EMERGE
Emerging Printed Electronics Research Infrastructure

D10.5 Developing of new functional materials for printed electronics

WP10 JRA2: Research on high throughput novel inks/pastes synthesis

The EMERGE project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement Nº 101008701

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List of abbreviations

1-MP – 1-methoxy-2-propanol
2D – Two-dimensional
2-ME – 2-methoxyethanol
ATR-FTIR – Attenuated total reflectance-Fourier transform infrared
CRE – Coffee ring effect
DPI – Dots per inch
EG – Ethylene glycol
e-skin – Electronic-skin
Eth – Ethanol
GO – Graphene oxide
GRMs – Graphene related materials
HMU – Hellenic Mediterranean University
ICN2 – Institut Català de Nanociència i Nanotecnologia
IoT – Internet-of-Things
MEGs – Moisture energy generators
M-GO – Alkali metal-doped graphene oxide
PET – Polyethylene terephthalate
SnO – Tin oxide
TFTs – Thin-film transistors
UNOVA – Instituto de Desenvolvimento de Novas Tecnologias
WUT – Warsaw University of Technology
WF – Work Function
XPS - X-ray photoelectron spectroscopy
ZnO – Zinc oxide
ZTO – Zinc tin oxide

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1. Executive Summary

At this early stage of WP10, the main ongoing research focus the zinc tin oxide (ZTO) semiconductor oxide-based inks for inkjet printing, graphene related materials (GRMs) inks and conductive pastes for screen printing, as well as the development and implementation of graphene based inks into consumer inkjet printers. In the next stages of the project, it is planned to expand the presented work and start new research in the topic of new functional materials for printing.

2. Description

During the reported period, work on developing new functional materials focused on the ZTO semiconductor oxide-based inks for inkjet printing (UNOVA), GRMs inks (HMU), conductive pastes for screen printing (WUT), and graphene based inks for consumer inkjet printing setups (ICN2). All materials are dedicated for printed electronics.

2.1. ZTO semiconductor oxide-based inks

UNOVA's work focused on the development of ZTO semiconductor inks for inkjet printing of functional layers with application in electronic devices. The inks solvent (ethanol, 2-methoxyethanol – 2-ME, 1-methoxypropanol – 1-MP), viscosity, film properties and printer settings (dots per inch – DPI, speed, #layers) were investigated to achieve optimal printed ZTO layers. These layers were successfully implemented in electronic devices, namely thin-film transistors (TFTs), as demonstrator.

2.1.1. ZTO inks preparation

Four separate zinc nitrate ($Zn(NO_3)_2 \cdot 6H_2O$, CAS 10196-18-6, 98% from Sigma Aldrich) precursor solutions (0.2 M) were prepared from either ethanol (CAS 64-17-5, 98% from PanReac AppliChem), a solution of ethanol (Eth)/distilled water (50/50 %V), 1-MP ($C_4H_{10}O_2$, CAS 107-98-2, >99% from Carl Roth) or 2-ME ($C_3H_8O_2$, CAS 107-98-2, 99% from Fischer Scientific). Similarly, tin chloride dihydrate ($Cl_2Sn \cdot 2H_2O$, CAS 10025-69-1, >96.0% from Sigma Aldrich) solutions of the same molarity were prepared for each solvent. The resulting zinc oxide (ZnO) and tin oxide (SnO) precursor solutions were stirred at room temperature

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until dissolution was complete and then mixed according to their solvents in a 2(ZnO):1(SnO) volume proportion. Multiple batches of Eth/Eth.H_2O/2-ME/1-MP based ZTO inks were produced and to each was added a different V% (0, 2.5, 5, 7.5 and 10%) of ethylene glycol (EG, $C_2H_6O_2$, CAS 107-21-1, >99,5% from Carlo Erba Reagents). All solutions were stirred for one hour at room temperature and subsequently stored in cold.

