Bulletin of the *Transilvania* University of Braşov • Vol. 10 (59) No. 1 - 2017
Series I: Engineering Sciences

EXFOLIATION OF GRAPHITE IN CARBON ARC DISCHARGE

M. FRONCZAK[1] M. BYSTRZEJEWSKI[1]

Abstract: *Herein a method for the synthesis of exfoliated graphite is presented. The method is based on the carbon arc discharge between two graphite electrodes under inert gas atmosphere (He and He-N_2). The process yields two types of products, i.e. the deposit from the cathode, rich in exfoliated graphite and soot, which contains various nanosized carbon particles. The products were investigated by thermogravimetry, scanning electron microscopy and Raman spectroscopy. The presented method is a novel approach for exfoliation of graphite and is characterized by high efficiency and simplicity.*

Key words: *exfoliation, graphite, few-layer graphene, arc discharge.*

1. Introduction and Objectives

Exfoliation of graphite is an excellent method for obtaining well defined graphene and few-layer graphene precursor. The exfoliation leads to an increase of the interlayer distance in the crystal of graphite. This process can be carried out with various routes, as for example via the incorporation of graphite with potassium [10] or lithium [12]. In this case the size of the guest ion is adequate to be inserted in the graphitic structure. The ultrasound treatment of graphite aqueous suspensions containing surfactants may be also applied [8]. The ultrasound energy destroys the graphitic lamellar structure, whilst the surfactants stabilizes the expanded materials.

Carbon arc discharge method is commonly used to synthesise various carbon nanomaterials, e.g. fullerenes [9], carbon nanotubes [7] and carbon encapsulated nanoparticles [2]. In this method the cathode emits electrons, which are accelerated in the electric field gradient. The electrons collide with the surface of the anode and lose their energy. This effect increases the temperature of the anode head, and subsequently the anode material start to sublime. The growth of the fullerenes, carbon nanotubes or carbon encapsulated nanoparticles is based on condensation of the vapours originated from the anode sublimation in the arcing [2, 7, 9].

The aim of this research is demonstrate the exfoliation of graphite in carbon arc discharge and to show how the operational parameters influence the exfoliation process. The obtained materials were investigated to determine the thermal stability, morphological features and the degree of graphitization. The novelty of this approach lies in the systematic studies on the arcing of pure graphite and optimization of pressure to obtain the exfoliated graphite with high efficiency.

[1] Faculty of Chemistry, University of Warsaw, 1 Pasteur Street, PL 02093, Warsaw, Poland.

2. Experimental

The experiments were carried out in the reactor, which is presented in Figure 1. The discharge were conducted under pure helium or the mixture of helium and nitrogen (1/1 v/v). Before the test the reaction chamber was evacuated and filled with the gas to the desired starting pressure (5-50 kPa). The pure graphite rods (diameter 8 mm) were used as the cathode and the anode, respectively. The discharge current was fixed at 30 A. Two types of the products were collected: the deposit from the cathode and soot from the inner walls of the reaction chamber. The typical arcing time was between 15 and 50 minutes.

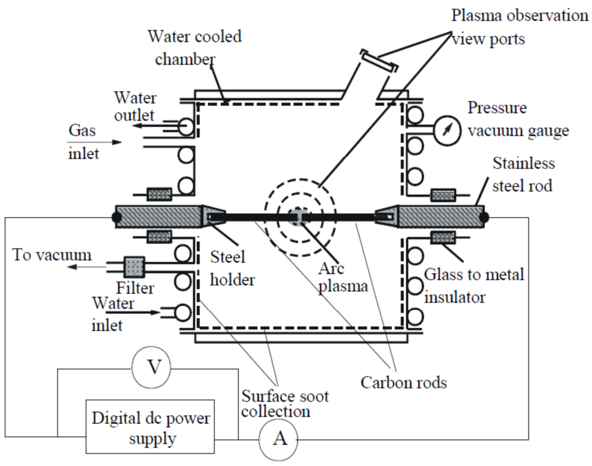

Fig. 1. *Scheme of carbon arc discharge reactor*

All products were examined with scanning electron microscopy (Zeiss Merlin electron microscope) to observe the morphological details. Moreover, the thermogravimetry (TA Instruments Q50 equipment) under the atmosphere of oxygen and nitrogen (5 % vol. of O_2) was also applied to determine the thermal resistance of the products. The Raman spectra of the products were also acquired (Jobin Yvon-Spex T64000 Raman spectrometer).

