Material inkjet printing of advanced systems suitable for polymer electronics

Bc. Martin Holek

nascannované zadání s. 1

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Příjmení a jméno: Martin Holek   Obor: IP

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ABSTRAKT

Tato práce pojednává o přípravě grafen oxidu ve formě nano "sheetů", jež jsou dále použity pro přípravu inkoustů pro materiálový tisk s využitím inkjetové technologie. Grafen oxid je charakterizován pomocí XRD, AFM, SEM, FTIR a Ramanovské spektrometrie. Připravené inkousty jsou charakterizovány s využitím viskozimetru, dále pak je měřeno povrchové napětí. Z připravených inkoustů jsou natisknuty elektronická zařízení (senzory), která jsou testována na senzitivitu vůči parám organických rozpouštědel.

Klíčová slova: Grafen oxid, grafit oxid, GO, inkjetový tisk, senzor, polymerní elektronika, flexibilní elektronika

ABSTRACT

This master's thesis deals with preparation of graphene oxide in form of nano-sheets which are intended as an active material in inks for inkjet printing. Synthesized graphene oxide was characterized by XRD, AFM, SEM, FTIR and Raman. Prepared inks were tested using viscometer and surface tension meter for liquids. Final electronic devices (sensors) were printed from prepared inks and these devices were tested on the sensitivity to organic solvent vapour.

Keywords: Graphene oxides, graphite oxide, GO, ink jet printing, sensor, polymer electronics, and flexible electronics

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I hereby declare that the print version of my Master's thesis and the electronic version of my thesis deposited in the IS/STAG system are identical.

CONTENTS

INTRODUCTION

Polymer electronics grew to a huge area of science and industry nowadays and material printing including inkjet printing, screen printing and gravure printing are technological methods often used in this industry.

Inkjet printing has been one of the most studied printing technologies not only for printed electronics but even for biological science in the field of microbiological patterning. Today, inkjet printing belongs to very versatile technique in the lab scale, if the thin patterns with relatively high resolutions are desired. Thus, the inkjet printing asserts itself also in sensing, where materials based on carbon are more and more used.

Carbon is one of the most important elements and it is the main building element of life on the Earth. Except the organic compounds, carbon can form many structures such as diamond or graphite. Over the last few decades the graphene, two dimensional monoatomic layer of carbon, is one of the most studied materials because of its remarkable properties. Only in last few years, graphene derivatives are intensively studied as very promising materials in many applications.

Graphene oxide, oxidized form of graphene, is mass produced insulating hydrophilic material with possibility of reversed reduction to graphene (reduced graphene oxide). Chemical structure makes graphene oxide possible material for applications such as water purification technique, supercapacitors, field emitters or bio and chemical sensors.

The main goals of the research presented in this thesis are preparation of graphene oxide and study of its properties considering the structural shape and ability to prepare suitable ink formulations for material inkjet printing.

Further aim of this thesis is to prepare and test functional gas sensor using digital inkjet printing from graphene oxide based ink, whereas the graphene oxide must be prepared at first, followed by ink preparation with fulfilled technological aspects of printing to ensure high resolution and quality of printed pattern.

I. THEORY

1 INKJET PRINTING

Inkjet printing is a method of printing digital text or image onto a substrate using ink, most often water-based. It is a contactless method, where droplets of liquid are jetted from a print head in precise locations onto a substrate. Conventionally inkjet printing has been used for repeated reproduction of the information many times onto a paper. In last few decades it has been also used for electrical and optical devices, for 3D printing, proteins or nucleic acids production, etc. So, in present, inkjet technology has an increasing impact on printing for industrial world. With so many variations of inks (even metals, polymers, ceramics, etc.), substrates (need not even be solid), printing techniques and methods, there exists very wide group of application. With inkjet printing can be also achieved many types of structure and patterns which cannot be created by other methods because of any limitation. [1, 2, 3]

Inkjet printing is very complex process during which many involvements can occur. These obstacles have physical, chemical or physicochemical nature. For optimal ink jet printing three main parts (print head, ink, and substrate) have to be optimized. Inkjet printing is described in more details below.

1.1 Ink print heads – drop generation methods

Principally, two kinds of methods for inkjet printing are introduced, continuous inkjet (CIJ) and drop-on-demand inkjet (DOD). In both methods liquid is ejected through nozzles. The difference between them is that in case of continuous inkjet the flow of droplets is continuous (*Fig. 1*, left) and in case of drop-on-demand droplets are ejected only when required (*Fig. 1*, right).
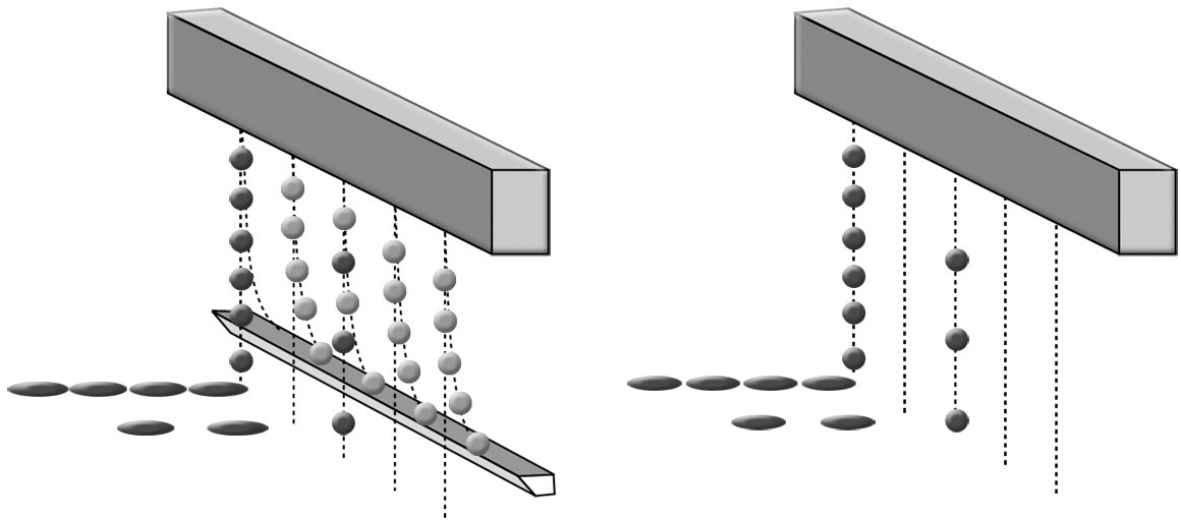
Fig. 1 Continuous inkjet (left) and drop-on-demand inkjet (right) schema. [1]

1.1.1 Continuous inkjet (CIJ)

In this method, droplets of ink are jetted continuously through nozzles. Today's printers can form large number of droplets with a well-controlled size and spacing. The jet formation is driven by vibrating piezoelectric crystal at high frequency (50-175 kHz).

Immediately after ink leaves the nozzle, Rayleigh-Plateau instability causes that ink has tendency to form continuous stream of droplets. The surface tension of liquid ensures forming of stable stream of droplets.

As drops are produced continually, some of them have to be selected. Drops go through an electrostatic field where are charged. Then, stream of drops flies through a deflection field and drops which are not required for printing are deflected and returned for reuse (***Fig. 1***, left). [1-4]

1.1.2 Drop-on-demand inkjet (DOD)

Except printers used in research institusions, the modern printers can have print heads with hundreds or thousands nozzles which can be also used in combinations. With these heads there does not exist the need to have deflection system, so these heads are smaller than for CIJ. Big difference is also that each nozzle works only when required. DOD printheads are subdivided into two main categories: thermal and piezoelectric. These heads differs in way of creating the pressure pulse for droplets forming. [1-4]

1) Thermal print head

This head is the most common in home or office inkjet printers. In this print head, drops are formed by heating of small resistive heater. If such element would work precisely, two assumptions exist: The heater must be in good contact with the ink and must be heated very quickly (few micro seconds between drops). This small heater causes a vaporisation of the ink, formed bubble quickly expands and it causes pressure pulse for jetting of the droplet when the bubble collapses and pressure drop sucks fresh ink. And the cycle repeats. [1, 2]

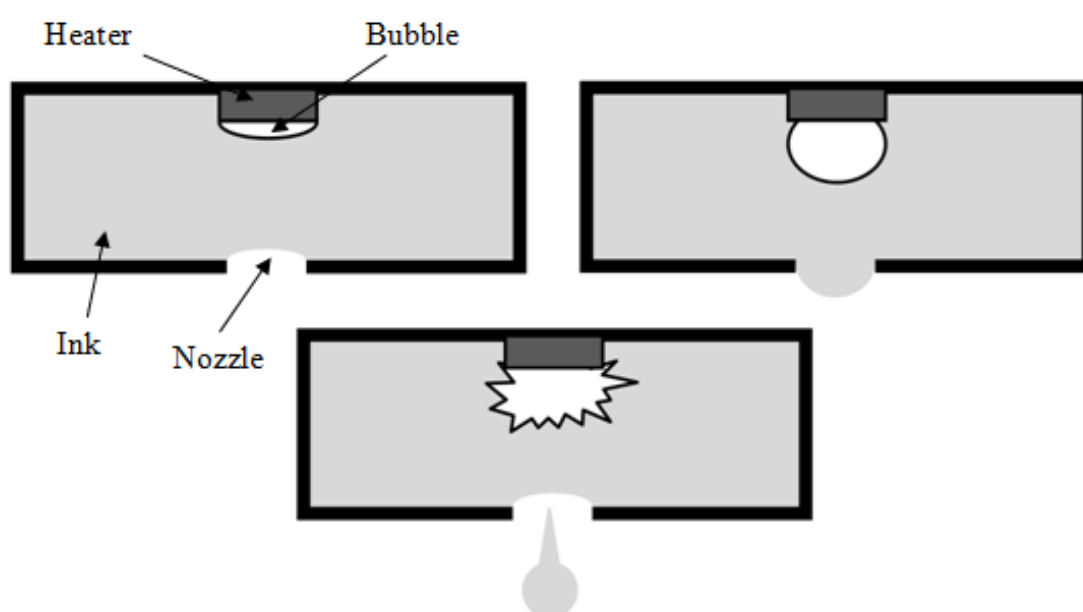Fig. 2 Printing cycle of thermal inkjet print head.

2) Piezoelectric print head

The crystal, which is used in these print heads, has piezoelectric properties and ability to generate mechanical stress if an electric field is applied. "Lead zirconium titanate" (PZT) - a ceramic material with strong piezoelectric effect is mostly used in printers. [2, 5]

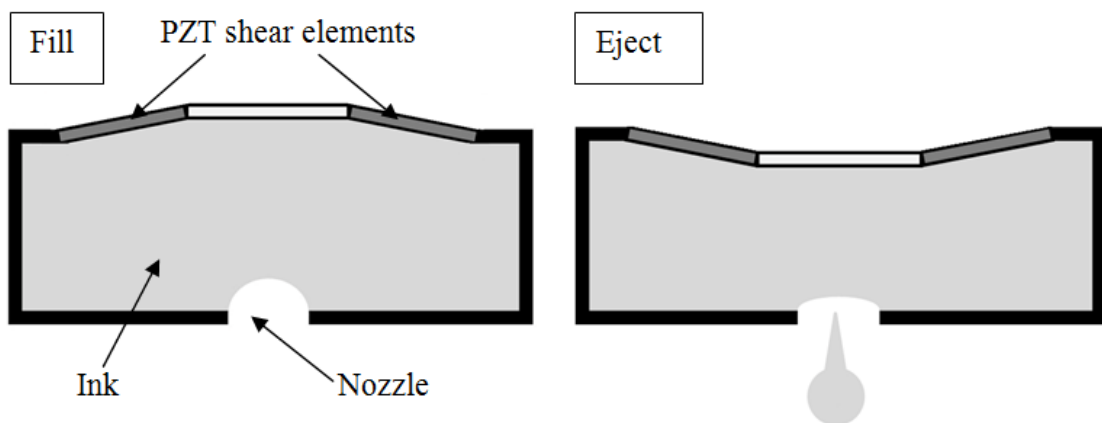Mechanism of piezoelectric inkjet shows *Fig. 3* below.

Fig. 3 Printing cycle of piezoelectric inkjet print head.

1.2 Substrates

The best possible interaction of every ink with the substrate must be ensured, especially in case of printed electronics. These interactions have influence on durability and abrasion resistance, adhesion, compactness of the printed patterns, distribution of the ink on the substrate, definition of the edges, layer thickness and ink wetting intensity. Two types of substrates can be used:

A) Porous – paper, textile, silica, gelatine, cellulose derivatives...

B) Non-porous – glass, metal, polyimide (PI), Polyethylene terephthalate (PET), polycarbonate (PC) foil...

Higher quality during printing on non-porous substrates can be achieved by heating of the substrate. In such case, ink viscosity decreases and evaporation rate increases. [6]

1.2.1 Wetting

The suitable functional molecules or groups must be contained in the ink to ensure good adhesion and wetting of droplets on the substrate.