2.1.2. Characterization of ZTO inks

The viscosity of all samples was determined in a CAP 2000+ Viscometer (from Brookfield) using a Brookfield Cap09 Spindle. The viscosity greatly influences the inks compatibility with inkjet printing. From the average of 5 measurements for each ink was then determined the Z value which according to the scale proposed by Jang et al. should be between 4 and 14. [doi: 10.1021/la900059m] The following Figure 1 shows the Z and viscosity results of ZTO precursor solutions.

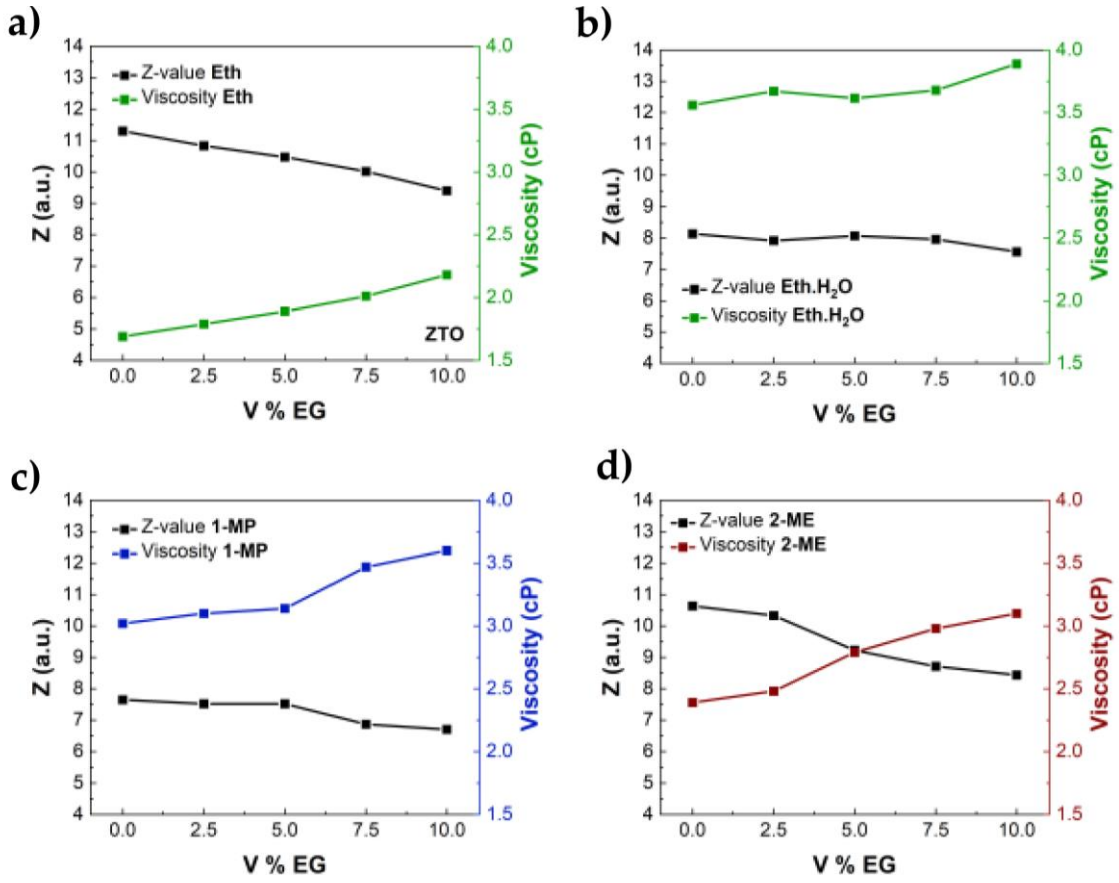

Figure 1. Viscosity measurements and Z value determined for ZTO inks by increasing V% EG for different solvents: a) ethanol, b) ethanol (50%):water (50%), c) 1-methoxypropanol (1-MP) and d) 2-methoxyethanol (2-ME).

