Experimental tests for carbon nanomaterial synthesis using DC plasma jet

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Abstract. In the frame of this work some experimental tests were performed in the plasma jet. Pure ethanol vapour alone or with the addition of fine iron powder were used to synthesize few-layer graphene or carbon-encapsulated iron nanoparticles, respectively.

1. Introduction
Carbon-encapsulated magnetic nanoparticles (CEINPs) were discovered in 1993 during the intensive studies on fullerene and nanotube formation using the carbon arc process. Recently, carbon encapsulates containing ferromagnetic phases have attracted significant interest. This is primarily due to their great potential for applications in biomedicine (e.g. contrast agents in magnetic resonance imaging [1]), drug delivery [2], hyperthermia [3], catalysis, and environmental protection (removal of heavy metal ions from aqueous solutions [4]). Hence, the development of efficient and selective synthesis routes for carbon-encapsulated magnetic nanoparticles is very important.

The flowing plasma jet is a powerful alternative to the conventional synthesis route of carbon nanomaterials using carbon arc discharge. These two methods of CEINPs synthesis have a very similar approach. The high temperature causes vaporization of carbon and iron precursors, and nucleation of Fe-C nanoparticles. When they leave the elevated temperature zone, the solidification of Fe–C nanoparticles with simultaneous expulsion of the crystalline carbon coating takes place. The major advantage of a flowing plasma jet over its predecessor stems from the fact, that it can be operated in a continuous regime. Additionally, the starting materials can be introduced into the reactor in any state, i.e. solid, liquid or gaseous. As for example carbon nanotubes have already been synthesized in a thermal plasma jet from ethanol [5], coal particles [6] or via ablation of a catalyst doped graphite rod [7].

This work has an exploratory character, as it was aimed at establishing the optimal conditions for the nanomaterial synthesis via dc plasma jet and carrying out several preliminary tests involving starting materials required for the formation of CEINPs.

2. Experimental
The experimental tests were carried out in a flow-through dc plasma jet reactor (figure 1). The pictured setup consists of two main sections: a plasma torch, where the reactants are introduced, and a water-cooled chamber, where the products condense. The starting materials were in this case ethanol and fine iron powder (10 µm). Previous studies have shown that ethanol is an optimal carbon precursor, since its processing in high temperature plasma environment results in formation of highly graphitic materials [8]. Importantly, the products formed from ethanol do not contain amorphous
carbon. The alcohol was delivered into the reaction zone in a form of vapor. The iron powder was
delivered by a powder feeder using Ar as a carrier gas. The reactant flow rates ranged between 8 and
35 g min$^{-1}$ for ethanol, and between 2 to 7 g min$^{-1}$ for iron powder. According to the presented flow
rate values the experiments were grouped into two categories: low ($m_{Fe}/m_{EtOH} < 0.1$) and high
($m_{Fe}/m_{EtOH} > 0.1$) Fe content.

Argon was the main plasma gas with the mean flow rate of 30 (or 21 - 35) slpm. The dc arc current
was 600 A, and the voltage drop ca. 22 V. During the tests, the emission spectra of hydrogen atoms H$_{\alpha}$
(656.2 nm) and H$_{\beta}$ (486.13 nm), and C$_2$ (d-a, $\Delta v$=0, 516.56 nm) Swan band were recorded (figure 2)
through an optical fiber inserted into one of two small view ports, close to the nozzle and 6 cm below
(figure 1). On the basis of Stark broadening of hydrogen lines the mean electron density and
temperature was evaluated. Obviously lines of Ar I and O I were also detected (figure 2).

The products were collected from different parts of the reactor system and subjected to a two-step
purification procedure consisting of boiling for 5 h in 3M HNO$_3$ and afterwards for 2.5 h in 30% 
H$_2$O$_2$, in order to remove the non-encapsulated iron particles and some insufficiently graphitized
carbon (if any).

![Figure 1. Reactor set-up.](image)

3. Results and discussion

3.1. Plasma spectroscopy

Figure 2 shows emission spectra of hydrogen lines, C$_2$, Ar I and O I. The Stark broadening of H$_{\alpha}$ and
H$_{\beta}$ lines was used to evaluate the mean electron density along the observation path (i.e. the optical
axis). To obtain information on temperature the thermodynamic calculations of plasma composition
(including electron density) were performed assuming the local thermodynamic equilibrium. The
dependence of electron density on temperature is shown in figure 3. Using the data from figure 3 and
the experimental mean electron density the mean temperature was drawn out. The electron density and
mean temperature for various Ar flow rates are shown in figure 4. The mean electron density and
temperature at the nozzle was about 6x10$^{16}$ cm$^{-3}$ and 12000 K. These values describe the plasma jet at
its middle zone. The mean temperature evaluated from the emission spectra of C₂ radical was found to be between 5800 and 6200 K. The atomic spectra recorded 6 cm below the nozzle were very weak. However, at this site in the reactor the molecular emission band of C₂ was acquired and used for estimation of the mean gas temperature, which was 3800 ± 500 K. It means that at 6 cm below the nozzle the vaporization of iron powder is still possible.