In case of large dots, ink should have lower surface tension than surface energy of the substrate. Otherwise, if small dots and better resolution are desired, surface tension should be as high as possible. [6]

Both, substrate and ink can be modified for optimal wetting and spreading and optimum arises if surface tension of ink and substrate is equal. Surface tension of the ink decreases with using wetting agent (surfactant) or low surface tension solvent. Surface treatment

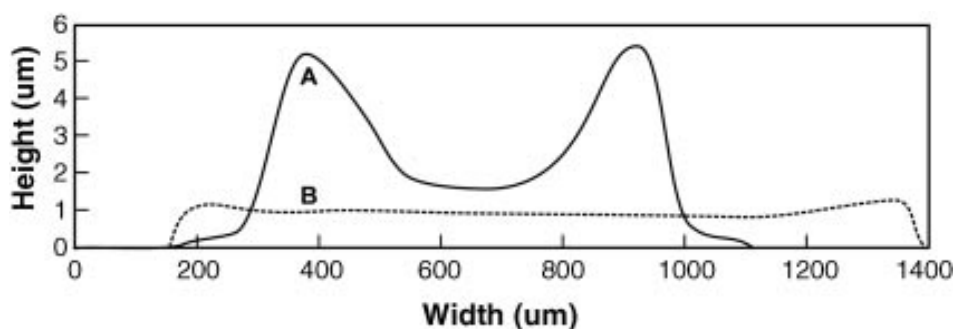such as plasma, ultraviolet/ozone or chemicals (cleaning, etching), modifies surface energy. [6, 7, 8]

Fig. 4 Wetting agent effect. Ink with wetting agent (B) and without (A). [6]

High quality of the pattern and substrate-ink compatibility can be achieved also with using substrate with special deposited thin layer on the surface. For thin layer deposition are used for example physical or chemical vapour deposition, ceramic coating, thermo-reactive deposition, electroless platting and much more. [9]

1.3   Inkjet inks

For inkjet technology has been found large number of inks with different properties intended for many application. There are five main categories: phase-change, solvent-based, water-based, UV curable and advanced ink systems (see **1.3.2.**). All of them have the same or similar requirements. Inks, at least during printing, should accomplish specific physico-chemical criteria.

Ink system can contain besides pigment and solvent also resin, additives and varnishes.

1.3.1   The main requirements on inks

1.   Stability

Stability of ink is defined as ink with constant properties over time. There are two types: with undissolved particles and without them.

If ink does not contain undissolved particles, stability is caused by temperature, interactions between parts of the ink (resin-solvent) or phase separation.

Ink which contains these particles is prone to aggregation of the pigment with following sedimentation on the bottom. It is due to van der Waals forces when particles try to reach

minimum potential energy. For example, it is hard to disperse well carbon black in water because it is hydrophobic. On the other hand, if functional groups with oxygen (graphite oxide) are on surface of carbon black, this pigment becomes hydrophilic and very well stable in water (see **2.1**). [1, 10]
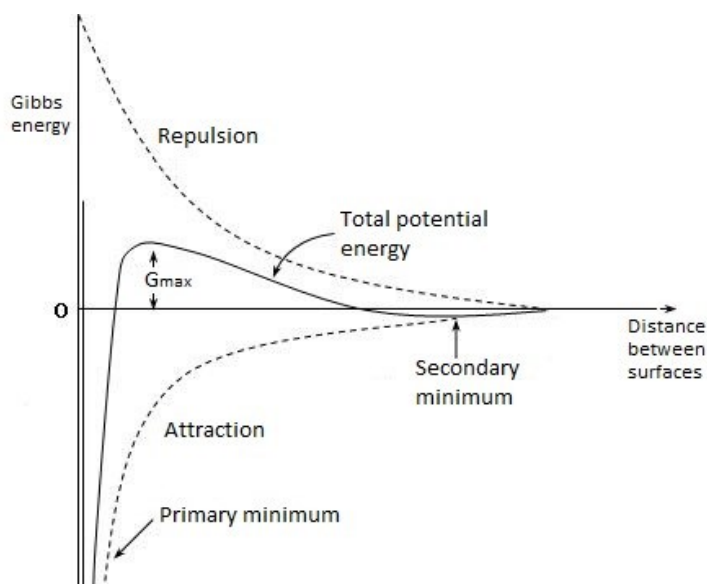
Fig. 5 Van der Waals potential energy curves as a function of distance between surfaces

2. Surface tension

It is one of the most important properties of the ink. Surface tension mostly determines forming of droplets, their size, shape and especially the structure of the printed pattern on the substrate. [11] With high surface tension ink can form only one big blot. In this case, surface tension must be modified with surfactants (for example isopropanol in case of water-based inks). It is also very useful that concentration of the added surfactant can be very low (even below 0,1 wt%).

It is also very important consider all components of the ink when preparing, because surface tension could be affected by interactions between them each other [1, 4, 12]

3. Viscosity

The viscosity is very important during jetting and deposition onto substrate. Inkjet printing requires viscosity around 20 mPa·s, depends on print head type. Because of big shear rate changes during printing, Newtonian inks are more desired. So, additives like polymers can cause changes in viscosity and can introduce non-Newtonian behaviour thus printing setting problems. From the other perspective, pseudoplastic materials have high viscosity

during storage and low during printing what can solve problem of stability. In particle inks sedimentation of the particles causing local changes in viscosity can arise. With decreasing size of particles contained in the ink the better stability is obtained. [1, 4, 12]

4. Other properties

pH may be important factor for water-based inks, which contains components stable or soluble only in specific range of pH. Problematic components are often polymers or resins. With polymers can be achieved better stability while they are charged. And the charge usually depends on pH of the ink. [12]

Ink conductivity has to be considered during inkjet printing. For continuous printing (CIJ), the conductivity is problematic due to the presence of electrical charge. It could be solved with adding charge control agents, which are electrolytes or ionic surfactants. But these salts can interact with other components, so there is very important to control changes in conductivity. Charged or uncharged polymers which act as insulators can be also used. To obtain conductive pattern, special treatment after printing is needed. [1, 12]

1.3.2   Ink types

Due to the huge number of possibilities how to prepare printable inks, it is hard to separate and classify every ink and determine any specific borders. In general, five main categories are described below.

1. Water-based inks

These inks have several advantages applying on the world market of common printers. They are relatively simple, environmentally friendly and cheap. That is the reason of using them in majority of office and home printers. But for industrial printers, they are not sufficient. Technologies using piezoelectronic industrial printing heads need quick penetration of the substrate and water-based inks require porous or treated substrates to contribute durability.

With technical improvement some water-based inks for printing of packaging materials such as food, wine, toys or drugs are used in industrial printing. [12, 13]

Water-based inks can be composed of colorants, surfactants, co-solvents, defoamers, buffers, polymeric binders etc. Typical ink formulation is given in **Table 1**.

Table 1 Typical water-based inkjet ink composition [14]

Component	Function	Concentration (wt%)
Deionised water	Aqueous carrier medium	
Water soluble co-solvents	Viscosity control, enhance dye solubility, humectant	5-50
Colorants, pigments	Provides colour, produce vibrant	0,5-10
Surfactants	Penetration and wetting	0,1-10
Polymeric binders	Improve gloss and durability	0,1-10
Biocide	Prevents biological growth	0,05-1
Buffer	Controls the pH	0,1-0,5
Other additives	Anti-corrosion, defoamers, chelating agents	>1

2. Solvent-based inks

These types of inks are widely used in industrial sector due to: quick drying, quality of printed pattern and compatibility with many substrates (from glass to leather). Most common solvent-based ink formulations are short-chain alcohols, lactates or glycols. More aggressive solvents as toluene and other aromatics are used less frequently. [12, 14]

These inks stand for a risk for the environment or health and due to the quick drying there is always risk of clogging the print head nozzles, especially for DOD print heads. [13]

3. UV curable inks

These inks are monomeric or oligomeric epoxides or acrylates. After printing onto substrate are polymerised by UV light. These inks must content a photo-initiator but not volatile substances; they can be printed onto various substrates (also in 3D structures). Printed patterns have a great resistance and high durability. UV curable inks are also stable in liquid phase until irradiated. High cost of material and device are disadvantages of these inks. [12, 14]

4. Phase-change

Also called hot-melt inks. As name suggests, these inks are melted in print head and they are deposited onto the substrate in form of solid structure. These inks are mostly formed of

mixture of waxes (natural or synthetic). Due to the solid state, there is no need to control the storage conditions as much as for liquid inks. Printing with these inks enables good flat covering, thus porous substrates are not required. As each type of ink, this has also disadvantage in low durability and abrasion resistance. [12, 14]

   5. **Advanced ink systems**

One type of the advanced ink systems are micellar inks. Micelles can have polar or non-polar core, can be hydrophobic or hydrophilic. Thus, polar parts of the ink can be located away from the non-polar and conversely. In another case, these systems can solubilise some compounds or stabilise dissociated ions and act as surfactant. Micelles can be also used for drug delivery and can help to drive pH changes. [1, 15]

Emulsion inkjet inks compose of two immiscible liquids and can form thermodynamically stable isotropic systems. If some particles are dissolved in the liquid and this liquid is dispersed in another liquid, those particles can be prevented from aggregation and sedimentation, high quality patterns are obtained and surface tension, local viscosity changes and stability properties are improved. [16]

1.4   Polymer electronics

Polymer electronics has been continuously developing industry in two last decades. Polymeric materials replace conventional materials due to their advantages. Silicon is one of the conventional materials used in electronics. It is the major component of semiconductor industry. As compared with silicon, polymers are flexible, low cost and very good processable. Polymers can be stored in no special environment, melted, dissolved and easily form films. With these advantages polymers can be used in all sorts of electronics. It could be used in applications such as light emitting diodes (LED), sensors, flexible displays, solar cells, transistors, biomedical devices, radio-frequency identification tags, wearable sensors and so on. [17, 18]

Polymer electronics can be classified into two main groups:

   1. Polymer serves as substrate – flexible carrier of the device, for example polyethylene terephtalate (PET) and polyimide (PI)
   2. Polymer serves as an active material – for example polymer as an emitter in pOLED

By combining the flexible and printed electronics, new generation of electronic devices can be created – Printed polymer electronics. Printing of conductive (or semiconductive) structures on the polymeric (flexible) substrate or printing of flexible material solves many technological problems, for example creation of complex structures, composites or assembly of several devices, etc.

1.4.1 Printed polymer electronics

Over last ten years, low cost mass production of polymer electronics (flexible photovoltaic systems, flexible electroluminescence foils) has been developing as a product with using spin coating, doctor-blading or material printing. Using printing technology is very profitable due to printing patterns directly onto the substrate. Polymer electronics grew to a huge area of science and industry and nowadays, conductive polymers and advanced systems, like a graphene or graphene oxides represent very interesting classes of materials for the future. The light emitting devices made from polymers, flexible electronic components or photovoltaic applications promise the broadening of current applications. Indeed examples of innovative solutions penetrated reached recently commercial market by such products as organic light emitting devices (OLED) displays, TV screens, solid state lighting and flexible photovoltaic cells. [18, 19]

In field of electronics, new progress is offered by the flexibility and relative simplicity (compared to photolithography process) of the printing process and variability of polymer substrates. On the other hand, conventional photolithography can produce electronic patterns with 50 nm width of lines. Industrial ink jet printer can only produce patterns with 20 μm width of lines. Except these small devices, the printed polymer electronics provide low cost and technological advantages. [1, 17, 18, 20]

The most printed materials for printed electronic devices are semiconductors – organic and inorganic. Semiconductor as an active material is main part of the printed device. Inorganic semiconductors have better electrical properties and higher environmental stability than organic semiconductors. Organic semiconductor devices are cheaper due to their ease of solution processing under less controlled environments. Thus, on the one hand we have inorganic devices for high performance electronics and the other organic low cost devices.

Inorganic semiconductors for printed electronics can be: one dimensional 1D (nanowires), 2D (graphene) or 3D exfoliated crystalline structures.

Over the last few years, the organic molecular electronics and carbon/graphene printed electronics have been most investigated. Ink jet printing is the most used printing technique in research sphere due to versatility, ability to print exactly digital pattern using of different kinds of inks. Main advantages are that inks do not need binders and with decreasing viscosity the resolution improves and that ink jet printing allows usage of both inorganic and organic materials. These are several reasons why this thesis is based on graphene oxide printed sensors.