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Ethylene glycol (EG) increases the boiling point, improves the stability of solutions and because it is more viscous than the remaining cosolvents it increases viscosity as shown in all measurements. These benefits lead to thicker films with decreased coffee ring effect (CRE) effects. From the produced ZTO inks, those using 2-ME as solvent showed a perfectly centered Z value when mixed with 5%V EG. 1-MP is the most viscous solvent and EG should only be added for the previously mentioned benefits. Ethanol is much more fluid and 10%V EG showed the value closest to the middle of the scale. Comparing the solutions with 0%V EG across all solvents it is also observed that the viscosity increases with increasing hydrocarbon chain length.

2.2. Conductive pastes for screen printing

2.2.1. Paste preparation

The first stage consists of the preparation of the carrier, i.e. polymer + solvent. The polymer is to constitute a matrix for the paths, therefore, for different applications, other carriers are used - selected in terms of physicochemical parameters. The carrier is prepared by dissolving a weighed amount of polymer in a solvent by stirring for at least 24 hours at a temperature adapted to the components of the carrier.

The carriers tested are:

- 8 wt% of Poly(methyl methacrylate) with an average molecular weight of 3.5 · 105 u dissolved in 2-(2- butoxyethoxy) ethyl acetate;
- 24,3 wt.% Laroflex M35 with a density of 1.24· 103 kg/m3, dissolved in a mixture of 2-(2- butoxyethoxy) ethyl acetate (97%) and 2-butoxyethanol (3%);
- 15 wt.% Elastollan® soft 35AP which has a density of 1.18 - 103 kg/m3 dissolved in N, N - Dimethylformamide;
- TPU soft, and TPU hard carriers.

In the second stage, the paste is ground with an agate mortar, after weighing the appropriate amounts of the carrier and the functional phase - the powder of the material with the desired properties, e.g. nanosilver flakes or graphene. The process of grinding in a mortar lasts about 20 minutes.

Subsequently, depending on the needs, the paste may be rolled using a triple-roll mill. Appropriate values of gaps and roll rotation speed should be set on the triple-roll mill. Moreover, an optional pre-step for some functional phases is sonication in the presence of

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a surfactant in a solvent for at least 30 minutes using an ultrasonic cleaner or an ultrasonic homogeniser.

2.3. GRMs inks polymer based

HMU has worked on developing functionalised GRMs and preparing the respective inks in various solvents and/or aqueous polymer media. These GRM inks are being prepared and optimised with the aim of applying them to printable electronics and textiles. This project involves continuous expansion of the GRM functionalisation methods and optimisation of the ink preparation.

Graphene oxide (GO) inks are being prepared and characterised as hygroscopic nanomaterials for the development of Moisture Energy Generators (MEGs). GO is prepared in-lab via improved Hummers' method. GO inks are then prepared in polar solvents (i.e. H_2O or isopropyl alcohol) and deposited to form moisture absorbing films that are apllied into MEG dvices and evaluated for there moisture-based power generating abilities. Currently, we are employing and assessing a variety of polymers to increase the printability of the GO-based inks with the end goal of developing flexible, wearable self-powering devices such as autonomous "Internet-of-Things" (IoT) sensors, electronic-skin (e-skin) patches developed onto bendable and stretchable substrates. This method can be applied to flexible substrates such as polyethylene terephthalate (PET), paper or textiles.

