

Graphene printing for textronic devices

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Graphene has been proved to be an excellent nanomaterial for modern electronic applications such as biosensors, transistors or heaters. The natural point of view is to use this new nanomaterial for the development of unique textronic devices. The current state of the art of the materials science shows design possibilities of the smart textiles with graphene. The authors show the results of implementation of 2D carbon structure into the textronic devices. The development inks and pastes give interesting properties of textile such as electro conductivity and sensitive to the volatile organic compounds.

Key words: *graphene, textronic, ink-jet printing, screen printing*

1. Introduction

The achievement of the science in the recent years, which is graphene, sets new challenges also in the field of modern electronics including textron-

ics. Graphene is a two-dimensional (2-D) sheet of carbon atoms in a hexagonal configuration with atoms bonded by sp^2 bonds. These bonds and the electron configuration are the reasons for the unique properties of graphene, which include a very large surface area, high electrical and thermal conductivity, high optical transparency in visible light spectrum,

high mechanical strength (200 times greater than steel) and flexibility [1]. The first work confirming the manufacturing of this new form of carbon for the purposes of electronics was demonstrated by Geim and Novoselov in 2004, for which the scientists were granted in 2010 the Nobel Prize from the field of physics. The graphene quickly becomes an object of

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interest for many scientific groups dealing with different fields of science, from quantum mechanics [2] to bioengineering [3]. The unique properties amassed in graphene make it the preferential material for modern electronics and textronic application. The one of the most promising applications of graphene for the design of novel smart textiles is the development of inks and pastes for printing conductive and sensory tracks on the surface of the textile materials.

Nowadays, conductive inks dedicated for production of textronic materials are prepared by the use of metal nanoparticles, carbon nanotubes, carbon black or electro conductive polymers as well [4-5]. The developed solutions among many advantages have some disadvantages. The most important are: (i) low optical transparency in visible light spectrum and (ii) low electrical conductivity of obtained materials. The low electrical conductivity of textronic materials is compensated by increasing the content of used nano-filler. Due to the high cost of obtaining high-quality nanomaterials, the production in industrial scale of current textronic materials cannot be profitable. Thus, the development of novel materials for smart textile design is still important. Graphene, because of its exceptional properties such as very good electrical conductance, flexibility and high optical transparency in visible light spectrum, can replace nanomaterials used nowadays. The present state of the art confirms the possibility of graphene application for production of novel conductive inks. The promising works show lower percolation threshold of graphene inside polymer matrix than carbon nanotubes [6] and high electrical conductance of printed graphene layers by using Ink-Jet printing method [7].

In the frame of the project titled „Production of graphene-based inks and pastes and development of the technology of printing for flexible electronics - GRAPH-PRINT realized under the GRAF-TECH Program

supported by the National Centre for Research and Development of Poland, the novel inks and pastes contain graphene was developed.

The prepared chemical composition could modify the surface properties of fabrics and nonwoven obtained from cotton, polyesters and para-ar-amides and gives unique properties such as surface conductivity and sensitive to volatile organic compounds (VOCs).

2. Screen printing VOCs sensors

2.1. The base of idea

The screen printing method is the one of the fastest and the most popular method of surfaces modification of textile fabrics. It is also the popular method of printing electronic devices such as circuit boards or touch-panels. The electronic devices are mainly printed by the using silver or graphite base pastes. During the evolution of electronic trends to the flexible electronic, the pastes are also prepared by the use the conductive polymers such as polyaniline, and nanomaterials such as carbon nanotubes. The application of the novel materials, which are the semi conductive materials created as a base for the preparation of the first sensors and other unique materials.

The flexible and high quality over-prints which have more properties than only electro conductivity, it creates the inspiration to the preparation smart textiles materials. Preparation of comfortable textiles contained the electronic devices, which so called textronic devices is resulted in the developing of textiles for monitoring environment around us and the monitoring of human vital functions, became real.

The once of previously works realized in Lodz University of Technology have been focused on application of carbon nanotubes to the preparation unique textronic materials. The prototypes of screen printed electrodes for monitoring the breathing (Fig.1) was developed successful as well as the developing of chemical sensors [8]. The obtained by the using commercial available multiwall carbon nanotubes (MWCNT) chemical sensors ware characterized by high sensitivity to the organic liquid solvents such as methanol, toluene and acetone and its volatile form.

The success of first works has been an inspiration to the continuation of laboratory works and preparation novel materials by using other allotrope form of carbon – graphene. The part of reported in E. Skrzetuska et. al. (2014) works are presented below [9].

