



# Continuous and catalyst free synthesis of graphene sheets in thermal plasma jet



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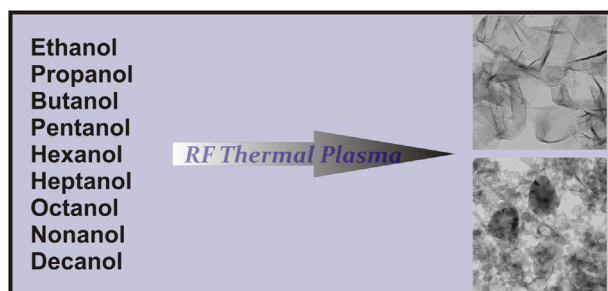
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## HIGHLIGHTS

- Plasma processing of alcohols yields graphene sheets and carbon particles.
- Graphene sheets are selectively synthesized from ethanol only.
- Graphene sheets are continuously produced with the production rate 1.5 g·h<sup>-1</sup>.
- Oxygen to carbon ratio is the key parameter which drives process selectivity.

## GRAPHICAL ABSTRACT



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## ABSTRACT

Herein we present a continuous and catalyst free method for the synthesis of graphene sheets from aliphatic alcohols in a radiofrequency thermal plasma jet. Nine aliphatic linear alcohols (ethanol–decanol) were tested as possible precursors for the massive production of graphene sheets. Moreover, additional tests were also carried out with the inclusion of gaseous oxygen in order to promote the formation of graphene and to eliminate the unwanted carbon byproducts. The obtained materials were investigated by electron microscopy, Raman and infrared spectroscopy. The thermal stability of products was also evaluated using thermogravimetry. The surface chemistry features were analyzed using acid–base titration and X-ray photoelectron and IR spectroscopy. Finally, the adsorption performance of graphene sheets was tested in the removal of 4-chlorophenol from aqueous solutions. The highest content of graphene sheets was found in the product obtained from ethanol with the production rate of ca. 1.5 g/h. The plasma processing of higher alcohols yielded a mixture of graphene sheets and spherical carbon nanoparticles.

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## 1. Introduction

The first described methods of synthesis of graphene materials was discovered independently by two research groups at the beginning of twenty first century. Graphene was obtained via thermal desorption of silicon from Si-terminated single crystal of silicon carbide in ultrahigh vacuum (ca. 10<sup>-8</sup> Pa) by electron bombardment [1]. In the second case, the mechanical exfoliation

of pyrolytic graphite was applied [2]. Nowadays, the exfoliation of graphite can be carried out using alkali metals, e.g. potassium [3] or lithium [4]. Moreover, graphite can be also exfoliated in carbon arc discharge under hydrogen atmosphere [5,6]. Furthermore, the exfoliation can be also carried out via ultrasound treatment of graphite in aqueous solutions of surfactants [7–10] or in supercritical CO<sub>2</sub>/H<sub>2</sub>O mediums [11]. The synthesis of graphene materials via exfoliation route is time-consuming (24–48 h) and do not lead to large amounts of the products at the laboratory scale. The current state of the art on graphene synthesis includes also chemical vapor deposition (CVD) onto silicon carbide [12–14] or copper

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[15]. It is also possible to obtain graphene via plasma-assisted CVD [16,17]. These processes require the use of an appropriate catalyst. Graphene materials can be also synthesized via reduction of graphene oxides using (i) chemical reducers [18–20], (ii) electrochemical processes [21–24] and (iii) thermal routes [6,25]. Finally, graphene materials were also obtained via combustion synthesis [26–28].

Graphene, few-layer graphene and graphene sheets exhibit unique physical and chemical properties and have a high potential to be applied in high-tech devices and applications. For example, graphene-based membranes are permeable for water vapor, but not for other liquids or gases [29]. This phenomenon can be used to preconcentrate aqueous solutions and in consequence to obtain pure water. Another possible application of graphene materials, taking advantage of their electrochemical properties, is to fabricate ultrathin electrodes, which can be used as the electrochemical sensor of dyes [30], hormones (for example serotonin) or glucose, which is very important in diabetics diagnostics [31]. Recently, Bahadır and Sezgentürk in their review [32] described a few-layer graphene based sensor dedicated to determine biomolecules, e.g. enzymes and DNA. Graphene-based materials and their composites have promising scope in energy storage, for instance as a component of rechargeable lithium batteries [33], or in construction of supercapacitors [34,35].

In this work, a novel approach to the synthesis of graphene sheets is investigated. We used oxygen-containing compounds, namely various aliphatic alcohols, as promising and low-cost precursors of graphene sheets. Another goal of the research was to study the role of gaseous oxygen added to the plasma gas on the formation of graphene sheets. The presence of oxygen and various oxides has a great influence on the growth of carbon nanomaterials (graphene and carbon-encapsulated magnetic nanoparticles) during thermal plasma synthesis [36–38]. It is noteworthy, that the use of in-flight plasma processing allows to carry out the experiment in a continuous manner and without the necessity of using the catalyst. A similar approach, in a microwave plasma system has already been published [17,39,40]. However, in these papers only two carbon precursors (methanol and ethanol) were tested and the process was assisted by the presence of a catalyst system. Nevertheless, the obtained products were inhomogeneous, as they contained graphene materials and multi-wall carbon nanotubes. Our work is focused on the systematic studies on the plasma processing of a wide range of aliphatic alcohols without the presence of catalyst as possible precursors of graphene sheets. Amirov et al. studied the decomposition of hydrocarbons in the direct current thermal plasma jet without catalyst and obtained porous multi-layer graphene materials [41]. Graphene sheets were obtained from ethanol by Dato et al. [42,43] in the microwave plasma system. In these works the catalyst was not used to promote the growth of few-layer graphene.