2.3.1. Alkali-doped GO inks

Alkali metal (Li, Na, K, Rb, Cs)-doped GO powders (M-GO) are synthesised and dispersed in water or organic solvents (i.e. chlorobenzene). To evaluate the chemical composition of the as-prepared M-GO samples, X-ray photoelectron spectroscopy (XPS) was performed. The results are presented in Figure 2a. The characteristic peaks of each alkali metal are present in all the M-GO samples, indicating sufficient doping upon reaction with the respective M_2CO_3 salt. All MGO samples have a higher %C-C sp^2 concentration compared to GO. This indicates partial restoration of the sp^2 carbon arrangement and therefore partial chemical reduction upon reaction with M_2CO_3. This is also supported by the lower %C-OH concentration in all MGOs. The Work Function (WF) values of each sample were obtained via Kelvin Probe measurements (Figure 2b). Upon M-doping, the WF value decreases by 0.4-0.7 eV when compared to pristine GO (WF=4.9 eV). The WF increases from 4.3 to

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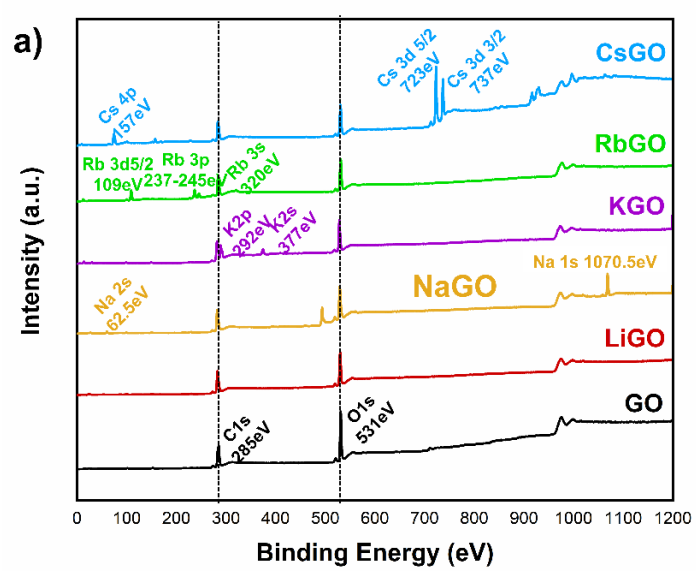
4.5 eV with the atomic number (Z) of the alkali metal dopant, until we reach Rb and Cs, for which the WF decreases to 4.2 eV for both metals.



b)

Sample	WF (eV) (+/- 0.05 eV)
GO	4.9
LiGO	4.3
NaGO	4.4
KGO	4.5
RbGO	4.2
CsGO	4.2

Figure 2. a) XPS spectra of M-GO powders with GO precursor as reference. b) Work Function (WF) values of M-GO and GO films prepared by spray coating aqueous dispersions onto glass subtrates.

Table 1. Carbon components concentration derived from the C1s peaks deconvolution.

Sample	C-C sp^2	C-C sp^3	C-O(H)	C=O	COOH
GO	34.3	5.5	48.8	8.2	3.2
LiGO	57.9	6.9	23.2	9.6	2.5
NaGO	47.7	11.0	27.1	10.8	3.3
KGO	53.2	17.1	16.2	13.5	0
RbGO	44.5	13.3	29.1	9.8	3.1
CsGO	44.7	14.3	28.4	9.4	3.2

The UV-Vis absorption spectra are featured in Figure 3, while the attenuated total reflectance-Fourier transform infrared (ATR-FTIR) and Raman spectra are shown in Figure 4.

