USE OF CARBON NANOSTRUCTURES FOR SENSOR PREPARATION

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Abstract

Graphene oxide is a carbonaceous material that has unique physicochemical properties (specific surface area, pollution resistance, conductivity, high mechanical strength) and can be produced in large quantities with relative ease. It is a material formed by the oxidation of graphene, which can be further modified with, for example, ascorbic acid to form reduced graphene oxide (rGO), or with hydrogen peroxide to form holey graphene oxide (HGO). The application of graphene oxide and its modifications in processes leads to improved sensitivity, electrocatalytic behavior and reduced fouling. Thus, a kampron, which is an electronic component with graphene oxide derivatives fabricated using 3D printing technology, has been experimentally prepared with the advantage of applications in various fields – physical, chemical and biological. Thus, in several stages, the action in the physical domain (pressure), chemical domain (gases and vapors) and biological domain (gases exhaled from the lungs) will be investigated. The changes caused by the investigated influences on the sensors are reflected by a change in the voltage on the sensor. This paper focuses on the first stage of the research, i.e. the fabrication and verification of reactivity of sensors printed in a single layer, which are similar to conventional comb or spiral sensors. The next stages of the research will focus on the investigation of sensors arranged in multiple layers, with the final stage involving the preparation of sensors with complex spatial shapes, while higher sensitivity is also expected. Carbon materials in the form of filaments will be used for 3D printing.

Keywords: Graphene oxide, sensors, kampron, 3D printing

1. INTRODUCTION

Graphene oxide and materials based on it are widely used materials mainly because of their excellent optical, mechanical and electrical properties, which can be used for a wide variety of applications. Attention is currently focused primarily on research into the industrial synthesis of graphene, with an emphasis on premium quality, while at the same time establishing a cheap and simple processing method to promote practical and industrial applications. [1] The materials are generally synthesized by long-established processes (Hummers method), whereby the graphite powder is oxidized to form graphene oxide (GO). From GO, it is possible to prepare, for example, rGO, i.e. reduced GO, by reaction with ascorbic acid, or HGO (holey graphene oxide, also referred to as perforated graphene), which can be prepared by the action of hydrogen peroxide. [2] The GO modifications differ quite significantly in properties from the original GO, for example in terms of electrical conductivity, mechanical strength or hydrophilic nature of the structures. [3] Reduced graphene oxide is a graphene material that is formed by reducing the number of oxygen groups of GO. After such reduction, the most resistant oxygen groups remain on the edges of GO. rGO has different electrical properties than graphene oxide, in particular conductivity. This is why the purpose is to take advantage of possible changes in conductivity due to the action of different sensor reagents. Holed graphene oxide (HGO) is then a graphene material with a large number of holes and pores in its basal plane. The last material is graphitic carbon nitride ($g\text{-}C_3N_4$), which appears to be promising for photocatalytic technologies (water splitting), for applications in supercapacitors (high charge density), or as a flame retardant. It is this material that was used for printing the

sensors tested in this work, where the material consisted of a PP filament with 10% g-C_3N_4. Thus, in summary, all of these materials can be used, for example, to purify wastewater from drugs, drugs, metabolites, microorganisms, pollutants, dyes, radioactive isotopes and heavy metals [4], and for biomedical applications such as magnetic field-controlled nanobots - targeted delivery of drugs, antimicrobials, interaction with molecules, or possibly cancer diagnosis. [5 - 8] The last application can be for the preparation of sensors and biosensors, as they are active cells working due to changes in electrical properties during electrochemical processes (physical applications of GO in the form of sensors) [9, 10].

Sensors of all types are proven to improve the quality of life in homes and industry. Electrodes are the most important part of sensors, as they enable data reception and analysis. The most commonly used materials for the development of electrodes are gold, silver, aluminum and carbon, in the form of graphene can be described as a frequently chosen option due to its excellent electrical and crystal properties. In force sensors, for example, the signal response, limit of detection, maximum sensing range and potential reproducibility of the response are all of interest - and it is these properties that are of high importance in graphene oxide. Electrochemical sensors then take advantage of the relatively large specific surface area when working with biomolecules, where the speed of transport and small band gaps cause an interaction between the electrode and the substance being analysed. The undeniable advantage of this material is also its low environmental burden, making it a popular material compared to the other metals mentioned. [11, 12] The purpose of this paper is then to verify whether materials from the graphene family are indeed suitable for the preparation of sensors and for which purposes these sensors can be used.

2. EXPERIMENTAL PART

The following section briefly describes the materials used and the experimental procedure.

