown that it is possible to synthesis of few-layers graphene material at decomposition of hydrocarbons in plasma jet reactor based on DC plasma torch with expanding channel-anode, and with helium, argon or nitrogen used as plasma forming gas. The kind of plasma forming gas and the precursor influences the morphology of graphene materials, their amount and the value of specific surface area. When using propane-butane mixture as a precursor solid products with a high content of pure carbon are formed. The highest value of the specific surface area (500 m$^2$/g) was found for the samples obtained by the decomposition of acetylene. The effect of the electrolytes on electrochemical properties for graphene materials as the electrode for supercapacitor and has been investigated by cyclic voltammetry, good chemical stability are established. A simple and cost-effective oxidation technique of graphene materials with good capacitive behavior encourages their possible use in commercial applications as catalysts carriers for fuel cells electrodes, electric current sources, conducting additives for electrodes in non-aqueous electrolytes.

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6. References
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