1.4.2 Sensors

Typical sensor is composed of two main parts: sensitive element and transducer. Sensitive element interacts with a target substance which causes a change of chemophysical properties. Transducer converts one form of energy to another (transduction) and depends on essential character of sensitive element. With the operation change, transducer converts the signal to readable data. The term "transducer" is also uniform name for many devices such as sensors, transistors or actuators. For transistors and actuators an important factor is the conversion efficiency. Sensors have other important factors such as selectivity or sensitivity. Thus, the term sensor is typically meant as only sensing element. [21]

Sensors are widespread all over the world in huge number of systems and play very important role in everyday life. Each application has specific requirements and according to that sensors can be divided into categories such as:

- Industrial applications – automotive, machine control, chemical...
- Military equipment
- Biomedical technologies
- Security devices
- Consumer electronics

To raise awareness of variety of applications, here are examples of safety sensors in cars: Belt, acceleration, steering wheel angle, torque, tilt, safety distance sensors. It proves that sensors are widespread and very important devices in all kinds of applications. [21]
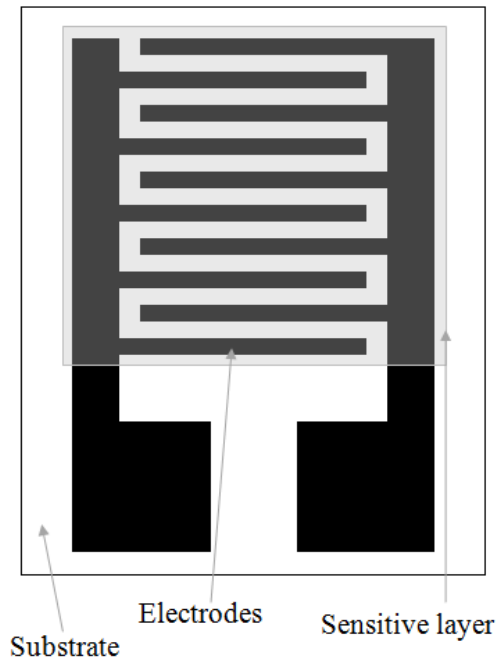
Fig. 6 Schema of an interdigital tranducer

1.4.2.1 Electrochemical sensors

It is the largest and the oldest category of chemical sensors. This category includes for example pH or gas sensors. Sensor responds to interaction between sensitive layer and the chemical substance. Generated signal depends on various aspects such as sensitivity, thickness, structure and dielectric properties of the sensitive layer, diffusion processes of the chemical, reactivity and thermodynamics between chemical and sensitive layer, distance between the electrodes, resistance of the electric circuit, and so on. [21, 22]
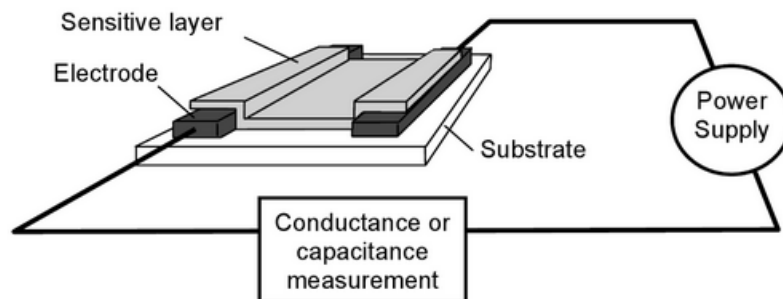

Fig. 7 Electrochemical transducer setup [22]

2 GRAPHENE AND CHEMICALLY DERIVED GRAPHENE

Carbon is one of the most important elements in the periodic table. Carbon atoms can form complicated networks such as polymers what makes them main building element of life on the Earth. Elemental carbon forms many of different allotropes such as three dimensional (3D) diamond and graphite, two dimensional (2D) graphene, one dimensional (1D) nanotubes and zero dimensional (0D) buckyballs structures.
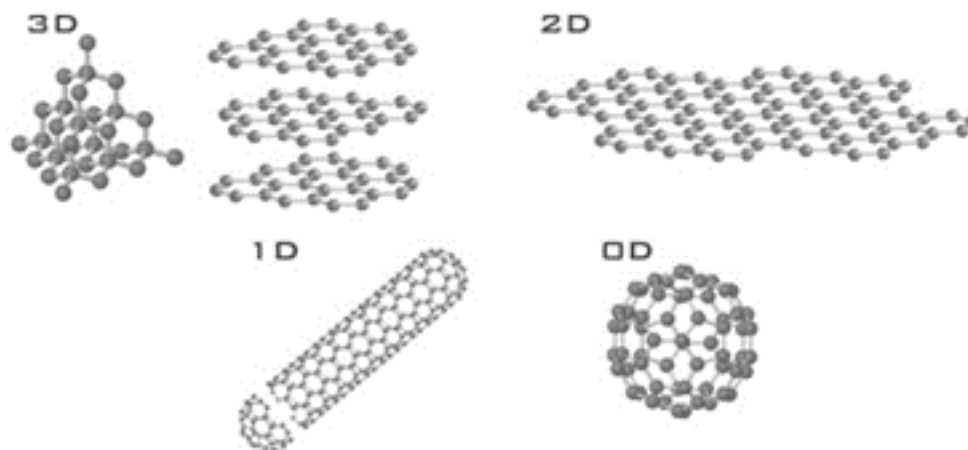

Fig. 8 Different carbon allotropes: 3D – diamond (left), graphite (right), 2D – graphene, 1D – nanotubes, 0D – buckyballs. [23]

Graphene is remarkable material. It is a single layered two-dimensional sheet of carbon atoms (*Fig. 9, a)*) and it is the basic structural element of graphite, carbon nanotubes and fullerenes. Graphene and its derivations have been found to possess interesting properties which could be useful for sensing, optoelectronic, energy storage and catalysis applications. [24]

Correctly, name graphene or graphene oxide should be used only for single atomic layered structures. But, in general, graphene oxide or graphite oxide are both called GO (*Fig. 9, b)*), because there is no big difference between them, even in the context of electronic structures and properties. Also when GO is prepared by wet chemical process, and there is big amount of GO flakes in solution, it is at least partially exfoliated by the solvent molecules, therefore it is called graphene oxide solution. Otherwise, GO in solid state is mostly graphite oxide. [25, 26]

Pristine graphene sheets are only flats of carbon atoms with thickness of ~0,34 nm. Graphene oxide sheets have a thickness around 1~2 nm. Graphene sheets are thinner due to the absence of sp^3 hybridized carbon atoms and of covalently bound oxygen atoms. Graphene

oxide is a graphene sheet with carboxyl (–COOH), hydroxyl (C–OH), ketone (C=O), epoxy (C–O–C), ester (–O–C=O) and lactol (–O–C–OH) functional groups. [25, 26]
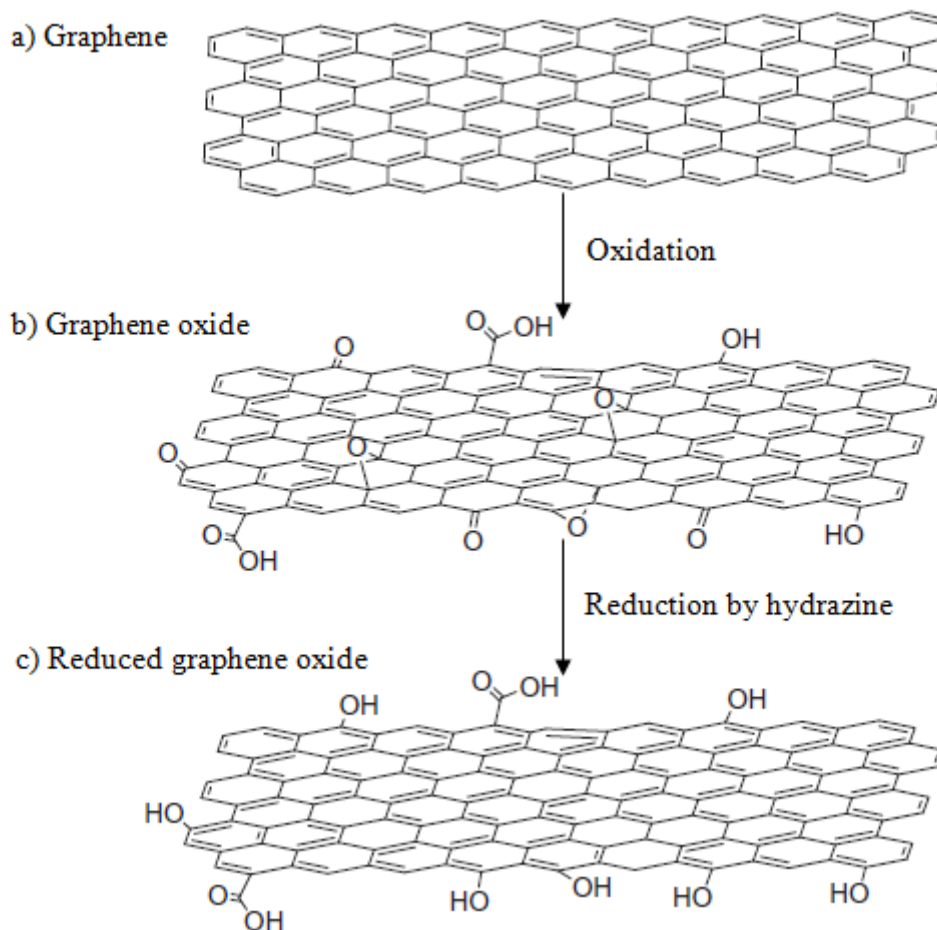
Fig. 9 - Oxidation of graphene to graphene oxide and proposed reduction by   hydrazine [27]

2.1   Graphite oxide and reduced graphite oxide

Graphite oxide (GO) is a structured compound obtained by oxidation of graphite and for the first time was discovered in 1859 by Benjamin Brodie and named graphitic acid or graphite oxide. At least six different structure models have been suggested with characterisation of GO (***Fig. 10***). Hofmann, Nakajima-Matsuo, Scholz-Boehm and Ruess models are only based on XRD data, elemental analysis and reactivity observations. Last two models (Lerf-Klinowski and Décány) are most recent and include NMR data what makes them most reasonable structures of GO. In spite of these theoretical models, precise structure remains elusive. [28, 29]

GO is highly hydrophilic and can be readily exfoliated in water. Due to the exfoliation, dispersion is consisted also of single layered sheets – graphene oxide. These colloidal suspensions prepared by sonication are clear, homogeneous and greatly stable. Perfect stability of this suspension is obtained not only due to the hydrophilicity but also the electrostatic repulsion. Surface charges on graphene oxide are highly negative when dispersed in water due to the ionisation of the carboxylic acid and the phenolic hydroxyl groups. [25, 30]
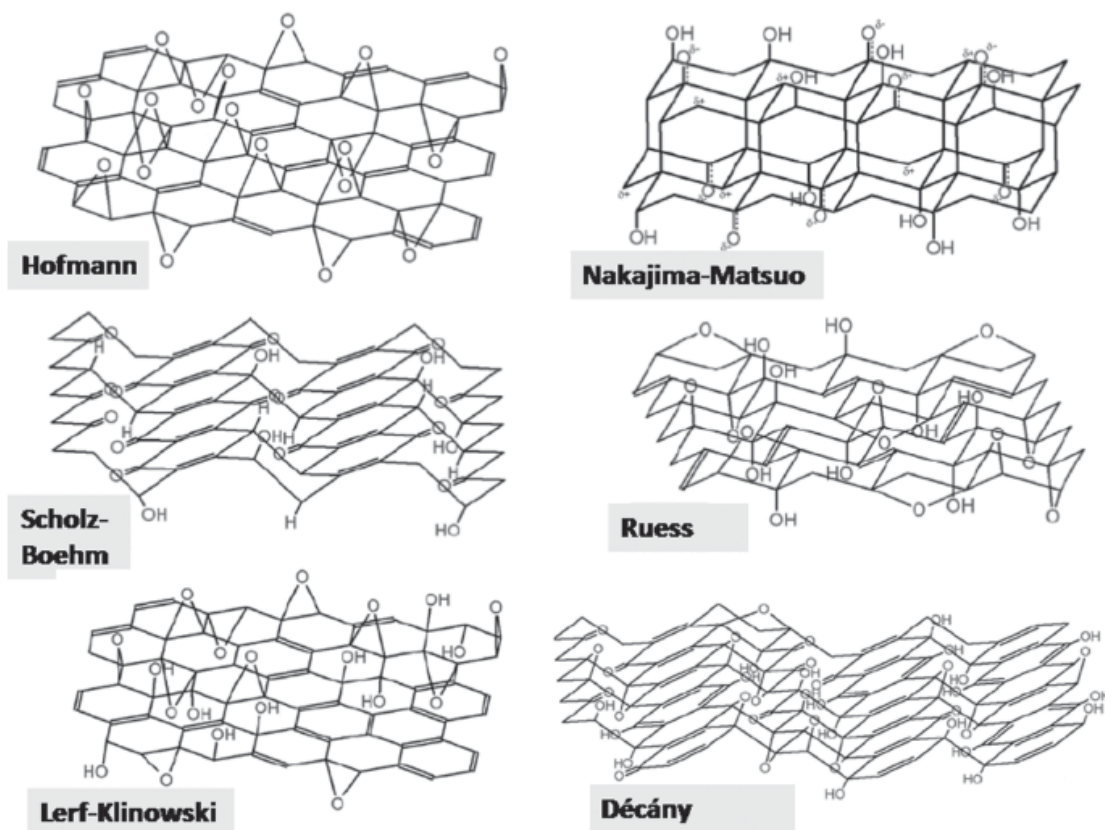
Fig. 10 – Proposed GO structure models [26]