2.1 Materials and methods

Comprehensive research on the reactive properties of graphene derivatives (GO, rGO, HGO, etc.) requires the development of a stable platform for future sensors. The preparation of these modifications is, however, protected by a patent and for this reason, only the term "kampron" will be used, which is a collective term for electronic components and devices with graphene derivatives created using 3D printing technology while being cheap, fast, reliable and repeatable technology with great potential for the development of sensors in various application areas - physical, chemical and biological. It is important to note that this term has not been used in history before and is solely a designation created by the authors. The Kampron is capable of detecting different types of reactions and interactions both in the physical (measurement of physical quantities, such as force, pressure, temperature, etc.) and chemical (gases and vapors detection) domains. Biological measurements, i.e., measurements related to the physiological functions of organisms, will also be investigated. For this reason, the research has been divided into three stages, with the first stage focused on the production and research of reactivity sensors that are similar to conventional comb or spiral sensors and are printed in a single layer, the second stage is then dedicated to the production and research of reactivity sensors that are comb (spiral) but arranged in multiple layers, and the essence of the last stage is the production and research of reactivity sensors that will have more complex spatial shapes. Thus, higher sensitivity is also expected.

The following section then focuses on the results of the experiments performed in the first stage of the research - i.e. measuring the reactivity of GO derivatives using a kampron printed in a single layer. The following materials were used for the experiments - PLA (polylactid acid) conductive filament, PETG filament (supplier PRUSA Research) and GO, prepared according to the procedure of Hummer W.S. - Offerman R.E. 195. The following equipment was then used for the experiments - a cell for testing the kampron with gas inlet and outlet, an Arduino UNO microcontroller with Data logger shield for SD cards and a SHITO force gauge, type FS-500N.

First, the kampron was prepared by printing the electrodes for sensing the electrical voltage (resistance or conductance measurement) from PLA material with 10% graphite. The electrodes are on a non-conductive

surface (PETG material). GO nanoparticles (100 nm on average) in an aqueous suspension were deposited on the electrodes, which formed an active layer at 40 - 50°C after 12 hours of drying, see **Figure 1**.

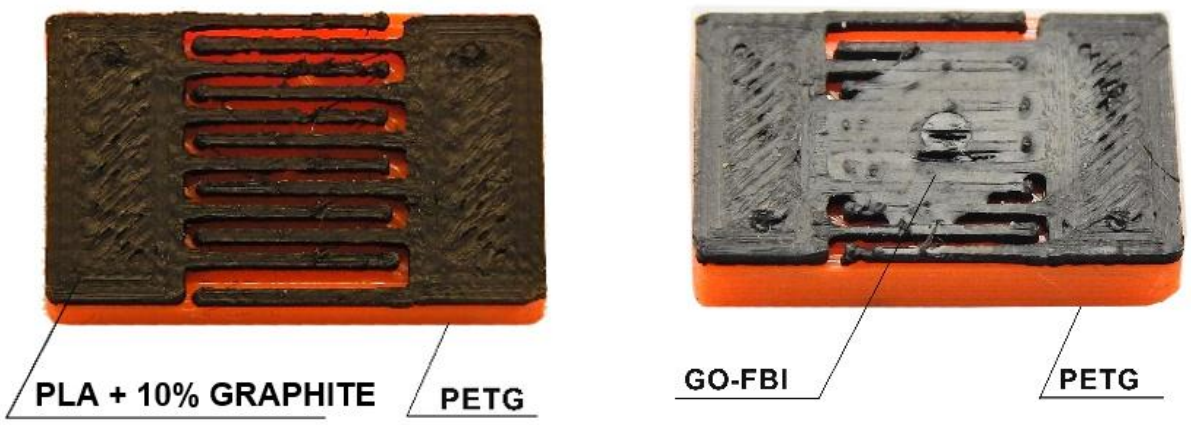

Figure 1 Kampron electrodes on insulator (left), GO on electrodes (right)

The kampron was then placed in a closed cell (**Figure 2**) with inlet and outlet for gases and vapors for reactivity measurements. The electrodes were connected to a voltage source produced by a microcontroller that simultaneously detects changes and stores the measured data on an SD card.