## 2. Materials and methods

### 2.1. Chemicals

Aliphatic n-alcohols (ethanol- decanol), sodium hydroxide and hydrochloric acid were purchased from Avantor Performance Materials Poland. The plasma gases (Ar 99.996%, He 99.999% purity) were from Messer Hungarogáz Kft. (Hungary). 4-chlorophenol (>99%) was purchased from Sigma Aldrich. Potassium bromide (IR grade) was from Across Organics.

Sodium hydroxide solution (0.05 mol·dm<sup>-3</sup>) and hydrochloric acid solution (0.1 mol·dm<sup>-3</sup>) were prepared using volumetric stock standard solutions. The working solutions of 4-chlorophenol were

prepared by diluting the stock solution (1000 mg·dm<sup>-3</sup>) in volumetric flasks.

### 2.2. Plasma decomposition of alcohols

The decomposition of aliphatic n-alcohols was carried out in an RF thermal plasma system, which consisted of an RF inductively coupled plasma torch (TEKNA PL-35) connected to a high frequency (4–5 MHz) LEPEL generator, a reactor, a cyclone, a filter unit and a vacuum pump (see [Supplementary Data, Fig. S1](#) and papers [44,45]). The double-wall, water cooled cylindrical reactor was made of stainless steel with the inner diameter of 19.7 cm and length of 121.6 cm. The delivered net power was 25 ± 1 kW. The alcohol precursors were delivered by a peristaltic pump (Masterflex) to an atomizer probe (2.16 mm inner diameter), and was fed coaxially into the hottest part of the plasma jet with the feeding rate of 7.5 ± 0.5 cm<sup>3</sup>·min<sup>-1</sup>. Argon with the flow rate of 7.5 dm<sup>3</sup>·min<sup>-1</sup> was used for atomization. The experiments were carried out under the atmosphere of argon and helium. The flow rates were as follows: sheath gas- argon 40 dm<sup>3</sup>·min<sup>-1</sup> and helium 27 dm<sup>3</sup>·min<sup>-1</sup>, plasma gas- argon 15.5 dm<sup>3</sup>·min<sup>-1</sup>. Two additional tests with n-decanol were also carried out under atmosphere enriched with 1% (1 dm<sup>3</sup>·min<sup>-1</sup>) and 5% (4.75 dm<sup>3</sup>·min<sup>-1</sup>) of oxygen added directly to the plasma gas. The experiments were conducted at the pressure of 70 ± 3 kPa.

### 2.3. Characterization of the products

The products, in the form of black and dusty powder were collected by a brush from the inner walls of the reactor and then weighted. The morphology of the carbon products was investigated using scanning (SEM; Zeiss Merlin) and transmission (TEM; Zeiss Libra 120) electron microscopy. The Raman spectra of the solid samples were acquired using a Jobin Yvon-Spex T64000 Raman spectrometer equipped an Ar-ion excitation laser (514.5 nm). The spectra were registered in the range of 800–3000 cm<sup>-1</sup>. The infrared spectra were recorded using a Thermo Fisher Scientific Nicolet spectrometer. A petite amount (ca. 1 mg) of a sample was mixed with 300 mg of potassium bromide, then, the mixtures were pressed into pellets using a laboratory hydraulic press. The spectra were acquired in the transmission mode in the spectral range of 400–4000 cm<sup>-1</sup>.

Thermal stability of carbon products obtained in the particular tests was studied by thermogravimetry (TGA) using a TA Q50 instrument. The measurements were performed under oxidizing atmosphere (N<sub>2</sub>/O<sub>2</sub> 95/5 vol.%) with the heating rate of 10 °C·min<sup>-1</sup>.

The Boehm titration method [46–49] was used to determine the content of surface acidic groups. 50 mg ± 1 mg of the material was put into 50 cm<sup>3</sup> of sodium hydroxide solution (0.05 mol·dm<sup>-3</sup>) at 23 ± 1 °C. After 24 h the concentration of NaOH was determined by potentiometric analysis using an automatic Metrohm Titrando 888 titrator.

The XPS spectra were acquired using a Kratos Axis Supra 5 spectrometer with monochromatic Al K $\alpha$  radiation (1486.6 eV). The samples were placed into brass holders.

The adsorption properties of the obtained materials were evaluated for 4-chlorophenol. The tests were carried out at 23 °C ± 1. 50 mg of the studied material was added to 50 cm<sup>3</sup> of 4-chlorophenol aqueous solution in a plastic vial and shaken for at least 6 h. Afterwards, a Shimadzu UV-2401 PC spectrometer was used to determine the equilibrium concentration of 4-chlorophenol.

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