3. Results and Discussions

The pressure during the experiments increased 1.2-1.5 times in the case of pure helium and 1.6-2.0 times in the case of the atmosphere of helium and nitrogen. This effect is connected with heating of the buffer gas, because the temperature of the carbon arc plasma between the electrodes exceeds 4000 K (i.e., the sublimation point of graphite). Importantly, the pressure increase in the case of helium is lower, because the heat capacity of helium under constant volume is 3.12 $kJ \cdot kg^{-1} \cdot K^{-1}$, whilst in the case of nitrogen it is 0.743 $kJ \cdot kg^{-1} \cdot K^{-1}$. The anode erosion rate is a parameter which shows the unit mass of the anode material which is transformed to gaseous phase in a unit time. The erosion rate in the test conducted under pure He atmosphere diminishes linearly with the pressure increase (Figure 2). This effect is expected since lower pressure favours the sublimation. The inclusion of nitrogen to the buffer gas significantly changes this dependence (Figure 3). The erosion rate rises with the increase of pressure. This is connected with the reaction between nitrogen and carbon leading to the formation of cyanide radicals. Importantly, helium does not react with carbon, so in consequence the anode erosion is connected only with the heat transfer.

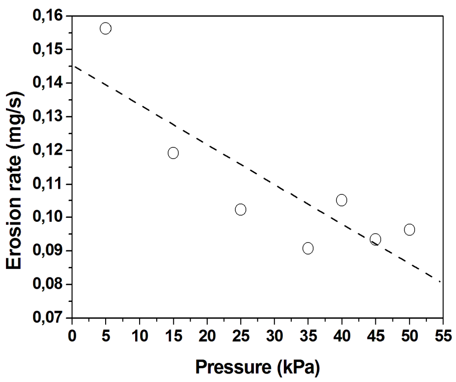

Fig. 2. *Anode erosion rate (He atmosphere)*

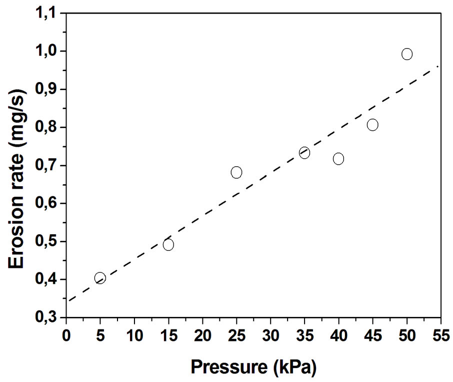

Fig. 3. *Anode erosion rate (He and N_2 atmosphere)*

Figure 4 shows the soot formation yield vs. the pressure. Importantly, the soot was obtained at 'visible' amounts (>5 mg) only in tests conducted under nitrogen-helium atmosphere. The soot formation yield increases with increase of initial pressure to 40 kPa, and after this point the yield decreases. It can be seen that the initial pressure is a key parameter which influences the soot formation yield. Figure 5 shows the deposit formation yield (the mass of the deposit formed from the unit mass of the anode). The pattern in Figure 5 corresponds to the changes of the erosion rate vs. pressure.

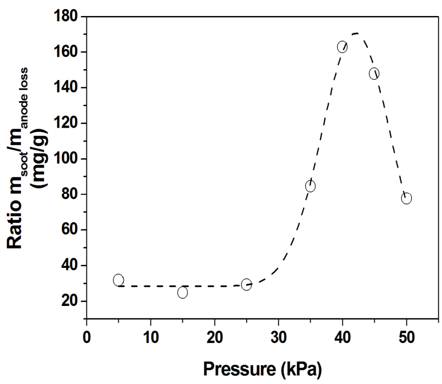

Fig. 4. *Soot formation yield (N_2-He atmosphere)*

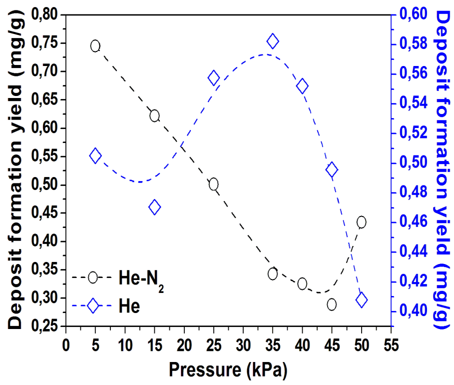

Fig. 5. *Deposit formation yield*

The deposits from the cathode obtained under helium contain exfoliated graphite and carbon nanotubes (Figure 6 and Figure 7). The amount of exfoliated graphite is higher in the products obtained at lower pressure. This finding shows that lower pressure favour the exfoliation process. In the case of products obtained under He-N_2 atmosphere the trend is opposite. The exfoliated graphite is found in the products obtained at lower pressure, whilst carbon nanotubes and carbon spherical nanoparticles are formed at higher pressure (Figure 8 and Figure 9). The exfoliated graphite lamellas have similar thickness (50-70 nm) and these values do not depend on the buffer gas atmosphere.