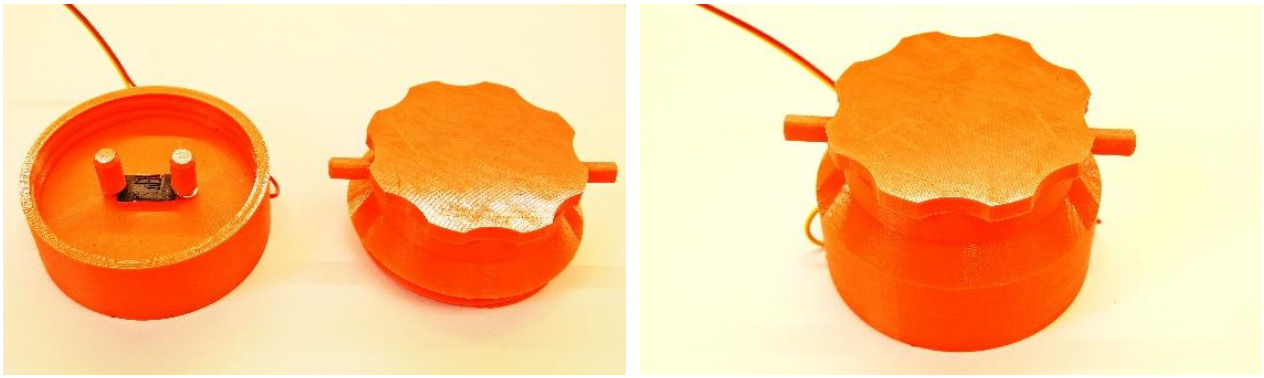

Figure 2 Open cell with kampron (left), closed cell (right)

2.2 Results

The measurement itself was performed using a microcontroller that contains an analog-to-digital converter that reads the changing voltage on the kampron and converts it to numbers between 0 and 1023 (it is 10-bit - it distinguishes 210 possible values). The maximum voltage on the microcontroller pin is 5 V. This value corresponds to 1023. For example, the numerical value 260 corresponds to a voltage of 1.27 V. To better plot the data in the graph, a converter was used. **Table 1** shows the conditions under which the measurements were performed and the following graphs show the results of physical, chemical and biological measurements. Chemical measurements were conducted using a 2-liter air tank, which was inflated with atmospheric air using a compressor set to a pressure of 1.2 bar. A material soaked in acetone or gasoline was placed in the intake where, due to the pressure, the vapors came into contact with the kampron. For the biological measurements, human exhalation lasting 20 seconds was used, which was then gradually atmospherically ventilated for 30 seconds.