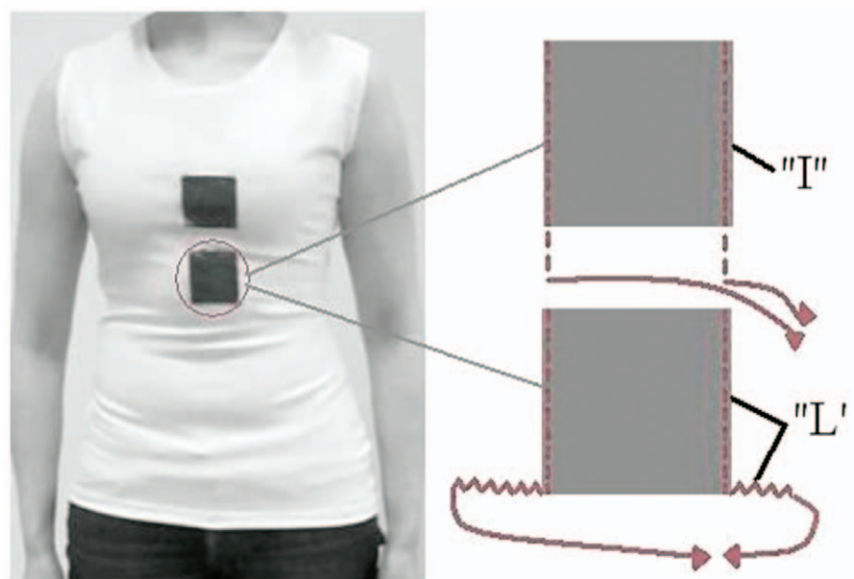


Fig.1 The breathing sensor contain MWCNT developing by TUL [8].

2.2. Preparation of screen printing sensors contains graphene

The paste was prepared by mixing commercially available nanomaterials, graphene powder from Graphen Supermarket (USA) and water dispersion of multi wall carbon nanotube from Nanocyl (Belgium). The aliphatic urethane acrylate and photoinitiator was added to the cross-link nanomaterials with textile fabric surface. The printing process on the cotton fabric with a twill weave was realized by means of a screen printing machine with an automatic squeegee manufactured by PrintingMachine (Poland). Sheets of A4 were printed using a screen with a 49 mesh/cm². The obtained prints were fixed using the cross-linking process by exposing the sample to an IR emitter (250 W) for 30 minutes (Fig.2b)

2.3. Results and discussion

In the first analysis was the comparison of the electrical properties of cotton fabric overprinting by multi wall carbon nanotube (MWNT) and MWNT with addition of 1%wt and 3%wt of graphene powder. The surface resistivity of the printed cotton woven fabrics was measured according to the standard EN 1149-1:2008 Protective clothing-Electrostatic properties Part 1: Surface resistivity (Test method and requirements). The obtained results clearly have shown the increase of conductivity of surface with increasing of graphene concentration. The surface resistance was decrease from the 13 k Ω for the carbon nanotubes to the 4.7 k Ω for the samples contain 3%wt of graphene powder.

More interesting results was obtained for the test of sensitivity of samples to VOCs. To test vapour sensitivity, two solvents were selected (acetone and methanol according to standard EN 14605+A1:2010), and measurements were carried out with the use of a laboratory measurement system. The sensitivity of each printed fabric to the chosen vapours was evaluated

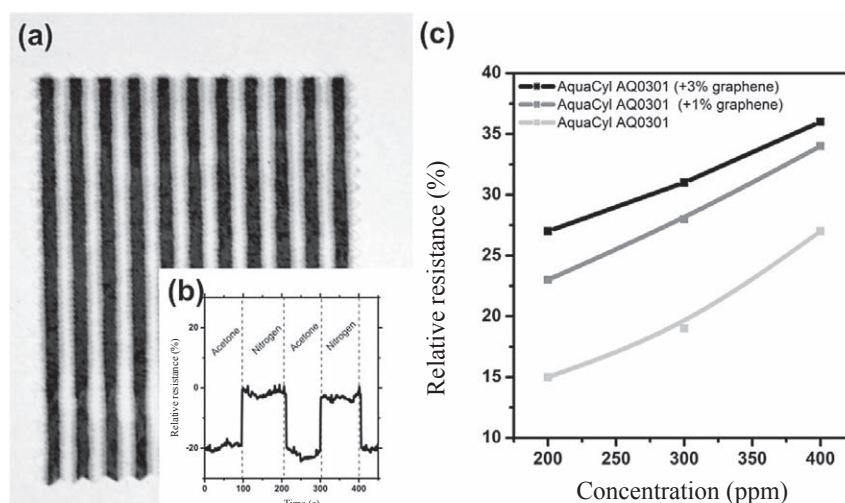


Fig.2 The screen printed VOCs sensor: (a) sensor, (b) cyclic reaction to the acetone vapours and (c) sensitivity to the various concentration of acetone [9]