Similar results were obtained in the work of Wu et al. [11]. They oxidised graphite by Hummers method and the as-obtained graphite oxide was used as the anode additive. The tests were conducted under Ar-H_2 atmosphere (9/1) and the products resembled few-layer graphene. The materials had high thermal stability and good electrical conductivity. The paper by Cataldo et al. [3] describes the process in which the carbon arc was conducted in a liquid (oleum). In their work the swelled, partially exfoliated graphite was obtained. In comparison to the presented results our approach does not require neither the preliminary chemical treatment of graphite, nor using of dangerous and highly oxidative environment. Moreover, the obtained exfoliated graphite has desirable morphology and it can be used in subsequent separation of the lamellas in order to obtain few-layer graphene.

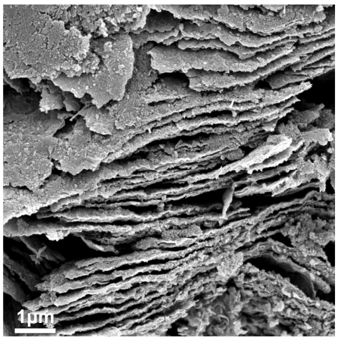

Fig. 6. *SEM image of the deposit from cathode (He 15 kPa)*

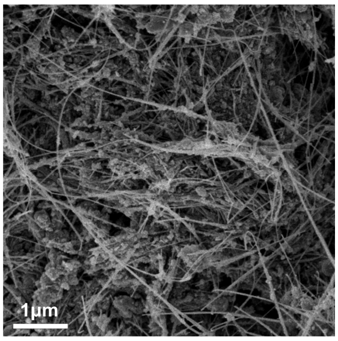

Fig. 7. *SEM image of the deposit from cathode (He 50 kPa)*

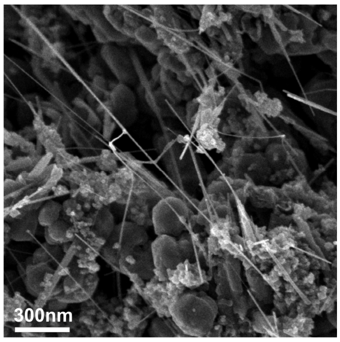

Fig. 8. *SEM image of the deposit from cathode (He + N_2 15 kPa)*

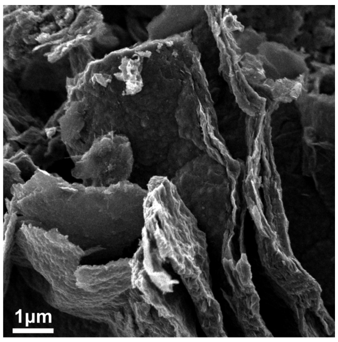

Fig. 9. *SEM image of the deposit from cathode (He + N_2 50 kPa)*

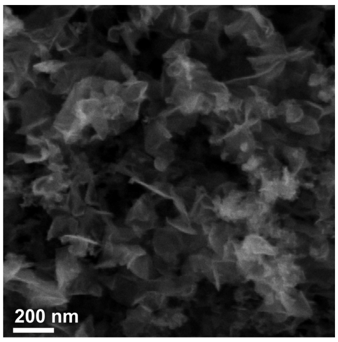

Fig. 10. *SEM image of the soot (N_2-He 5 kPa)*

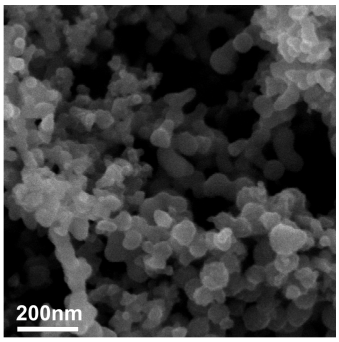

Fig. 11. *SEM image of the soot (N_2-He 50 kPa)*

The soot obtained in tests under He-N_2 atmosphere consist of nanoparticles (diameter ca. 50 nm) and nanoflakes, which resemble few-layer graphene. Interestingly, the product obtained at the lowest pressure (5 kPa) comprises mainly nanoflakes (Figure 10), whilst the product obtained at the highest pressure (50 kPa) is solely composed of carbon particles (Figure 11). The materials synthesized at the pressure between 5 and 50 kPa have a intermediate morphology, i.e. they contain both nanoflakes and nanoparticles. The content of the nanoflakes increases with an decrease of the pressure of the buffer gas.