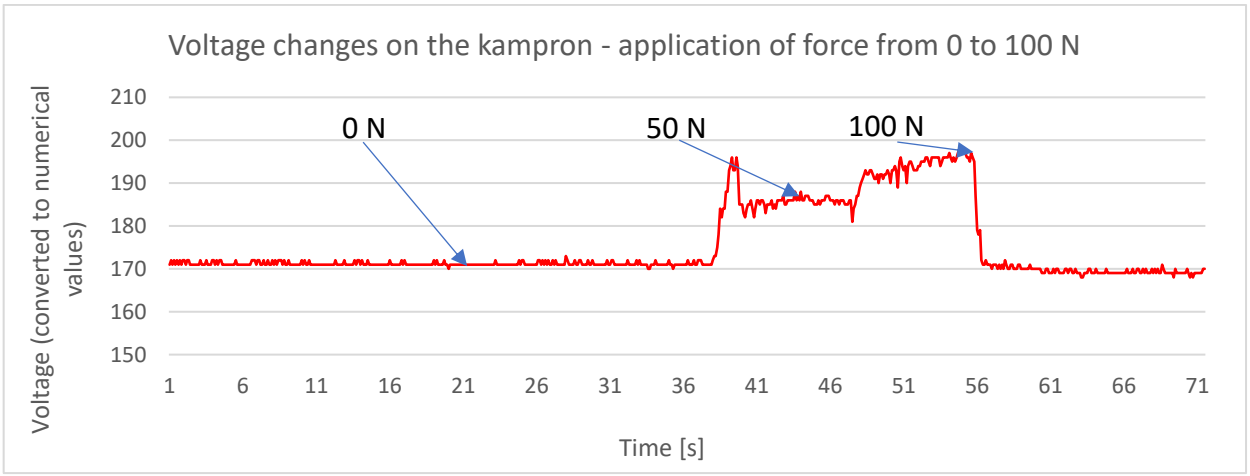

Figure 3 Voltage changes while testing force changes

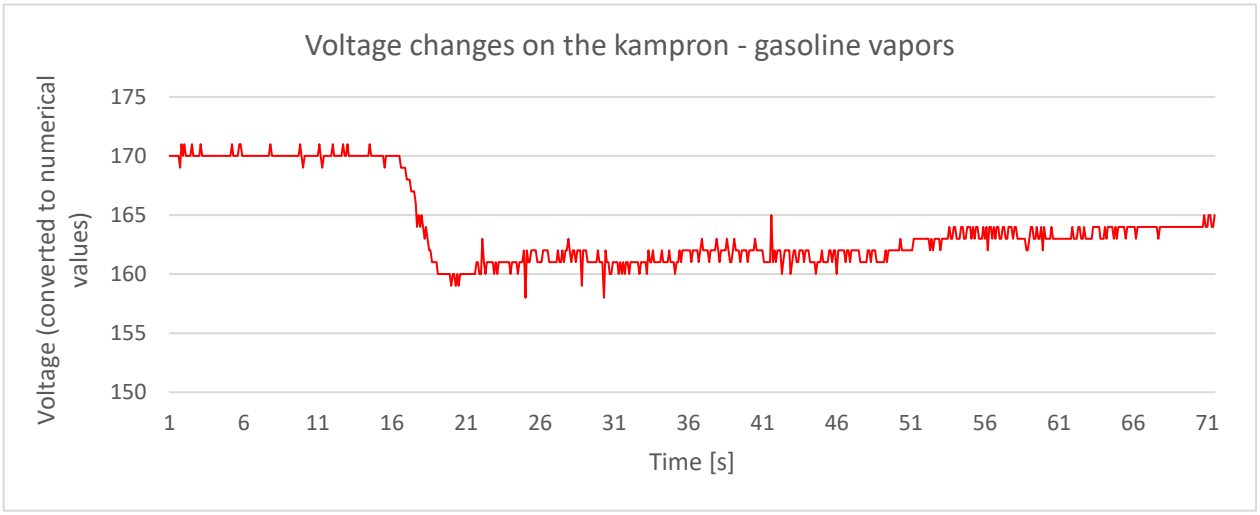

Figure 4 Voltage changes while testing vapors (gasoline)

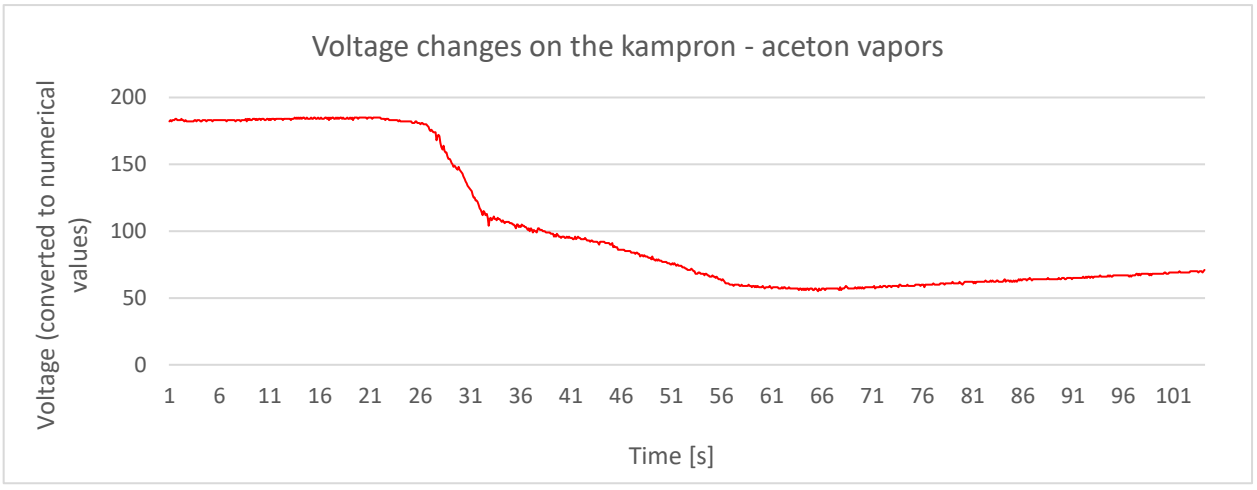

Figure 5 Voltage changes while testing vapors (aceton)