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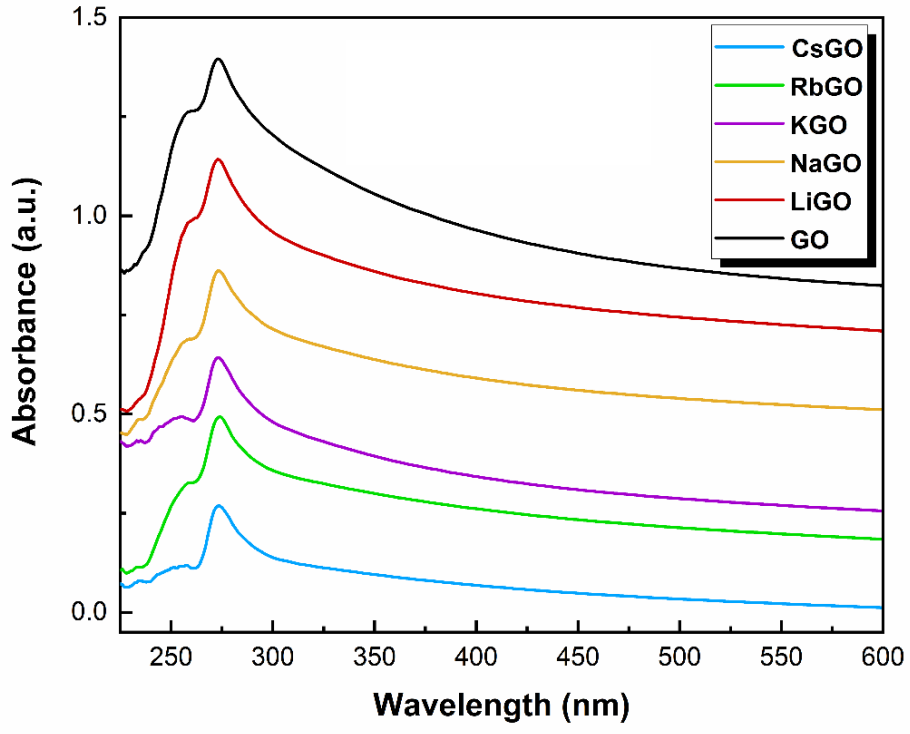

Figure 3. UV-Vis absorption spectra of M-GO and GO films prepared by spray coating aqueous dispersions onto glass substrates.

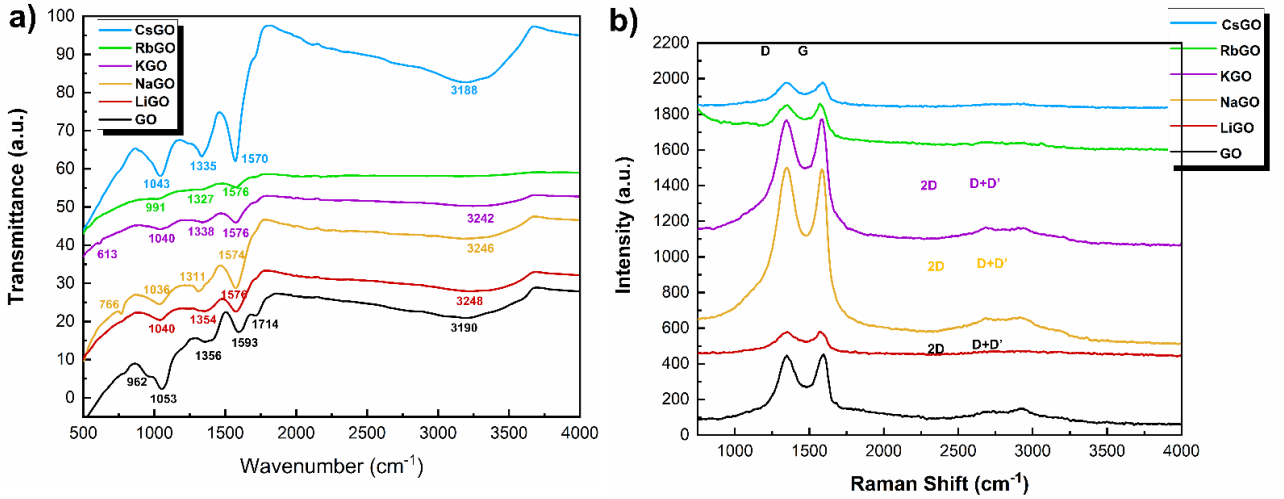

Figure 4. a) ATR-FTIR spectra and b) Raman spectra of M-GOs and GO powders.