GO offers potential of large-scale and cost-effective production of graphene-based materials. Large-scale fabrication of graphite oxide is highly important for industrial and academic applications of this material. The most common large-scale preparation method is the oxidation of graphite to graphite oxide using concentrated acids in the presence of strong oxidants. [28, 31]

Most common large-scale methods:

1. Brodie method – fuming nitric acid (HNO_3), potassium chlorate ($KClO_3$)
2. Staudenmaier method – concentrated sulphuric acid (H_2SO_4) with fuming nitric acid (HNO_3) and potassium chlorate ($KClO_3$)

3. Hummers method – concentrated sulphuric acid (H_2SO_4), sodium nitrate ($NaNO_3$) and potassium permanganate ($KMnO_4$)

4. Tour method – mixture of sulphuric acid (H_2SO_4) with phosphoric acid (H_3PO_4) and potassium permanganate ($KMnO_4$)

GO preparation by Brodie, was complex process needed few repetitions under oxidation environment. Due to this, it was difficult to hold original conditions each time. Almost 40 years later (1898) was prepared GO by Staudenmaier which was highly oxidized in a single reaction process, but very hazardous, because of forming of chloride dioxide (ClO_2). In 1958 Hummers and Offeman introduced new recipe for making GO. Oxidation process was finished in two hours and final product had higher degree of oxidation. This recipe is the most common and modified method. Modifications are continuously studied and improved for getting higher and higher degree of oxidation, because Hummers' product has not completely oxidized structure. New Tour method containing phosphoric acid instead of sodium nitrate was introduced in 2010. GO obtained from this method has higher degree of oxidation, recipe is much environmentally friendly (without forming of NO_2 or ClO_2) and final yield of GO is much higher than Hummers method. [28, 32, 33, 34]

Not only chemical way, but also type of graphite used as the starting material has a great influence on the final material. Purified natural graphite is the most commonly used for GO preparation. Due to the purification, there are defects in graphene sheets. These defects are susceptible to chemical oxidation and increase degree of oxidation. However, these defects and size variation cause that explanation of oxidation mechanism is complicated. For precise oxidation mechanism can be used graphite nanofibers which have approximately unified size distribution. [35]

For the formation of few layers or thin films (under 10 nm) are known these several ways: drop cast, dip coating, spraying, spin coating, Langmuir-Blodgett film and vacuum filtration deposition. [25]

Functional groups cause that the conjugated electronic structure is disrupted and graphene oxide becomes electrically insulating with irreversible defects. But with the chemical reduction of graphene oxide could be partially restored its conductivity at values below that of pristine graphene. [36]

Preparation of GO is one of the most important precursors to graphene (Reduced graphene oxide – RGO), thus lot of studies of reduction processes have been shown where their

properties have been measured and compared. There are two main groups of reduction processes – thermal and chemical. Temperatures even over 1000 °C are used for thermal reduction. Hydrazine is the most popular for chemical reduction (***Fig. 9, c)***). Recently, green reduction of GO has become famous, and there is number of studies on this topic using e.g. plant leaf extracts, mango bark extract, spinach... [26, 37]

2.1.1 Properties

Due to the presence of oxidized groups, GO is electrically insulating. When GO is reduced, many of the oxidized groups are removed, but there is always remaining part of oxidized groups which limits electron transport. It is known that conductivity and mobility values of RGO are lower than the pristine graphene. It is caused by these two things:

- As was discussed above, due to the remaining oxidized groups, charge percolation is limited by disconnected network of π delocalized tracks in the sheets.
- Because of defects in the sheets, mainly formed during reduction process.

Typically 60 % of the sheet area contains graphitic domains and the rest are topological defects and oxygen group areas. Increased conductivity of the material is caused by in- creasing of the charge percolation – in case of graphite it is increasing of sp^2. The degree of orderness can be measured by Raman spectroscopy where the G band (sp^2) has peak at ~ 1600 cm^{-1}, D band (sp^3) with peak at ~ 1350 cm^{-1} and 2D peak at ~ 2700 [25, 36]

2.1.2 Applications

In spite of functional groups and defects, GO/RGO can be used where extraordinary elec- trical properties are not required. On the other hand, they have to bond (non-covalently or covalently) various substrates what makes them an attractive material for large-scale man- ufacturing of graphene based supercapacitors, chemical or bio- sensors, photovoltaic de- vices, field emitters, electrodes and so on. [25]

1) Supercapacitors

In capacitors, dielectric constant $\boldsymbol{\varepsilon}$, surface area **A** and the distance between two electrodes **d** are important for capacitance **c** (formula below).

$$c = \varepsilon \frac{A}{d} \qquad\qquad \{1\}$$

Typical commercial supercapacitors use activated carbon as an electrode material. With RGO as an electrode, which can have specific surface area over 3000 m^2 g^{-1}, could be reached electrode with large electrode porosity for high ion diffusion. Key of too big specific area (which is higher than theoretical limit of graphene - 2600 m^2 g^{-1}) could be e.g. KOH etching creating holes in GO sheets. [38]

2) Electrochemical sensors and biosensors

GO and RGO are very promising for electrochemical and biological sensors. RGO is better for sensors, because of different functionalities on the edge. These functionalities are very sensitive to change in chemical or biological environment. Much depends on way of getting GO/RGO, on measurement, detection limits and substance which should be detected.

The most common sensors of GO/RGO are gas or vapour sensors. Very depends on the charge carrier transfer on surfaces caused by adsorption of e.g. NH_3, NO_2, CO, H_2O, Iodine, ethanol and many others. By controlling of reduction process of GO can be modified sensitivity and functionality of RGO sensors. [25]

3) Lithium ion batteries

Common materials used in lithium batteries are lithium cobalt oxide and graphite. GO/RGO is very promising material due to high surface area, good electrical conductivity and large porosity. In batteries GO/RGO are mainly used as a substrate for metal oxides as anodes. [29]

4) Water purifications

Again due to the large specific surface area and oxygenated groups, in few last years was found, that GO/RGO or GO-based nanocomposites can be efficient:

   a) Adsorbents on sand surfaces for mercuric ions and rhodamine B dyes in contaminated water. [39]
   b) In removing of radionuclides from water even in highly acidic conditions. [40]
   c) Adsorbents for arsenate, mercury (II) and arsenic ions. [29, 41]

5) Bio-applications

As known, GO can form very stable suspensions in water. With various modifications of functional groups GO can be soluble in other biological systems too. With studying of in vivo compatibility has been indicated that GO exfoliated by ultrasonic is compatible with several cell lines up to a certain level.

Sensing ability is highly sensitive to the C–O groups in GO. So, diversity of using increases with varying of synthesis methods, purification and others. GO interacts with biomolecules non-covalently and thus can be used as a biosensor for various chemicals or in drug delivery applications. It is also fluorescence quencher of many organic dyes, but GO absorbs strongly below 400 nm and quenching ability increases with reduction to RGO. [29, 42]

2.2 Toxicity

There are only few toxicity studies of graphene and its derivations, currently available.

Was reported that GO and RGO are toxic to Escherichia and Staphylococcus bacteria, where damage cell membrane, but another study verifies non-specific toxicity to both bacteria and tells that toxicity, reported before, could be only caused by carried impurities. [43, 44]

The toxicity to human depends on dose, exfoliation and sheet size. Unified view to the GO/RGO toxicity to human and reported toxicity levels it is not available for now. [45]

3   AIMS OF THE MASTER'S THESIS

The main goals of the master's thesis "Material inkjet printing of advanced systems suitable for polymer electronics" based on the assignment of the thesis can be summarized into following parts:

1) Literary summary, whereas the literary search on the topic "printed electronics" was carried out. The scope of the search was oriented mainly on the inkjet printing technology and carbon based materials with sensing properties.

2) Preparation and characterization of active material

3) Preparation and characterization of ink intended for inkjet printing

4) Printing and testing of electronic device

5) Evaluation of obtained results

6) Conclusion

II. ANALYSIS

4 EXPERIMENTAL PART

All used instruments, chemicals, utilities and other devices are listed in this chapter.

4.1 Laboratory devices and utilities

Beakers, magnetic stirrers, graduated cylinder, thermometers, pipettes, micropipettes, heaters, oven, analytical weight, pH meter Lab 870.

4.2 Instruments

1. **X-ray diffraction (XRD)**

Rigaku MiniFlex 600 X-ray spectrometer with a filtered cobalt source

2. **Scanning electron microscopy (SEM)**

Nova NanoSEM450, FEI company

3. **Fourier transform infrared spectroscopy (FTIR)**

FT-IR spectrometer Nicolet 6700 with extended range to FAR

4. **Raman spectroscopy**

Dispersive Raman Microscope Nicolet DXR, excitation laser with wavelength 532 nm

5. **Atomic force microscopy (AFM)**

Atomic force microscope Dimension Icon with resolution 1 nm

6. **Rheological properties measurement**

Viscosity – Viscometer Anton Paar LOVIS 2000 M/ME

Density – Density Meter Anton Paar DMA 5000M

7. **Surface tension measurement**

Tensometer K100MK3

8. **Electrical properties measurement**

Multimeter UT71D

4.3 Chemicals

Table 2 Chemicals used in experimental part

I. Graphite	II. Sulfuric acid
Producer: Sigma-Aldrich	Producer: Ing. Petr Švec – PENTA s.r.o.
Batch number: MKBW0432V	Batch number: 1609210911
CAS: 7782-42-5	CAS: 016-020-00-8
M_r: 12,01 g/mol	M_r: 98,08 g/mol
	Purity: p.a.
III. **Potassium permanganate**	**IV.** **Sodium nitrate**
Producer: Sigma-Aldrich	Producer: Lach-Ner, s.r.o.
Batch number: MKBV4591V	Batch number: PP/2015/06780
CAS: 7722-64-7	CAS: 7631-99-4
M_r: 158,03 g/mol	M_r: 85,01 g/mol
Purity: 97 %	Purity: p.a.
V. **Hydrogen peroxide solution - 35 %**	**VI.** **Tween® 20**
Producer: Sigma-Aldrich	Producer: Sigma-Aldrich
Batch number: SZBF2390V	Batch number: SLBL2583V
CAS: 7722-84-1	CAS: 9005-64-5
M_r: 34,01 g/mol, D: 1,13 g/ml	D: 1,095 g/ml
Purity: 97 %	
VII. **Dimethyl sulfoxide**	**VIII.** **Acetone**
Producer: Sigma-Aldrich	Producer: MikroCHEM®
Batch number: 1479637V	Batch number: A140775/01
CAS: 67-68-5	CAS: 67-64-1
M_r: 78,13 g/mol	M_r: 58,08 g/ mol
Purity: ≥99,8 %	Purity: p.a.
IX. **Ethanol**	
Producer: Ing. Petr Švec – PENTA s.r.o.	
Batch number: 1881061115	
CAS: 603-002-00-5	
M_r: 46,08 g/mol	
Purity: absolute for UV	

4.4 GO powder preparation

For GO preparation was chosen the Hummers method. For optimal preparation was this method modified in few ways: in duration time of mixing and in molar ratio of added chemicals and in different washing treatment.

Powdered flake graphite, sulphuric acid and sodium nitrate were put into the beaker with appropriate volume and stirred using magnetic stirrer. Temperature of suspension was hold in ice-bath at about 0 °C, the potassium permanganate was very carefully and slowly added to avoid temperature increase over 20 °C. When potassium permanganate was added, the ice-bath was removed and mixture was stirred at room temperature. The suspension was gradually thickened and became pasty with brownish colour. Then the suspension was diluted by water which was slowly added during stirring. The temperature of mixture was increased to 98 °C and suspension was again diluted. Solution of hot water and 35 % hydrogen peroxide was added to reduce the residual permanganate and manganese dioxide. Arising soluble manganese sulphate is colourless. Upon the hydrogen peroxide addition the colour of suspension changed to yellowish green. [1]

This suspension was left for few hours until heavier part settles. After separation into two parts the upper liquid was removed. Mixture of water, hydrogen peroxide and sulphuric acid was added into beaker with lower suspension. Diluted suspension was stirred for few hours for sufficient washing. Then the suspension was again left for the separation of mixture followed by decanting of upper liquid. Washing of lower suspension with water continued by centrifugation until the pH 5 was obtained. Dry GO powder was obtained by dehydration at 60 °C in vacuum oven followed by grinding in centrifugal rotor mill with sieve size 0,12 mm.

4.5 GO inks preparation

Purpose of ink preparation was to prepare in simply way environmentally friendly ink for inkjet printing. Preparation of GO (or graphene) inks has one big disadvantage. Particles are very thin in one dimension and in two other dimensions vary from few nanometres up to microns. This shape causes rapid increase of viscosity even at a low concentration range. Not forget to mention that the colloidal sheets clog the nozzles of the print head.