by observing changes in the electrical resistance caused by chemical stimuli. Changes were registered by a special system including a Keithley digital multimeter and the system used for chemical vapour detection, built in The Department of Material and Commodity Sciences and Textile Metrology [10]. The addition only 1%wt of graphene powder cause the increase of reaction to the selected vapours twice (Fig.2c). The mixing two types of carbon nanomaterials results in the increases the reaction to selected VOCs.

3. Ink-jet printing VOCs sensors

3.1. The base of idea

The novel conception of flexible electronic is the using of Ink-Jet printing method. That method has the higher resolution and is more efficient then screen printing method. Ink-Jet printing technique is successful used for preparation precision small conductive tracks, transistors, diodes OLED, and other devices. The commercial available inks mainly based on the silver nanoparticle, carbon nanotubes and electro conductive polymer such as PEDOT:PSS. Ink-jet printing according to its advantage is perfectly for developing unique electronic devices with micrometre precision.

The Ink-Jet method is also promising technique for the modification of textile fabrics. The previously our works was focused on preparation ink by using commercial available multi wall carbon nanotubes [10]. The developed ink allows modification of cotton fabrics and creation new properties such as antistatic and antibacterial properties.

In the frame of GRAPH-PRINT Projects the modification of textile surface by Ink-Jet printing method was evaluated. The developed inks based on graphene oxides (GO) are dedicated for flexible electronic and is also promising for preparation of wearable VOCs sensors. The part of reported in M. Rogala et al. (2015) works are presented below [11].

3.2. Preparation of Ink-Jet printing sensors contains graphene

The graphene oxide was prepared from graphite flakes by modified Hummers method. The water dispersion of graphene oxide was concentrated up to 10 mg/ml. The prepared liquid was the base for the ink. We developed the ink based on the mixture of GO water dispersion and propylene glycol. Such liquid is characterized by the optimal properties as viscosity, surface tension and density. The calculated Ohnesorge number

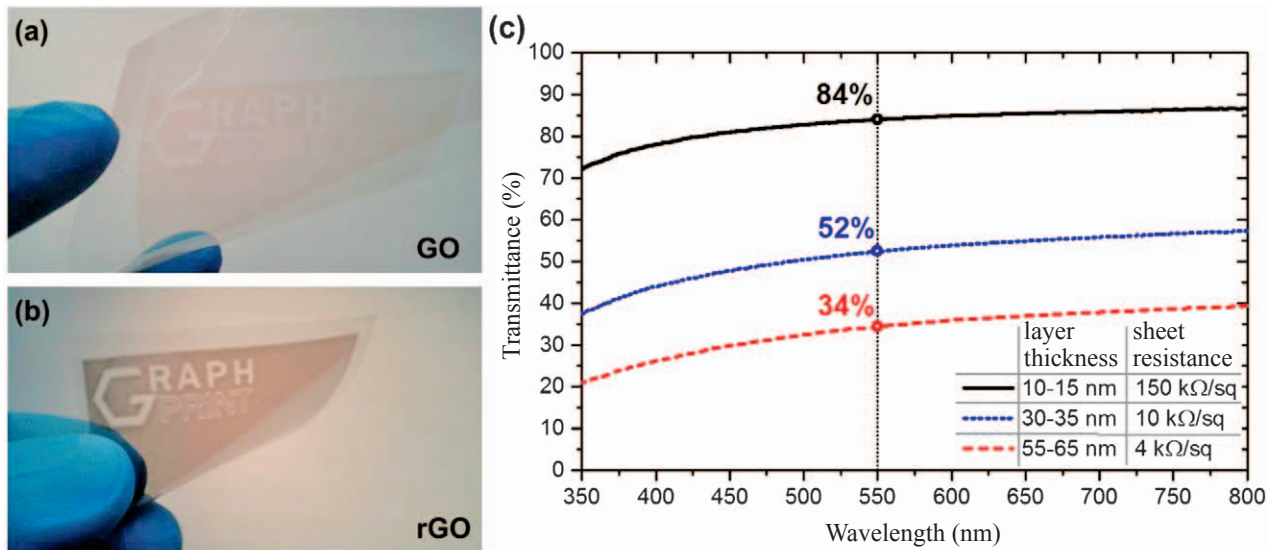


Fig.3 The graphene oxide overprint on PET foil (a) before and (b) after chemical reduction, and (c) transmittance spectrophotometry spectra for reduced graphene oxide overprints [11]