2.4. Graphene based inks for consumer/desktop inkjet printing

ICN2 during this initial period has worked on the development of two-dimensional (2D)-materials inks specifically tailored for use into consumer inkjet printing setup. The scope is to develop platforms and electrochemical devices useful in biosensing and biomedical applications. Some of the properties of the graphene like large surface area and the ease of

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functionalization show a promising future for advancement in the field of nanobiomedical technologies.

The requirements of desktop inkjet printer differ from standard research grade equipments. The inks have generally lower viscosities, and also there is the clear disadvantage of fixed printing parameters which does not let space for significant modulation. For these reasons, highly stable and reliable inks are a necessity.

In this period ICN2 focused the efforts into studying the adequate parameters for printing graphene based inks, using reference materials commercially available as a guidelines.

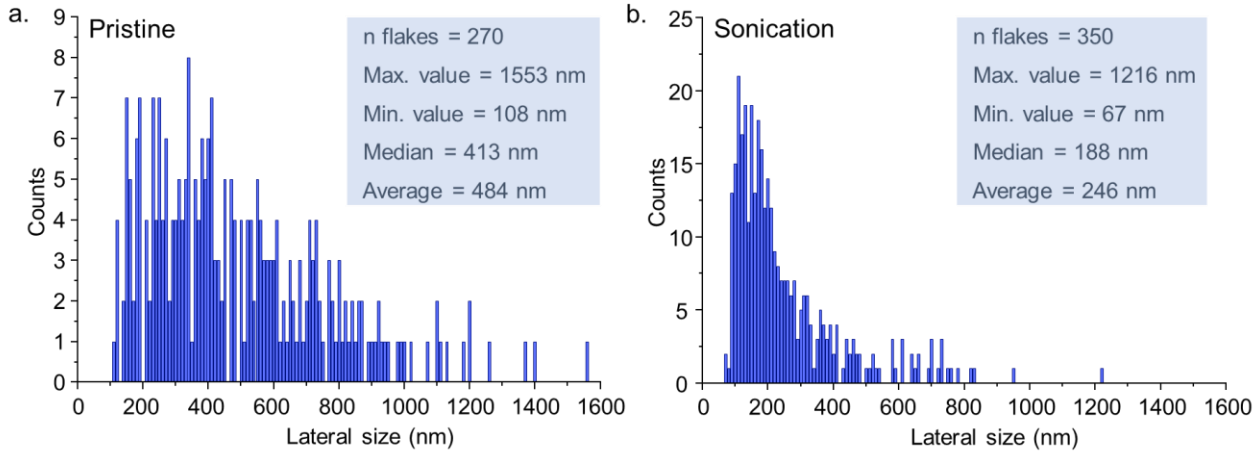

Figure 5. Pristine graphene size distribution before the sonication (a) and after the sonication showing the reduced size and narrower distribution.

It was found that the flakes size of the graphene should not exceed 400 nm so the graphene dispersions used have been sonicated to reduce the dimensions. The chemical stability after the treatment has been assessed using XPS, showing the sonication does not alter the chemical properties of the material.

After this step, the printability of the inks has been investigated showing how EG (25%), Eth (2%) and isopropyl alcohol (1%) were necessary to adjust the rheological parameters of the ink.

The graphene ink was successfully printed onto commercially available substrates and characterized to check the morphology.