As it follows from the morphology studies, the pressure and the buffer gas atmosphere influences the selectivity of the process. As it can be found in the review by Arora and Sharma [1], the pressure of the buffer gas plays an important role in the carbon arc discharge. In the case of helium, the higher pressure (50-70 kPa) favours the formation of carbon nanotubes, and in fact it has been also confirmed in our work. Similarly, our results in the case of nitrogen are also coherent with the statements from the work [1], i.e. lower pressure of nitrogen results in the synthesis of carbon nanotubes. Thus, it can be seen that our findings are in a good agreement with previous reported observations.

The representative Raman spectra of the products are shown in Figure 12. The spectra have three Raman bands, G-band, D-band and 2D-band at 1580, 1350 and 2700 cm^{-1}, respectively. These spectral features are typical for graphitic materials [4]. The degree of graphitization can be derived from the ratio between the G-band and the D-band areas. The calculated G/D ratio values are higher than 1.5 and this finding shows that the obtained materials have graphitic structure. The G/D ratio changes with the pressure (Figure 13). Interestingly, there is an opposite dependence of the G/D vs. pressure pattern for the products obtained under He and He-N_2 atmosphere. In the first case the increase of pressure causes the increase of the degree of graphitization, whilst the inclusion of nitrogen leads to the formation of products with lower graphitization.