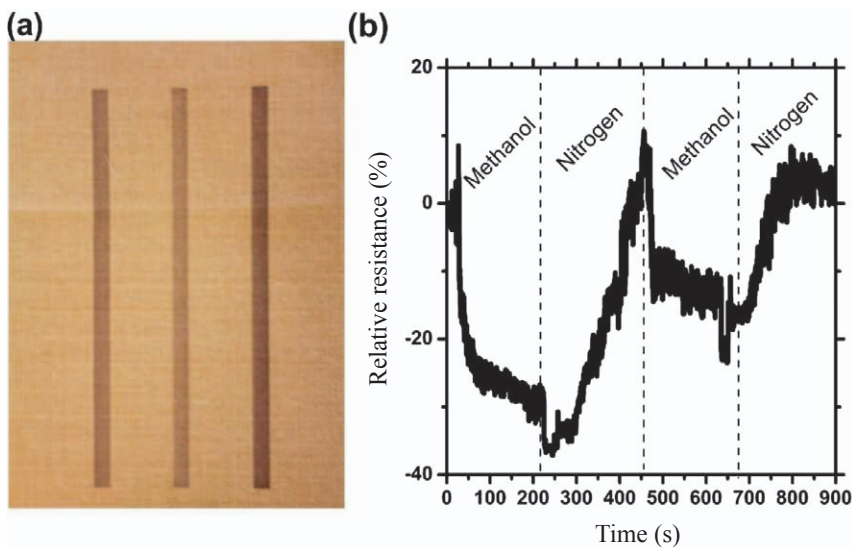


Fig.4 The graphene oxide overprint on Zylon[®] woven: (a) after chemical reduction and (b) cyclic reaction to the methanol vapours

(Oh) is close to 0.4, which gives the $1/Oh$ factor at the level of 2.3 and is in the range, as mentioned in previous papers for the ink and is between 1 and 14. The printing process on PET foil and Zylon[®] woven fabric was done by ink-jet printing machine LP20, manufactured by PixDro (Belgium). After printing process the printed GO layer was reduced in HBr bath at 80 °C for 60 min.

3.3. Results and discussion

In the first steps the overprint PET foil was analysed. The developed ink

and chosen reduction method gives interesting results. After reduction the printed layers thickness up to 65 nm was transparent for the visible light. The layers was also conductive and the measured resistance by for electrode method was 4 kΩ/sq for 60 nm overprint, 10 kΩ/sq for 30 nm and 150 kΩ/sq for 15 nm thick overprint. The results of this part investigation is presented in Fig.3.

The overprints on Zylon[®] woven fabric (Fig.4a) was also electro conductive but due to the topography of textile substrate the resistance, mea-

sured by the same method which was used for PET foil, was on the level 100 kΩ/sq. The prepared sample was stable and resistance insignificantly decrease up to 100 kΩ/sq after washing according to the standard PN-ISO 105-C06 at 40 °C during 45 minutes. This result is interested because does not exclude the application of overprints as VOCs sensors.

The measurements of methanol vapour sensitivity were carried out with the use of a laboratory measurement system (Fig.4b). The sensitivity of each printed fabric to the chosen vapour was evaluated by observing changes in the electrical resistance caused by chemical stimuli. The obtained results was similar to the sensors prepared by screen printed method. The most importance is the concentration of nanomaterials which was lower in the case of Ink-Jet printing (up to 1%wt) than in the case of screen printing (above 1% wt).

4. Conclusion

In summary, we have presented screen printing of networks of MWNT as well as MWNT containing graphene nanowires, from paste prepared by mixing commercially available nanomaterials, graphene powder and water dispersion of MWNT. Performed

investigations clearly have shown the increase of conductivity of surface with increasing of graphene concentration. The surface resistance was decrease from the 13 k Ω for the carbon nanotubes to the 4.7 k Ω for the samples contain 3%wt of graphene powder.

Obtained materials give unique properties such as sensitive to volatile organic compounds (VOCs). The addition only 1%wt of graphene powder to the printed wire cause the increase of reaction to the acetone vapours twice.

It was shown that ink-Jet printing method is suitable to print VOCs sensors containing graphene. Printing ink was composed with dispersion of graphene oxide in water and propylene glycol. In this method reduction treatment is necessary using HBr solution at high temperature. Obtained sensors as a layer with thickness up to 65 nm were transparent and have good VOCs sensitivity against methanol.

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