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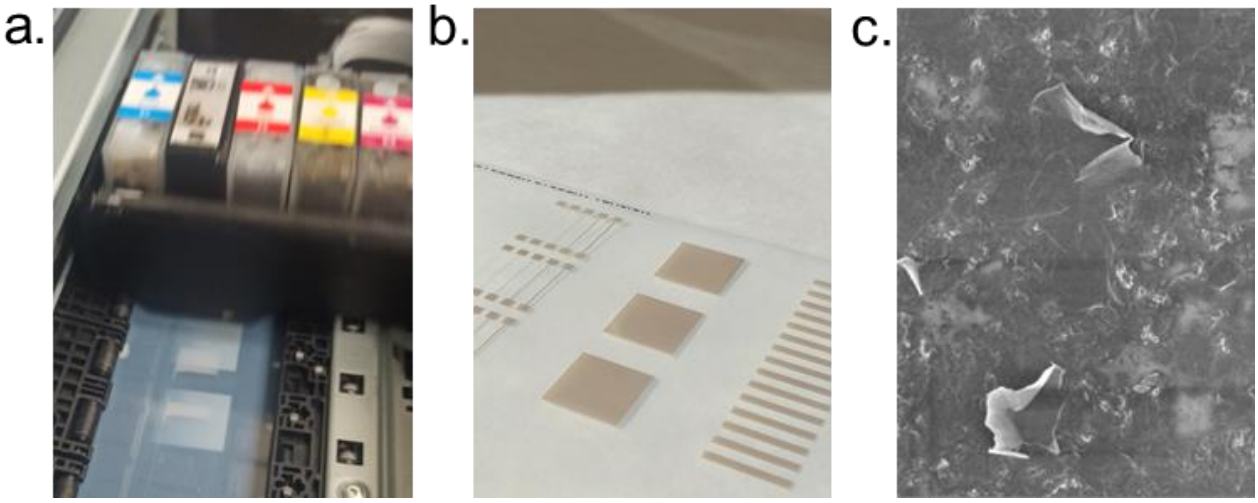

Figure 6. Consumer inkjet printing of the graphene dispersions (a). Printer graphene on a coated PET substrate (b). Morphology of the graphene printed with consumer inkjet printing on coated PET substrate (c). The morphological traits are the ones expected for this type of material.

The resistance has been measured at increasing number of deposited layers. After the printing the materials resulted in being non conductive, so annealing techniques are going to be necessary to achieve good electrical and electrochemical properties.

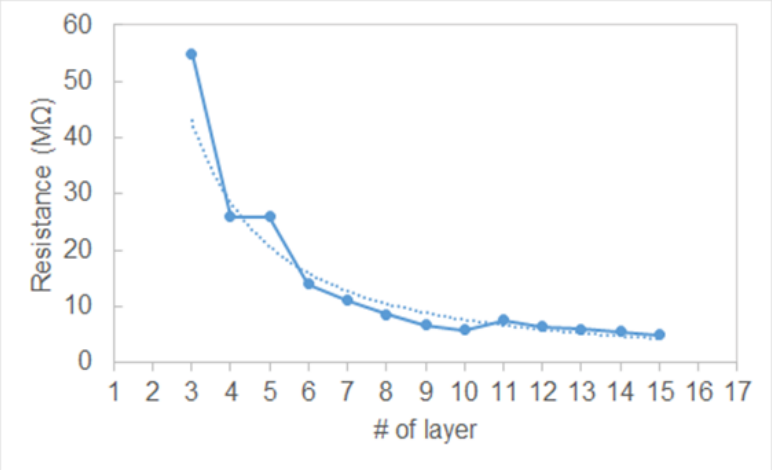

Figure 7. Plot showing the resistance of 2mm lines with the number of printed layers.

The main characteristics for printing the graphene-based inks has been established during the period covered by D10.5 as well as successfully printing the materials. The performed characterizations show the future steps to take for advancing this technology. In the future ICN2 is going to test other materials possibly collaborating with the partners. This will be carried on together with the investigation of possible annealing strategies and chemical treatments to echance the conductivity, as well as fabrication of test devices.

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3. Final Remarks

New semiconducting and conducting functional materials for printed electronics were developed in different ink forms: precursors solutions (ZTO), nanoparticle suspensions (graphene, GO, GRMs) and pastes (for conductive nanomaterials' integration, Ag and graphene). Depending on the ink formulation these materials can be printed using diverse printing techniques such as, flexoprinting, lab-scale and consumer inkjet printing setups and screen-printing. The developments achieved during this periode enhance the capabilities that EMERGE can provide to users.

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