It follows from the thermodynamic calculations that C₂ radicals can only be present in the periphery of the jet, where the temperature is substantially lower in comparison to the middle. To summarize, the higher and lower temperatures describe different plasma zones.

![Emission spectra recorded at the nozzle.](image)

**Figure 2.** Emission spectra recorded at the nozzle.
3.2 Plasma processing of pure ethanol

The plasma processing of pure ethanol resulted in a black powder, which was recovered from the inner wall of the cooling chamber. The TEM investigations (figure 5) show that the products are composed of few-layer graphene flakes. Their lateral size is between 100 and 500 nm. The thickness (evaluated from the bending zones) is between 2 and 10 nm. This finding informs that the graphitic flakes are comprised of ca. 5 to 30 individual graphene layers. Further structural details were derived from
Raman spectra (figure 6). The G band (located at 1590 cm$^{-1}$) has substantially larger intensity in comparison to the D band (1360 cm$^{-1}$). This observation proves that the obtained product has a relatively high graphitization degree.

![Figure 5. TEM of raw products obtained from pure ethanol.](image)

![Figure 6. Raman spectrum of products obtained from pure ethanol.](image)

Multi-layer graphene sheets have already been fabricated by decomposition of ethanol in thermal plasma jet [9].

3.3 Plasma processing of ethanol and iron
The TEM investigation of products obtained from all tests which involved both ethanol and iron as the starting materials revealed that all of them contain mainly agglomerates of nanosized Fe particles surrounded by a layer of carbon – carbon encapsulated iron nanoparticles (CEINPs, figure 7). As a
result of the purification procedure, the insufficiently protected iron was removed from the samples leaving behind some empty shells (data not shown). Importantly, there is a clear noticeable difference in the diameter distribution of CEINPs. The encapsulates with narrower diameter distribution are primarily synthesized at higher Fe content in the initial reactant mixture.

The Fe content in both raw and purified products was evaluated by thermogravimetric analysis (TGA, figure 8). The analysis is performed under oxygen and during the TGA measurement the solid carbon phase is gasified, whilst Fe-bearing phases are transformed to the solid iron oxide. The ratio between the solid residue collected after the measurement and the initial mass is an indirect indicator of Fe content. As it stems from the TGA curves the Fe content in the raw products and the products after each stage of the purification procedure do not depend on the Fe/EtOH ratio. The Fe content in the samples obtained after nitric acid treatment is ca 1.5-fold lower in comparison to the raw product. This observation is a consequence of irreversible dissolution of non-encapsulated Fe particles which

![Figure 7. TEM images of products obtained from Fe and ethanol mixtures in two different ratios: A - m_{Fe}/m_{EtOH} < 0.1 and B - m_{Fe}/m_{EtOH} > 0.1.](image)
are present in the raw product. Noticeably, the Fe content increases after H$_2$O$_2$ treatment. In this case it is resulted from the removal of some amount of carbon.

![Graph showing TGA of products on every stage of the purification process.](image)

**Figure 8.** TGA of products on every stage of the purification process.

The Raman spectra of CEINPs are shown in figure 9. There is no remarkable difference in the graphitization degree for the products synthesis at low and high Fe/EtOH ratio (please note the G and D bands are of similar intensity). However, the graphitization degree of CEINPs is lower in comparison to the products obtained from pure ethanol (figure 6). This is an expected result, because carbon coatings in carbon encapsulates contain more defects than the relatively flat few-layer graphene structures.

![Graph showing Raman spectra of purified products.](image)

**Figure 9.** Raman spectra of purified products.
The overall synthesis yield of carbon-encapsulated iron nanoparticles has been evaluated. The yield is defined as the ratio between the mass of products and the mass of the introduced starting material. Then, the yield is multiplied by the purification yield (this factor illustrates the fraction of a material which was recovered after purification). The overall yield was found to be ca. 1% and 5% for low ($m_{Fe}/m_{EtOH} < 0.1$) and high ($m_{Fe}/m_{EtOH} > 0.1$) Fe content in the initial mixture of starting reactants.

4. Conclusions
The plasma processing of pure ethanol and its mixture with fine Fe powder was studied. It was found that the mean temperature in the port where the initial reactants were introduced was ca. 2 times greater than the sublimation point of Fe and high enough for decomposition of the carbon precursor. The performed tests have shown that the plasma processing of pure ethanol results in formation of few-layer graphene flakes with the lateral dimension between 100 and 500 nm and the corresponding thickness up to 10 nm. The inclusion of Fe in the reactant system causes the production of carbon-encapsulated iron nanoparticles.

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