It is already known that sonication of GO results exfoliation of the particles. With smaller sheets increases viscosity and lower concentrations of GO must be used. First ink was pre-

pared by dilution of GO in water and then sonicated for one hour. Exfoliated GO in water with the concentration $3,\overline{3}$ mg/ ml was obtained - Ink 1.

Ink 2 was prepared by two steps:

- First part of process was the same as in case of Ink 1, only one modification was introduced; the concentration of GO was set as 10 mg/ ml.
- In second step, this suspension was diluted with dimethyl sulfoxide and Tween 20 followed by stirring for one hour. Ink with the concentration of $3,\overline{3}$ mg/ ml was obtained (same as Ink 1).

Specific composition of these inks is described in **Table 3** below:

Table 3 Specific composition of prepared inks

Final concentration of GO in inks: $3,\overline{3}$ mg/ml	GO powder (mg)	Water (ml)	GO + Water - 10 mg/ml (ml)	Dimethyl sulfoxide (ml)	Tween 20 (ml)
Ink 1	100	30	-	-	-
Ink 2 – first step	300	30	-	-	-
Ink 2 – second step	-	-	3,33	6,66	0,01

4.6   Printing of the device

Printing of final device (sensor) followed after preparation of inks with optimal technology properties. Sensors were printed using Dimatix Material Printer 2800.

Two different types of specimen were used for sensor printing:

1. Ceramic substrate with gold electrodes
2. Polyimide substrate with silver electrodes

As was described, with preparation of printed patterns, ink-substrate interactions as good as possible should be achieved. These interactions have an impact on distribution of the ink, wetting of substrate and so on. For printing only one ink was used – Ink 2, but as substrate there were 2 different – ceramic and polyimide. Thus, process of printing had to be optimized before printing of the particular device. Schema of the printed device was the same as in *Fig. 6*.

5   RESULTS AND DISCUSSION

5.1   GO powder characterisation

Prepared GO powder was characterised by X-ray diffraction and by Fourier transform infrared spectroscopy.
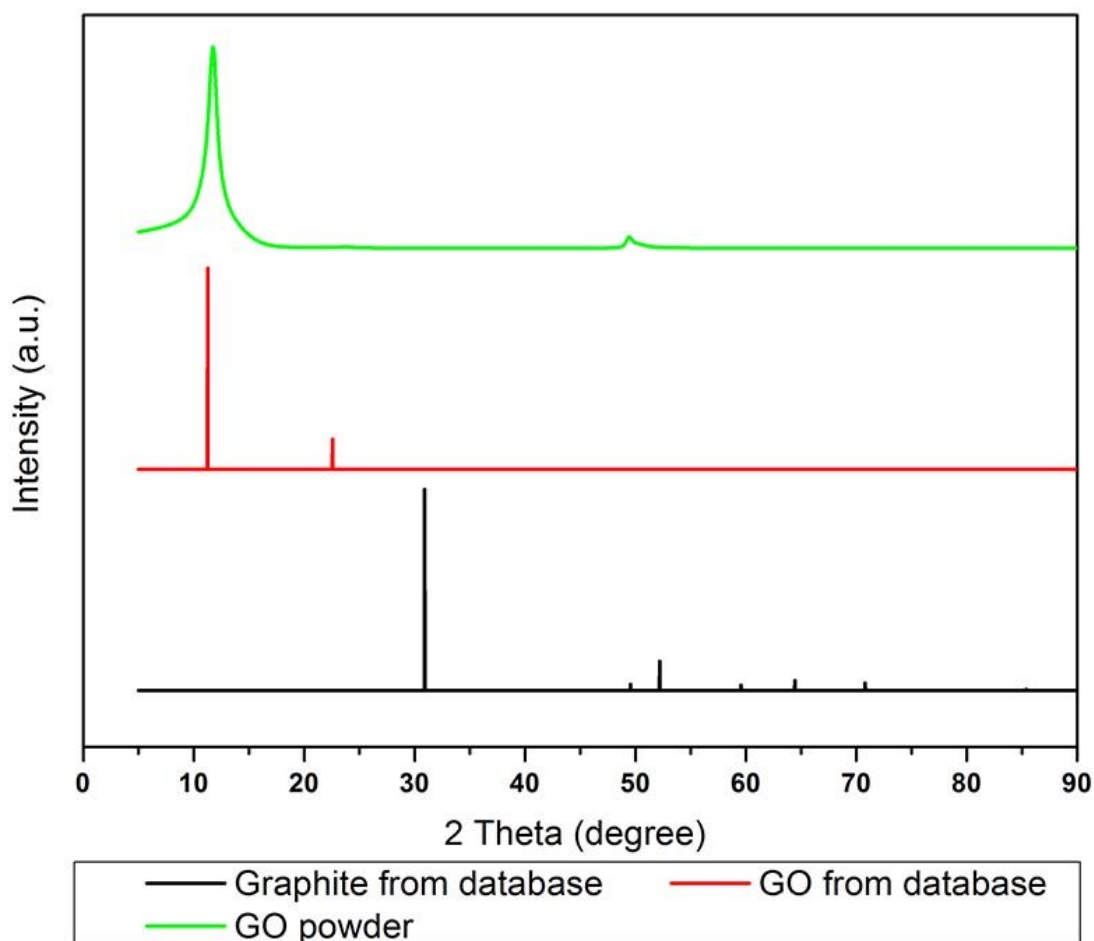

Fig. 11 Diffractogram of prepared GO powder (green curve) and comparison with database materials.

Diffractogram of XRD analysis of prepared GO powder is in ***Fig. 11***. For comparison of measured peaks with database data there are also XRD patterns of GO and graphite. In this figure we can see conformity of green GO powder line in both peaks with red line of GO from database. One more peak in green line identical with peak in black line of graphite from database was observed. This could be caused by any diffraction of higher order if GO sheets are stacked. Other peaks of graphite are not included in diffractogram of GO powder. Statement, that prepared material is GO, is in accordance with matching between measured and database diffractorgrams.
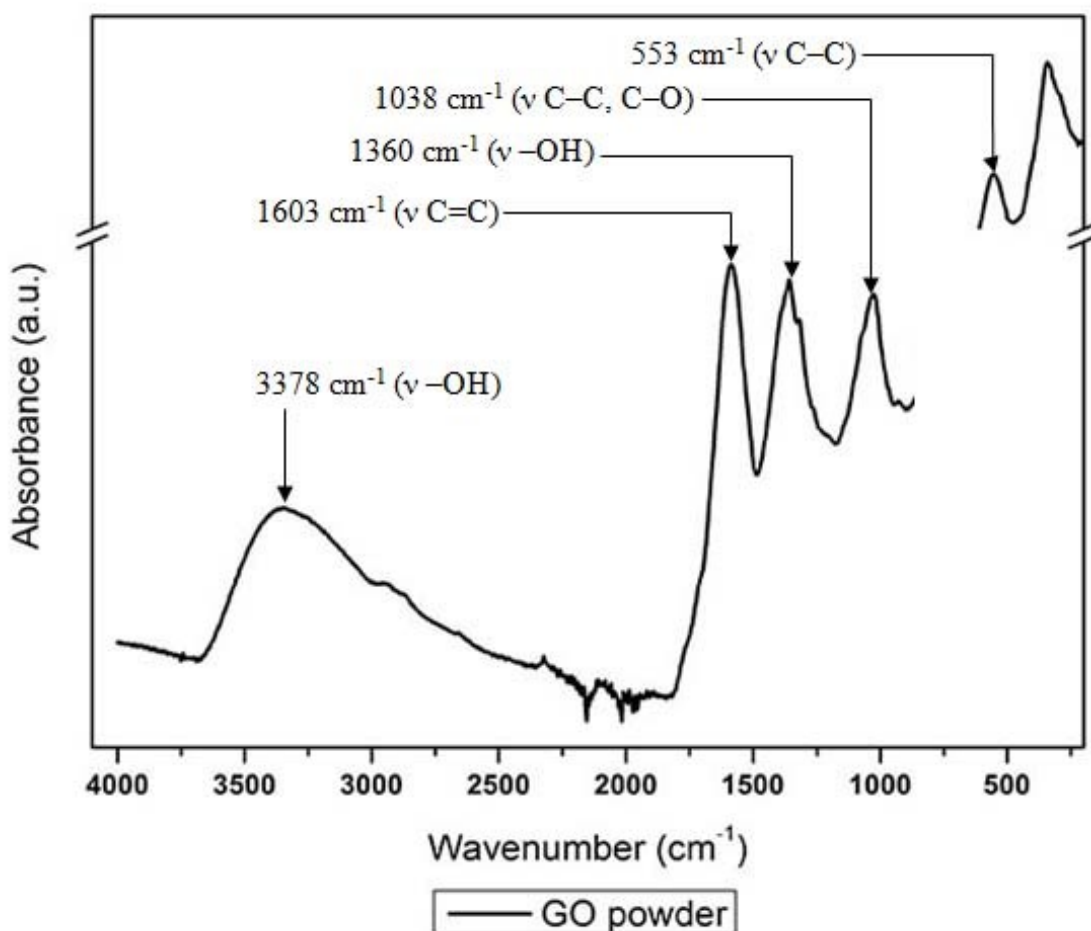
Fig. 12 Transmission FTIR absorbance spectrum of GO powder

Fourier transform infrared spectroscopy was used to characterise structure of functional groups of the GO powder. In *Fig. 12* we can see three peaks confirming oxidation of the graphite. Peak at 1038 cm^{-1} arises due to the stretching vibrations of the C–O and C–C. These two vibrations are located in close proximity thus it is very difficult to distinguish them, but they contribute to the intensity of the 1038 cm^{-1} peak. Peak at 1360 cm^{-1}, related to –OH bending vibrations in tertiary alcohols, is relatively wide and can hide other vibrations, for example organic carbonate vibrations (1384 cm^{-1}) or benzene ring vibrations (around 1400 cm^{-1}).

Around 1700 cm^{-1} is extension of C=C peak at 1603 cm^{-1}. This extension can be caused by C=O stretching vibrations (from 1710 cm^{-1} to 1735 cm^{-1}).

Both analyses confirm that prepared powder is formed of oxidized carbon layers thus we can suggest GO powder.

5.2 GO ink characterisation

For every ink, surface tension and viscosity are crucial parameters. In ***Fig.13*** operational window is depicted. Requirements for DMP 2800 on the inks are defined by blue region. Optimal surface tension in the middle parts of requirements was achieved with the Ink 2. On the other hand, viscosity was lower than DMP optimum requires, but still in the good position of operational window.
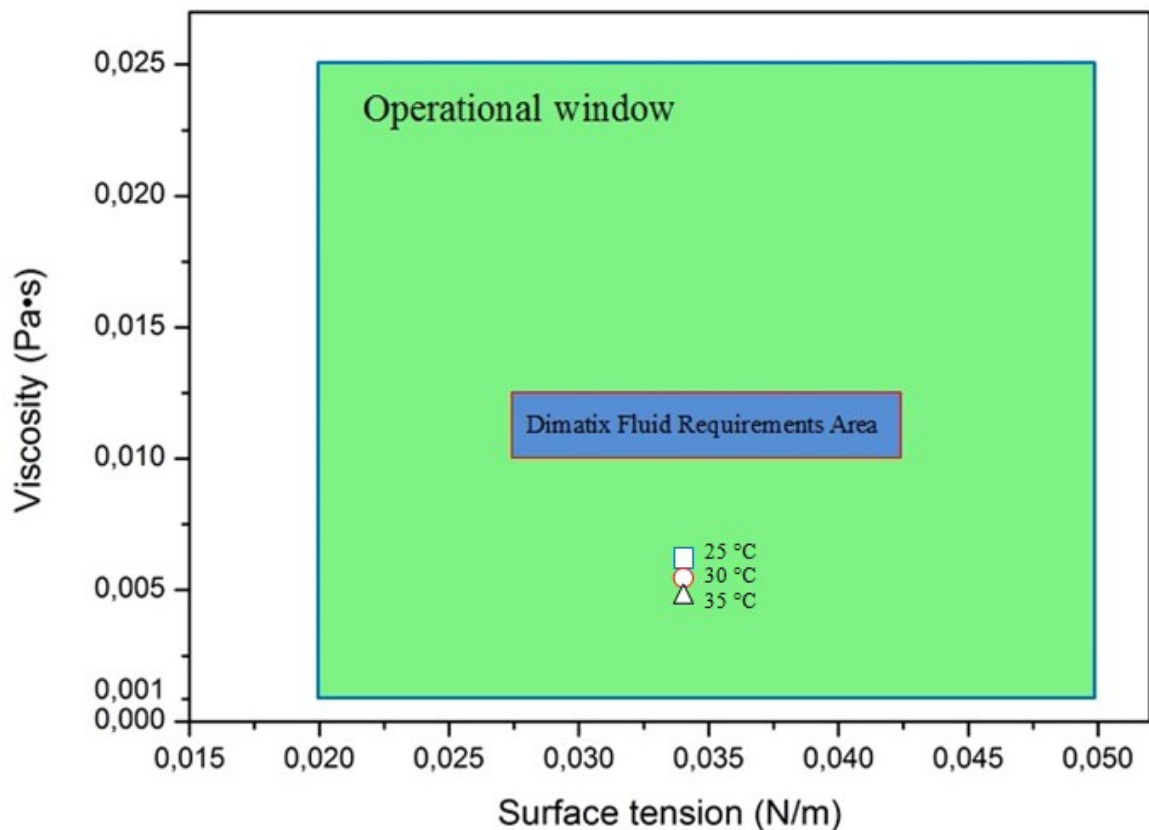

Fig. 13 Operational window of inkjet print head

Surface tension, one of the most important properties of the ink, was measured using Krüss tensometer K100MK3. This attribute was measured at three temperatures, 25, 30 and 35 °C, because during printing temperature can vary and better knowledge of the surface tension can help to better predict behaviour of ink in the temperature range. First prepared and measured ink is the Ink 1. The ink was before measuring stirred with magnetic stirrer to maintain same conditions of each measuring. As we can see from operational window for inkjet print head (***Fig. 13***), surface tension of the Ink 1 which is over 70 mN/ m at all temperatures (***Fig. 14***), is not sufficient for inkjet printing. Ink 1 achieves the same values as water due to the composition of the Ink 1 formed only of two parts: main part of water and

only few tenths of percent of GO. During measurement performed at 35 °C, other phenomenon was observed. The surface tension values decrease over time (*Fig. 14*). There could exist any temperature threshold (between 30 and 35 °C), where the behaviour of ink is changed. This could indicate changes of the distribution of GO particles in the system, where the particles can sediment and thus can change the environment of surface. It can be suppressed for example with longer time of sonication or by adding of a surfactant.