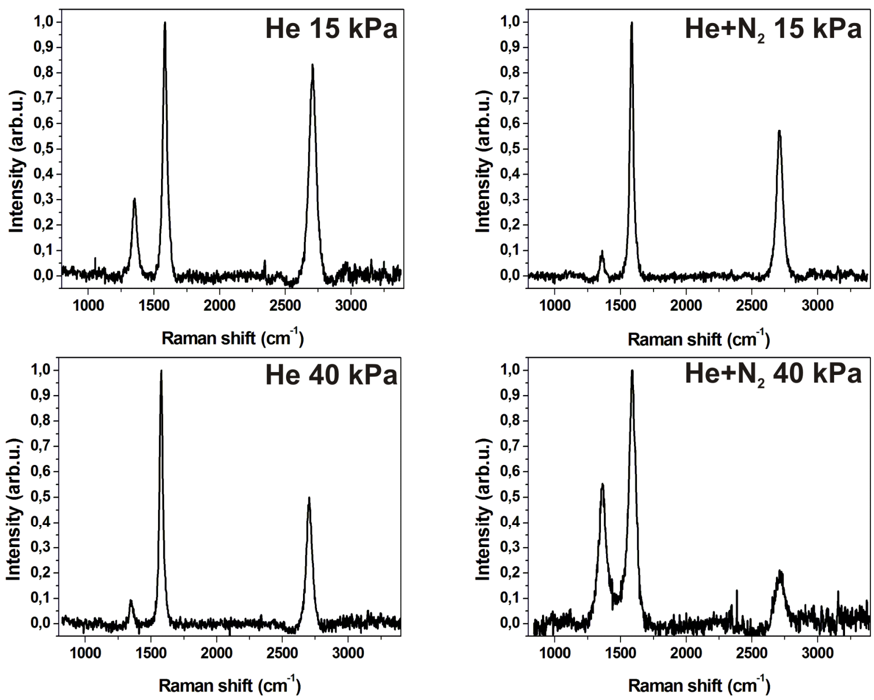

Fig. 12. *Raman spectra of deposits from cathodes (conditions in brackets)*

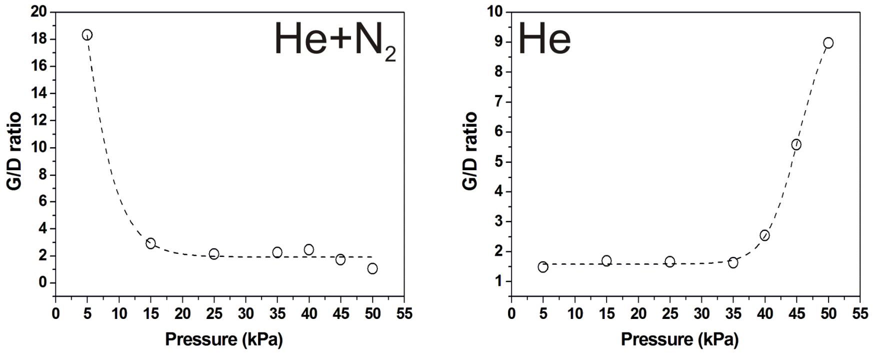

Fig. 13. *Relation of G/D ratio for deposits and initial pressure*

The Raman spectra and G/D ratio vs. pressure patterns for soot are shown in Figure 14. The degree of graphitization decreases with increase of pressure. This observation is in agreement with the morphological studies. The soot formed at lower pressure contain few-layer grapheme and this materials has higher G to D ratio than semi-graphitic carbon nanoparticles.

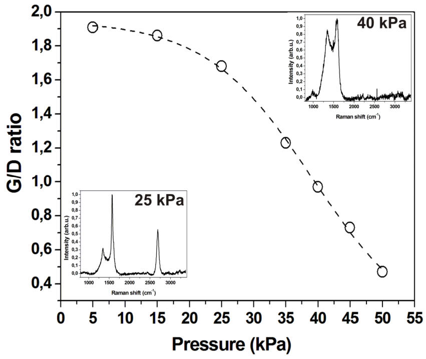

Fig. 14. *Relation of G/D ratio for soot obtained under nitrogen and helium and initial pressure (representative Raman spectra are in insets)*

The thermogravimetry curves of all products are shown in Figure 15 and Figure 16. The deposits starts to oxidize at temperature 600-620 ^{o}C and there is no correlation with the onset

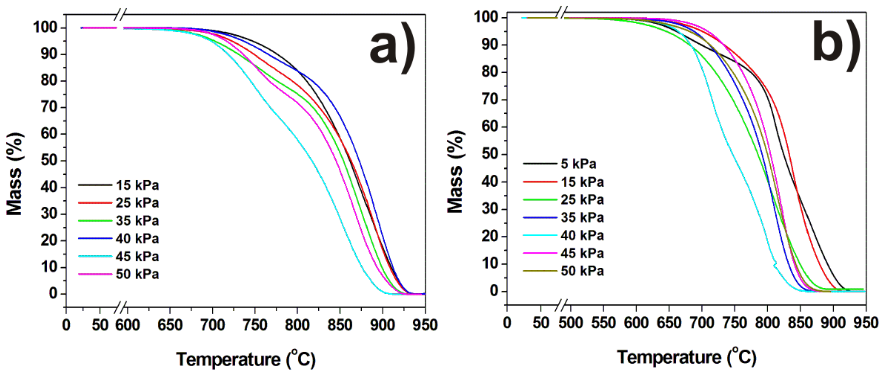

Fig. 15. *Sets of TGA curves of deposits obtained under a) helium b) nitrogen and helium*

temperature and the pressure. The thermal stability of the deposits obtained both under He and He-N_2 are similar to the thermal stability of pure graphite [5].

The soot has lower thermal stability because the combustion starts at 300-350 ^oC. This finding suggests that the obtained carbon nanoparticles and nanoflakes are defected and poorly graphitized. It is known that carbon materials combusts at lower temperature if they are weakly graphitized [6]. This conclusion is in a good agreement with Raman spectroscopy, because the soot has generally lower graphitization in comparison to the cathode deposits.