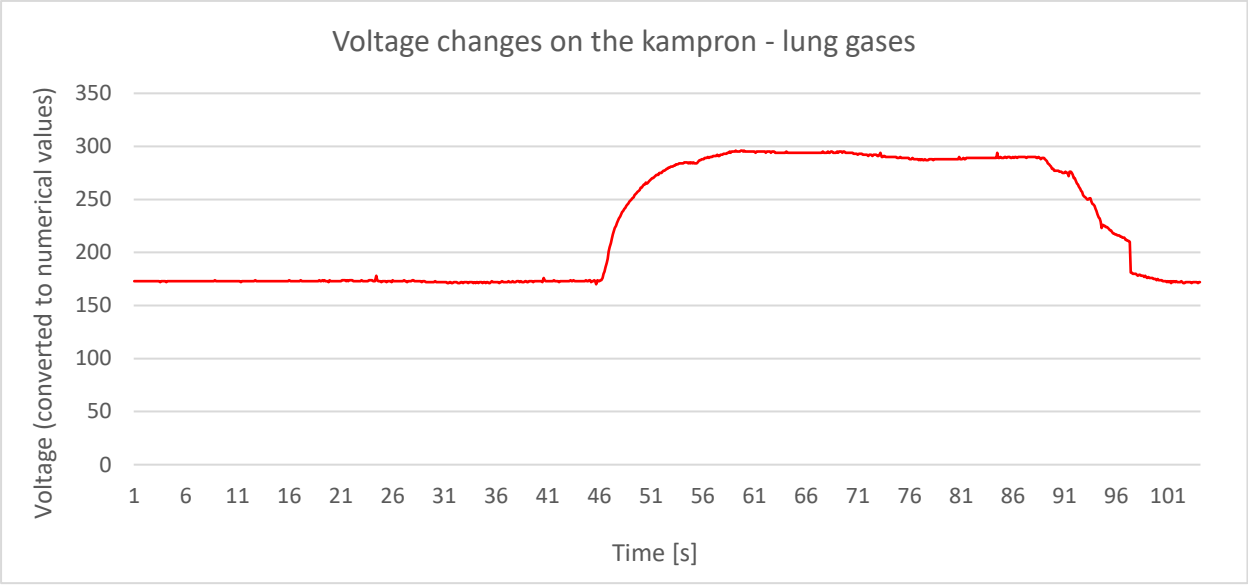

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Figure 6 Voltage changes while testing moist gases from the lungs

The table below summarizes the experimental values obtained from the measurements.

Table 1 Experimental conditions and values obtained by measurements

Experimental conditions	**Pressure measurement (physical measurement)**	**Measurement of flammable vapors (chemical measurement)**	**Measurement of flammable vapors (chemical measurement)**	**Measurement of gas mixtures (biological measurement)**
Kampron material	Single layer 10x16x2.6 mm kampron, PLA + 10% GO electrodes	Single layer 10x16x2.6 mm kampron, PLA + 10% GO electrodes	Single layer 10x16x2.6 mm kampron, PLA + 10% GO electrodes	Single layer 10x16x2.6 mm kampron, PLA + 10% GO electrodes
Temperature [°C]	22 (laboratory and sample)	22 (laboratory and sample)	22 (laboratory and sample)	22 (laboratory) 34 (sample)
Pressure [hPa]	999	974	970	970
Humidity [%]	37	33	30	35
Subject of testing	Force applied to the kampron 0 - 50 - 100 N	Medical gasoline (hydrogenated gasoline)	Aceton	A person exhaled gases at 87% humidity
Voltage [numerical value]	171 - 185 - 197	170 - 160	182 - 55	173 - 295
Voltage [V]	0.84 – 0.9 – 0.96	0.83 – 0.78	0.89 – 0.27	0.85 – 1.44

As can be seen from the figures, kampron has demonstrated, as a basis for further research, that convincing results were already obtained in the first stage when measuring GO reactivity. It is assumed that the measurable voltage changes are the result of interactions of the reactants at the contact points of GO with the electrodes. This assumption will be developed in the next stages of the research. The tested method can be considered promising (it is cheap, fast and modifiable), which makes it applicable in future physical applications (sensors, reactors, etc.).

3. CONCLUSION

It has been experimentally verified that the use of GO and its modifications has considerable potential also in the field of sensors, where physical, chemical and biological measurements of stress changes after exposure of the material to various influences have been performed. In the verification, a material called kampron was chosen (the name was assigned by the authors, it is not a previously known material), where single layer 10x16x2.6 mm kampron, PLA + 10% GO electrodes were used. Thus, it can now be stated that the kampron prepared in the first stage of the research (single layer), in conjunction with the electrodes prepared from GO, met the expectations in terms of results. Attention will now be focused on the second and third stages, whereby multilayered helical structures and subsequently much more complex shapes will be tested. The materials used appear to be quite reliable due to their low cost, ease of preparation - and hence reproducibility, which is a key aspect in the experimental validation of the suitability of the materials.

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