Table 4 Surface tension values of prepared inks

	Temperature	25 °C	30 °C	35 °C
Ink 1	Average surface tension (mN/m)	72,74	72,3	71,5
	Standard deviation	0,06	0,1	0,2
Ink 2	Average surface tension (mN/m)	34,9	34,4	34,1
	Standard deviation	0,2	0,2	0,2

Ink 2 differs from Ink 1 in one important thing; it contents surfactants. The DMSO and Tween 20 were added, as was written above (see Section **4.5**). Addition of surfactants into the ink system impacted surface tension significantly. As we can see in *Fig. 14*, the Ink 2 has much lower values of surface tension at all three temperatures. The trend of curves expressing measurement at different temperatures is very similar and it can be concluded that the problem with sedimentation of particles was suppressed. The surface tension values met requirement values for inkjet printing at temperature range between 25 °C and 35 °C what makes this ink suitable and stable for printing in this temperature range.

Based on these facts, composition of Ink 2 was chosen for further printing and finishing of electronic devices.
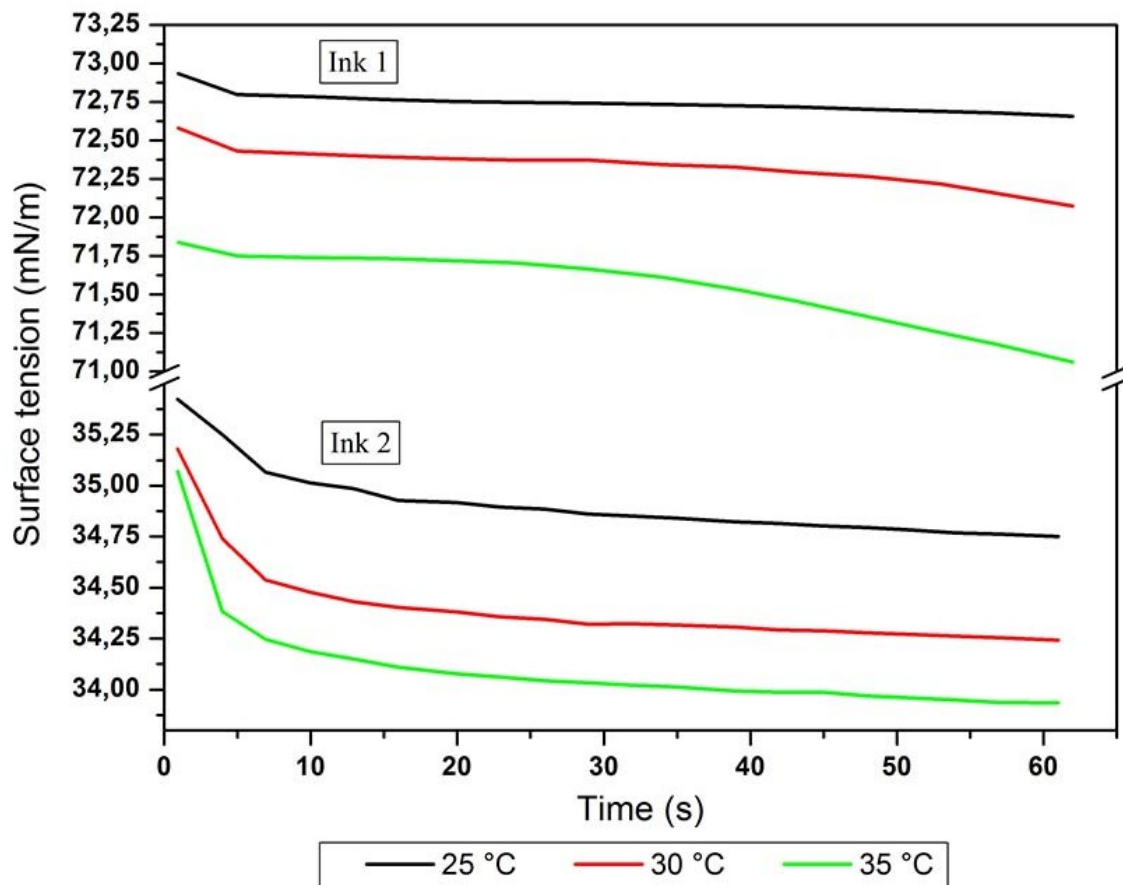
Fig. 14 Results of surface tension measurement of Ink 1 and Ink 2 at temperatures of 25, 30 and 35 °C

Table 5 Density and viscosity of the Ink 2 according to the temperature

Temperature (°C)	Density (g/cm³)	Viscosity (mPa·s)
25	1,0951	6,24 ± 0,07
30	1,0908	5,44 ± 0,03
35	1,0865	4,73 ± 0,01

The temperatures of the ink are during printing in range between 25 °C and 35 °C. Density and viscosity measurement of the Ink 2 took place at 25, 30 and 35 °C for knowledge of density and viscosity behaviour within these temperatures (**Table 5**). There are only small changes in temperature dependencies. It confirms that GO particles in this concentration do not have big influence on rheological properties.

Density values are closely over 1 g/cm³ what corresponds to density of mixture of DMSO and water where DMSO is major compound. Viscosity of this ink is lower than the Di-

matix Fluid Requirements Area for the inkjet printing (*Fig. 11*), nevertheless it meets the operational window for printing.

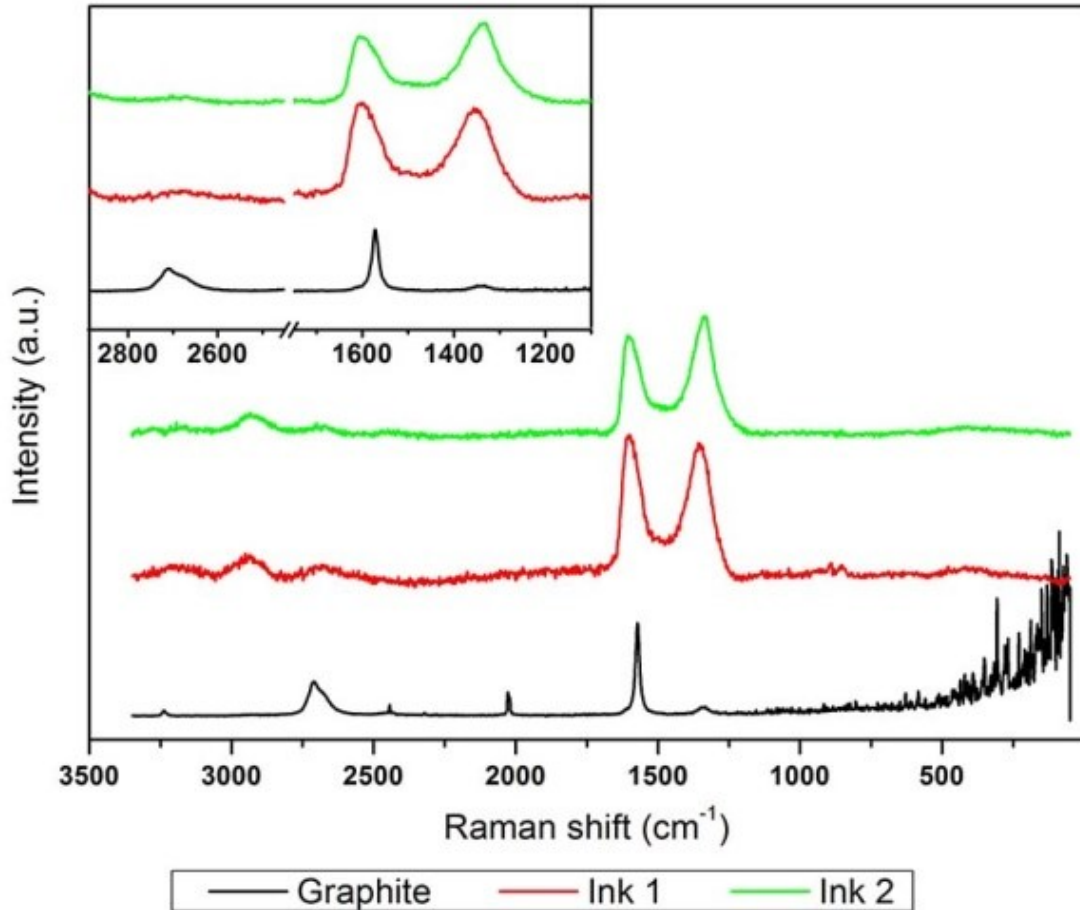### 5.2.1   Spectral characterization

Fig. 15 Raman spectra of graphite and prepared inks

Fig. 15 shows comparison of the Raman spectra between graphite and layers coated from inks. GO spectrum basically consists of 3 main peaks: D peak located at ~1350 cm^{-1}, G peak at ~1600 cm^{-1} and 2D peak at ~2700 cm^{-1}. **Table 6** shows exact values of peaks.

In Raman spectrum D peak appears due to the disordered atomic arrangement or edges of GO (graphite-based materials). For example: graphene spectrum should not contain D peak what confirms the absence of defects. G peak arises due to the graphitic domain vibration. The third important peak is 2D peak which has higher wavenumber with increasing number of layers. As is in **Table 6**, 2D peak wavenumber of Ink 2 is lower than graphite and even Ink 1, thus the Ink 2 has more exfoliated GO particles than Ink 1 and graphite.

Amount of defects within the crystal lattice can be detected with the D/G ratio. It is the ratio of peak intensities, I_D/I_G. Higher ratio means larger amount of defects. For graphite is the ratio 0,14 and for inks much larger, over 0,9. Oxidation cause the defects, thus this ratio shows the oxidation degree of the GO very well. Ink 2 has even higher D/G ratio than Ink 1 which can be due to the presence of surfactants, thus better distribution of GO particles in the liquid.

The G peak is due to the doubly degenerated zone centre E_2g mode in sheets and it means a primary in-plane vibrational mode. On the contrary, the G' band has nothing to do with the G peak, but is the second order of zone-boundary phonons. Since zone-boundary phonons do not satisfy the Raman fundamental selection rule, they are not seen in first order Raman spectra of defect-free graphite (black line). Such phonons give rise to a peak at 1350 cm^{-1} in defected graphite, called D peak and in the neat graphene sheet should be invisible. For clarity, it must be referred to the G' peak as 2D, which is a second-order overtone of a different in-plane vibration. From characterization point of view, Raman spectroscopy is very useful method because of characterizing disorder and many other properties in graphene, including the edges and grain boundaries of graphene crystals.