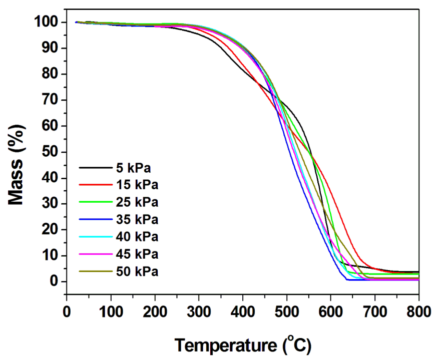

Fig. 16. *Set of TGA curves of soot obtained under nitrogen and helium*

4. Conclusions

The systematic studies on the exfoliation of graphite in carbon arc discharge are presented. The influence of two operational parameters (buffer gas atmosphere and its pressure) has been studied. The carbon arc discharge under pure He yielded cathode deposits which contained exfoliated graphite and carbon nanotubes. The products obtained at lower pressure under He contained mainly exfoliated graphite, whilst the increase of pressure resulted in formation of carbon nanotubes. The inclusion of nitrogen to the buffer gas increased the sublimation rate of the anode, and changed the trend, i.e. the exfoliated graphite was observed at higher pressure only. The pressure has been found as a parameter which drives the degree of graphitization. The thermal stability of obtained products was on a similar level as pure graphite powder. The obtained results brings a conclusion that carbon arc discharge is an promising method for the exfoliation of graphene. The obtained materials can be subsequently processed to obtain few-layer graphene.

References

1. Arora, N., Sharma, N.N.: *Arc Discharge Synthesis of Carbon Nanotubes: Comprehensive Review*. In: Diamond & Related Materials **50** (2014), p. 135-150.
2. Bystrzejewski, M., Łabędź, O., Kaszuwara, W., Huczko, A., Lange, H.: *Controlling the Diameter and Magnetic Properties of Carbon-Encapsulated Iron Nanoparticles Produced by Carbon Arc Discharge*. In: Powder Technology **246** (2013), p. 7-15.
3. Cataldo, F., Valentini, F., Cherubini, V., Ursini, O., Angelini, G.: *Synthesis of Expanded Graphite Plakes by the Submerged Carbon Arc in Oleum*. In: Fulerenes, Nanotubes and Carbon Nanostructures **20** (2012), p. 152-162.

4. Dresselhaus, M.S., Jorio, A., Saito, R.: *Characterizing Graphene, Graphite and Carbon Nanotubes by Raman Spectroscopy.* In: Annu. Rev. Condens. Matter Phys. **1** (2010), p. 89-108.
5. Kim, K.S., Jeon, I.Y., Ahn, S.N., Kwon, Y.D., Baek, J.B.: *Edge-Functionalized Graphene-Like Platelets as a Co-Curing Agent and a Nanoscale Additive to Epoxy Resin*. In: J. Mater. Chem. **21** (2011), p. 7337-7342.
6. Li, Z., Zhang, J., Li, Y., Guan, Y., Feng, Z., Li, C.: *Preparation and Characterization of Ordered Mesoporous Carbons on SBA-15 Template*. In: J. Mater. Chem. **16** (2006), p. 1350-1354.
7. Łabędź, O., Lange, H., Huczko, A., Borysiuk, J., Szybowicz, M., Bystrzejewski, M.: *Influence of Carbon Structure of the Anode on the Synthesis of Single-Walled Carbon Nanotubes in a Carbon Arc Plasma.* In: Carbon **27** (2009) No. 12, p. 2847-2854.
8. Łoś, S., Duclaux, L., Alvarez, L, Hawełek, Ł., Duber, S., Kempiński, W.: *Cleavage and Size Reduction of Graphite Crystal using Ultrasound Radiation.* In: Carbon **55** (2013), p. 53-61.
9. Saidane, K., Razafinimanana, M., Lange, H., Huczko, A., Baltas, M., Gleizes, A., Meunier, J.L.: *Fullerene Synthesis in the Graphite Electrode Arc Process: Local Plasma Characteristics and Correlation with Yield*. In: Journal of Physics D-Applied Physics **37** (2004) No. 2, p. 232-239.
10. Wada, T., Yasutake, T., Nakasuga, A., Kinumoto, T., Tsumura, T., Toyoda, M.: *Evaluation of Layered Graphene Prepared via Hydroxylation of Potassium-Graphite Intercalation Compounds.* In: J. Nanomater. (2014), p. 925253.
11. Wu, Z.S., Ren, W., Gao, L., Zhao, J., Chen, Z., Liu, B., Tang, D., Yu, B., Jiang, C., Cheng, H.M.: *Synthesis of Graphene Sheets with High Electrical Conductivity and Good Thermal Stability by Hydrogen Arc Discharge Exfoliation*. In: ACS Nano **3** (2009) No. 2, p. 411-417.
12. Xu, M., Sun, H., Shen, C., Yang, S., Que, W., Zhang, Y., et al.: *Lithium-Assisted Exfoliation of Pristine Graphite for Few-layer Graphene Nanosheets*. In: Nano Res **8** (2015), p. 801-807.