Table 6 Raman spectra positions and analysis of the graphite and prepared inks

Sample	D position (cm^{-1})	G position (cm^{-1})	2D position (cm^{-1})	D/G	2D/G
Graphite	1348	1572	2709	0,14	0,40
Ink 1	1357	1604	2707	0,91	0,98
Ink 2	1333	1606	2701	0,95	0,92

From the comparison of FTIR absorbance spectra (*Fig. 16*) there are obvious differences between neat GO powder and dried layers prepared from inks. In **Table 7** individual bands are assigned to wavenumbers. In all spectra, typical bands for GO can be observed. In spectra for layers deposited from inks, bands, which can be assigned to surfactants, are obvious (see details in **Table 7**).
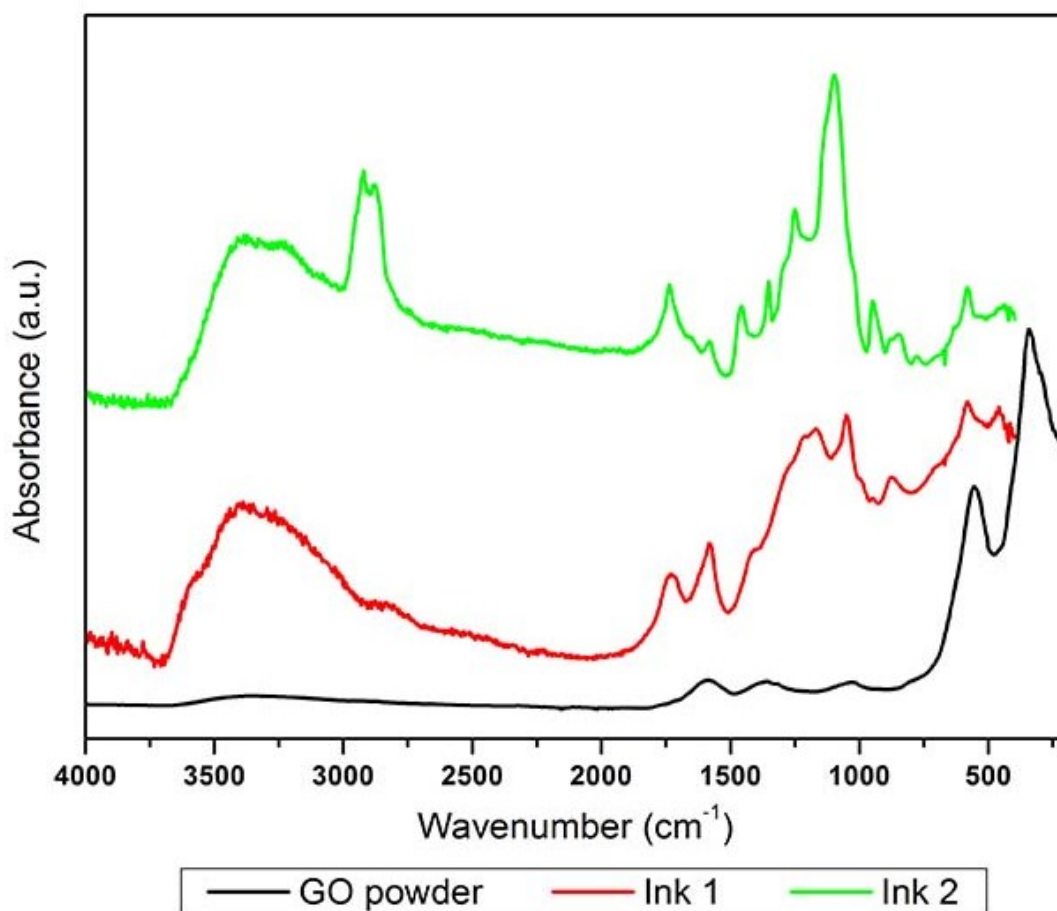
Fig. 16 Transmission FTIR absorbance spectrum of GO powder and prepared inks

Table 7 FTIR peak positions (in cm^{-1}) of GO powder and prepared inks

GO powder	Ink 1	Ink 2	Assignment
3378	3388	3386	ν stretching –OH
-	-	2921	ν asymmetric stretching CH_3
-	-	2808	ν symmetric stretching CH_3
1603	1581	1581	ν C=C in aromatic cycle
-	-	1458	ν bending CH_2, asymmetric CH_3
1360	1396	-	ν bending –OH
-	-	1352	ν geminal dimethyl
-	-	1248	ν a stretching S=O
1038	1050	-	ν stretching C–O, C–C
-	-	1097	ν s stretching S=O
553	582	580	radial motion: C–C deformations

In spectrum of Ink 2 we can clearly see peaks of DMSO proven by vibrations of CH_3, CH_2 and S=O groups (**Table 7**). In the spectrum belong to Ink 1, which is composed only of water and GO powder, are clearly seen peaks which can be assigned to GO powder and present of water.
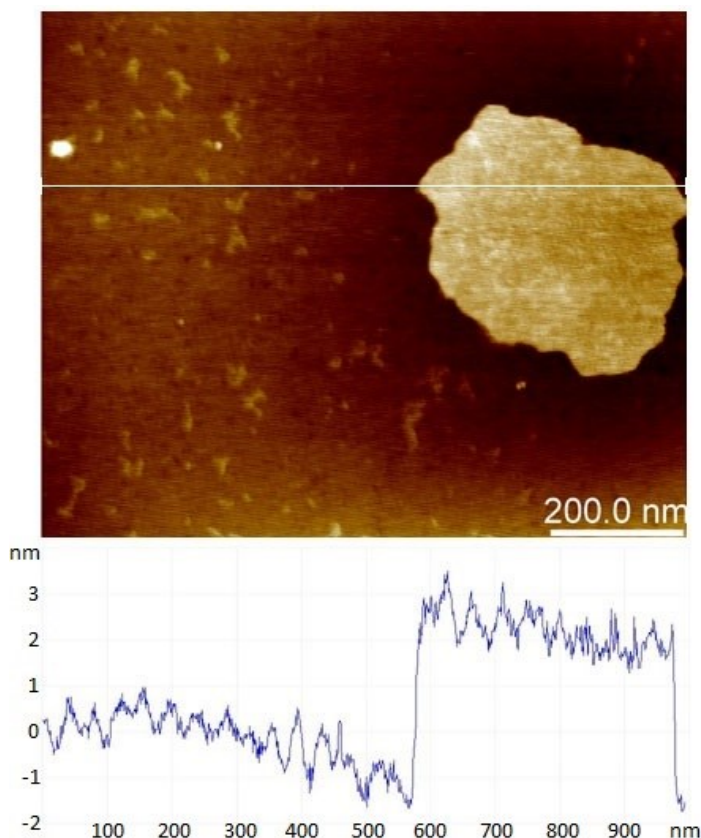
5.2.2   Topographic and SEM analysis

Fig. 17 AFM image with height profile of region marked in image (white curve).

Low concentrated suspension of GO powder in water was prepared for AFM measurement. Drop of this suspension was cast onto the polished silicon wafer and then dried in vacuum oven. Sample prepared by the same way was used for SEM imaging also.

Atomic force microscopy image (*Fig. 17*) shows individual sheet of GO and its height profile. This technique of imaging easily determines height of the sheets in resolution of 1 nanometer. *Fig. 17* confirms the 2D structure of GO sheets with height around 4 nm and XY dimensions from tens nanometers to microns. This image also confirms that exfoliation by sonication is nearly completed, only few atomic layers is stacked together.

SEM imaging is better for determination of bigger areas, compared to AFM. AFM shows only topographic and surface properties whereas SEM can be used for more complex structure determination.

In SEM image (*Fig. 18*) is located more sheets of GO for better imaging of size distribution of sheets (from tens of nanometers to one micrometer). In the middle of this image (darker area) we can see area with overlapped sheets.
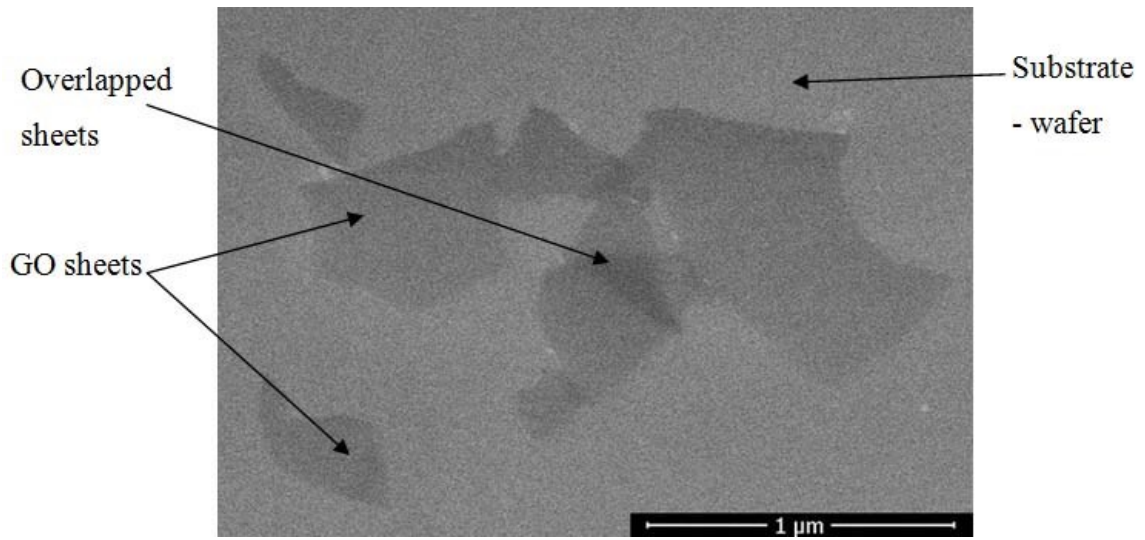

Fig. 18 SEM image of the GO particles

5.3   Device properties

For device preparation using inkjet printing only Ink 2 was used, as was discussed in term of operational window. This ink met the requirements for the inkjet DMP. SEM images (*Fig. 19* and *Fig. 20*) show printed layers from Ink 2 on ceramic substrates. Imaging of sensors on the ceramic substrates using SEM was performed only; because of high electron voltage causing burned surface of PI substrate and thus made imaging disabled.

In *Fig. 19* three areas of printed sensor are shown: substrate without printed layer, substrate with printed GO layer and electrodes covered by GO layer. In printed areas the ink is on surface well distributed in uniform layer without unprinted areas. There is also well visible definition of the edge of printed and unprinted area, what indicates precisely controlled printing process.
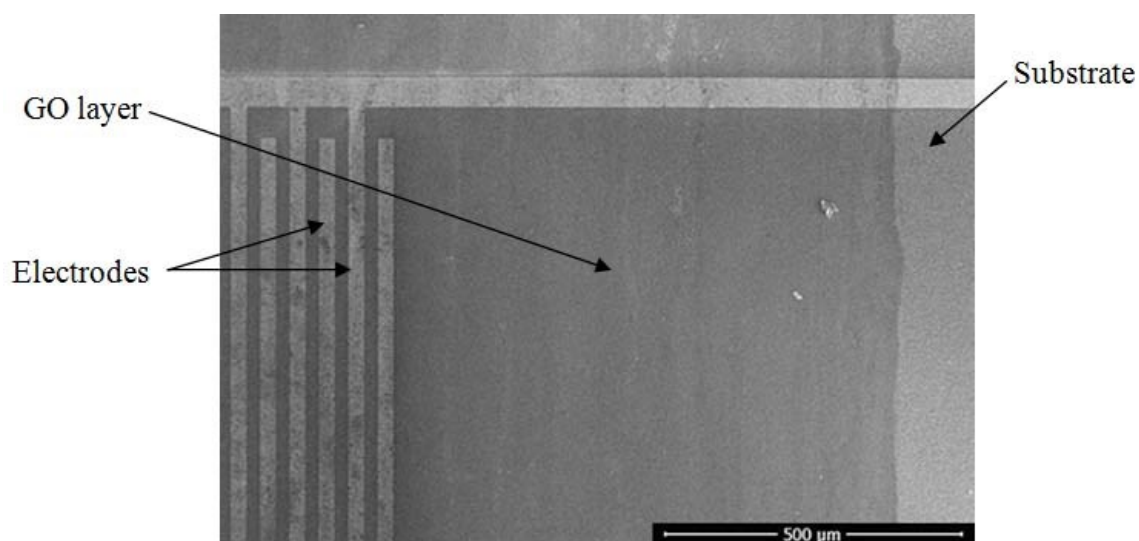
Fig. 19 SEM image of the ceramic sensor with printed GO layer

Compactness and coherence of the printed layer shown in the *Fig. 20* confirms the fact precisely controlled printing process. The charging of metal electrodes is more intensive, so the electrodes are brighter coloured and the substrate is darker. Nevertheless, the compactness and coherence is well visible – surface has same structure across the area of the image.
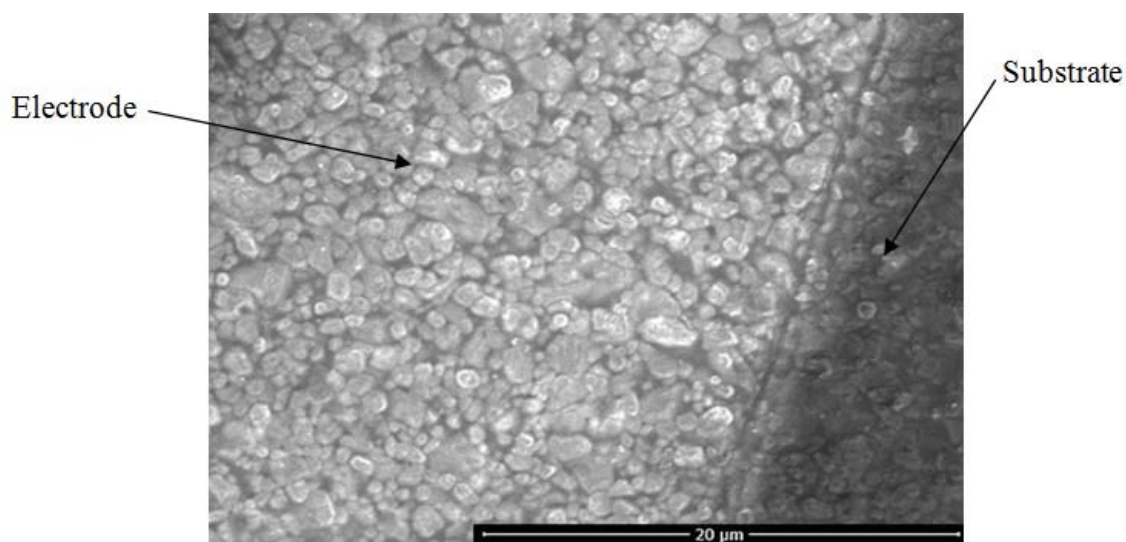

Fig. 20 SEM image of the coherent layer on substrate and metal electrode of the ceramic sensor

5.3.1 Device sensing

Last task of the experimental part was the measuring of response of printed sensors to vapour of organic solvents, namely ethanol and acetone. Measurements were carried out on the sensors printed from GO inks onto the polyimide and ceramic substrates. Measured response of sensors to vapour of organic solvents approved the sensitivity to these substances.

It was measured in closed tempered container at 40 °C with nitrogen inlet and single-way valve for gas outlet. Liquid chemical was dosed through rubber septum using needle with defined volume. Measuring was divided into two parts:

- Nitrogen blowing
- Response to exposure of chemical substance after dosing

Nitrogen was blowing to obtain steady signal of sensor in an inert atmosphere. Steady pressure in the box was ensured by one-way valve, and the pressure was set at 1 ATM. In second step, the nitrogen inlet was closed and the chemical substance was injected in liquid form. Tempered container set at 40 °C helped to faster evaporation of the chemical. After a defined period of time the nitrogen inlet was opened and cycle was repeated.

Fig. 21 shows responses of both prepared sensors (ceramic and PI substrate) to acetone and ethanol. Red curve belongs to acetone, black curve belongs to ethanol. Grey colour shows time range of nitrogen blowing and white colour shows time range of exposure to the chemical substance. Ceramic sensor response measurement is shown in *Fig. 21 A*. When the nitrogen inlet was closed, the defined amount of the chemical was injected into the container. Added amount corresponds to 50 ‰ of substance in the box atmosphere. In white areas of graphs we can see changing response to exposure of evaporating chemical. Signal was constant after some time period and no more changes were observed in the sensing curve (meant one sensing period blowing/sensing). The difference between signal from response to exposure of chemical and nitrogen can be seen when the nitrogen inlet is opened.

The same process was used for response measuring of sensor based on polyimide foil. Because of lower sensitivity of sensor printed on the PI substrate, higher amount of chemicals was added into to the container, where the measurement was performed. This added amount corresponds to saturated equilibrium of partial pressures of the mixture N_2/acetone(etanol) vapours.

Let us mention, that saturated equilibrium of partial pressure is in accordance to 562 ‰ of acetone in container and to 179 ‰ of ethanol respectively. Partial pressures were estimated from Antoine's equation and desired amount of substance corresponding to required gas volume fraction is calculated from following relationship:

$$\varphi = \frac{Q \cdot 22{,}4 \cdot D \cdot \rho \cdot 10^{-9}}{V \cdot M} \qquad \{2\}$$

, where Q (ml) is the liquid volume, V (ml) is the volume of the testing container, φ is the required gas volume fraction, M (g/mol) is the molecular weight, D (g/cm^3) is specific gravity, ρ is the purity of the volatile testing liquid [46].
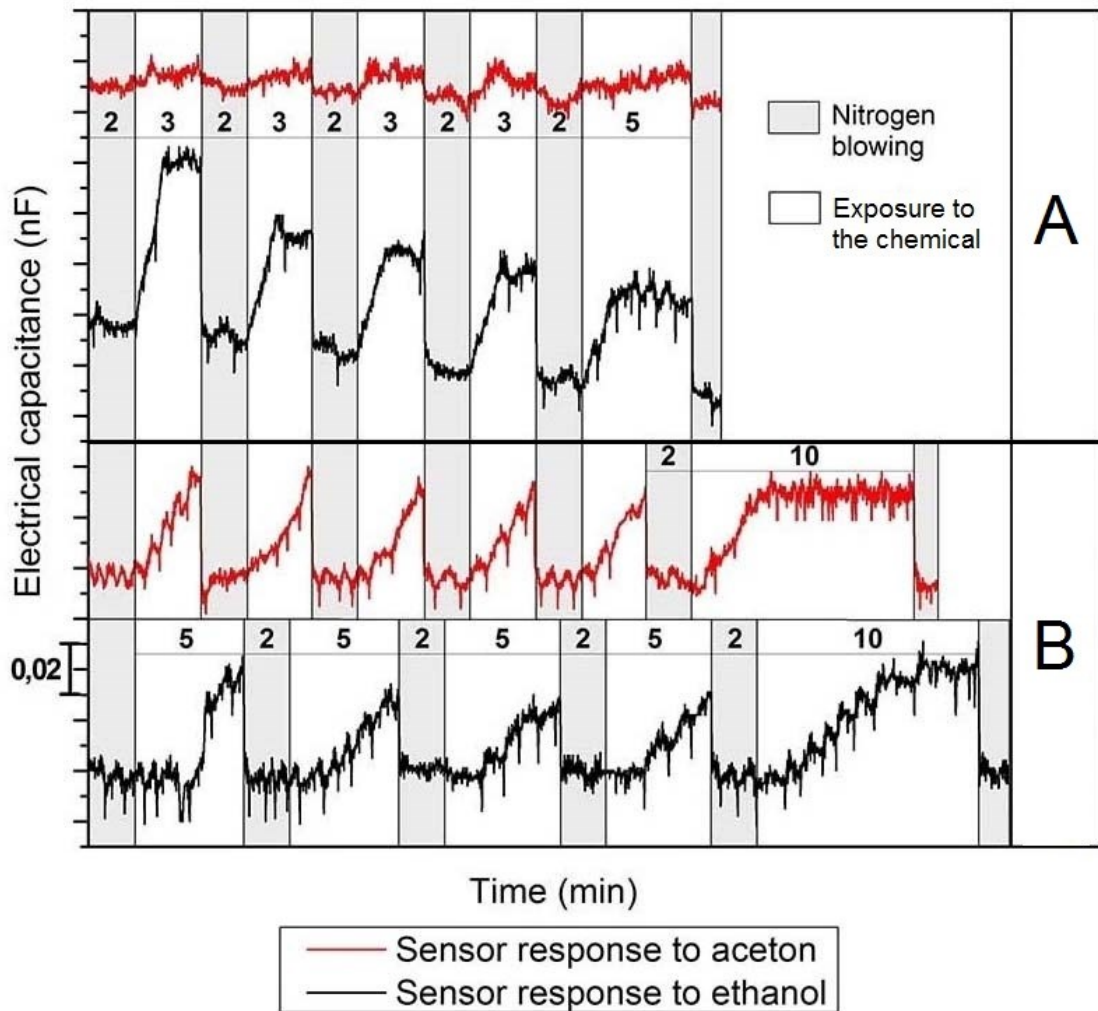

Fig. 21 Measurement of response to exposure to ethanol and acetone using sensors with printed GO layer onto ceramic (**A**) and polyimide (**B**) substrate.

If we compare individual response curves of sensor printed on the ceramic substrate, sensitivity is much higher to ethanol than the sensitivity to acetone. Based on this fact, we can

suggest that sensitivity of printed sensors should be highly selective. If we compare curves of sensor printed on polyimide foil, especially last cycle, responses to ethanol and acetone are similar, but the sensitivity of sensor printed on polyimide foil to ethanol is higher again like in case of sensor printed on the ceramic substrate. Selectivity expressed by variance in capacitance, around 0,01 nF, is well detectable difference. Thus, we suggest the sensitivity of sensor printed on polyimide foil is also selective.

Measuring of capacitance is more profitable method than measuring of resistivity because of fact that change of capacitance depends on the adsorption of the analyte on top of the sensitive layer and also on the absorption of the analyte within the sensitive layer. Both processes can change the thickness of the layer (swelling) and permittivity of the sensitive layer, what is covered by changes of the capacitance.

6 CONCLUSION

In this work, the literary background research on the topic "printed electronics" with special focus on the inkjet printing technology and carbon based material (better to say nanomaterial) intended for use as active material in electronic devices was performed. In **Chapter 1**, information about inkjet printing technology is introduced. Two main types of inkjet printing processes are specified – Continuous inkjet and Drop-on-demand processes. Furthermore, basic requirements on substrates are mentioned. Very important part of the first Chapter deals with inkjet inks and demands, which are required for no trouble processing. Next section of the first Chapter is focused on the polymer electronics and two points of view are defined. In the **Chapter 2**, knowledges about carbon based materials are summarized. There are discussed preparation, properties and applications. Based on the literary search, the main aims of this thesis were defined and they are introduced in the **Chapter 3**.

Experimental part of this thesis deals with preparation and characterization of the active material, which is used for inkjet inks preparation. Inks are further characterized. Methods of material synthesis and inks preparation are described in **Chapter 4**. Obtained results and their discussion are inserted in **Chapter 5**.

From the results obtained during the performing tasks specified in the assignment of the thesis, the contribution for research community can be concluded by these points:

1. Carbon based material was successfully synthetized via easy synthesis route based on Hummers method
2. Ink for inkjet material printing was successfully prepared
3. Flexible electronic devices on the polymer substrates were printed and tested; good response to organic solvents was proven.

Via Hummers method graphene oxide was successfully synthesized and characterized. Used characterization methods (XRD, FTIR, Raman spectroscopy, AFM, SEM) proved that prepared material is seriously graphene oxide with its unique properties – nanodimensionality, oxidized crystal structure.

Ink based on the prepared GO material was formulated and tested, if the properties of final ink fulfil requirements of inkjet material printer. Results are sufficient, lying in the general operational window estimated for inkjet printing, but not exactly lying in the operational window area recommended by DMP 2800 producer. Surface tension of prepared ink is about 35 mN/m, viscosity of this ink is about 5 mPa.s.

From prepared inks were printed sensors onto two types of substrates. Sensors sensitivity solvent vapour was tested. Graphene oxide seems to be selective material for different types of organic solvents, what can be very promising for real applications.

Achieved results and experience could help extend the use of carbon based material in printed electronics industry. Based on the knowledge gathered in this thesis, future research should be considered in three main directions.

First promising research route is expected to be the basic research oriented on the general study of graphene material, its properties, synthesis and possible routes how to modify this material because the reduction of GO can leads to more sensitive products and moreover, if such product will be modified by functional groups, the sensitivity and selectivity can be more improved.

The second direction considers the prospective of material printing. From the technological point of view of sample preparation, the work should continue by studies on the structures prepared by printing.

The last, third course, derived from the basic research, has to be the preparation of the final applications and devices – mainly sensor, where the experiences from fundamental research work will be applied, because preparation of selective sensors seems to be possible.

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LIST OF ABBREVIATIONS AND SYMBOLS

CIJ   Continuous inkjet

DOD   Drop-on-demand inkjet

GO   Graphite oxide

RGO   Reduced graphite oxide

LED   Light emitting diodes

OLED   Organic light emitting diodes

pOLED   plastic organic light emitting diodes

ε Dielectric constant

A   Surface area

d   Distance between two electrodes

c   Capacitance

UV   Ultraviolet

PET   Polyethylene terephtalate

PI   Polyimide

PC   Polycarbonate

3D   Three dimensional

2D   Two dimensional

1D   One dimensional

0D   Zero dimensional

PZT   Lead zirconium titanate

NMR   Nuclear magnetic resonance spectroscopy

SEM   Scanning electron microscopy

FTIR   Fourier transform infrared spectroscopy

XRD   X-ray diffraction

AFM   Atomic force microscopy

kHz   kilohertz

mPa·s   Millipascal seconds

nm   Nanometers

µm   Micrometers

mm   Millimetres

nF   Nanofarad

DMP   Dimatix materials printer

°C   Degree Celsius

ppm   parts per million

‰   Permille

Q   Volume of liquid

V   Volume of testing container

M   Molecular weight

φ Volume fraction of required gas

D   Specific gravity

ρ Purity of testing liquid

LIST OF FIGURES

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