D6.10 Interim Report on the Chemical formulation methods used

WP6

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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Document information

Project details	
Project Acronym	EMERGE
Project title	Emerging Printed Electronics Research Infrastructure
Grant Agreement Nº	101008701
Funding scheme	RIA - Research and Innovation action
Starting date	01/07/2021
Project coordinator	Rodrigo Ferrão de Paiva Martins (UNOVA)
Work package details	
Work package ID	WP6
Work package title	TA2 – Access to material synthesis and characterization
Work package leader	TUD
Deliverable details	
Deliverable ID	D6.10
Deliverable title	Interim Report on the Chemical formulation methods used
Delivery due date	30/06/2024
Author(s)	HMU, WUT, UNOVA
Responsible person for the deliverable	Eirini Koutsouroubi, Konstantinos Rogdakis (HMU)
Nature	Report
Dissemination level	Public
Report details	
Actual submission date	19/07/2024
Number of pages	11
Contact person	Konstantinos Rogdakis (HMU)

Report history

Version Nº	Date	Status	Changes	Contributor(s)
1.0	17/06/2024	*Draft*		(HMU) Eirini Koutsouroubi, Konstantinos Rogdakis, Katerina Anagnostou
1.1	12/09/2024	*Draft*	Content from WUT and UNOVA	Jakub Krzemiński (WUT), Rita Branquinho (UNOVA)
1.2	19/07/2024	*Final*	Final check and submission	Pedro Barquinha, Rodrigo Martins (UNOVA)

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1. Executive Summary

In this deliverable are reported the significant advancements made in the preparation and application of Graphene-Related Materials (GRMs) and oxide inks for various electronic and energy-harvesting devices. GRMs are synthesized from graphite, followed by liquid-phase exfoliation (LPE) to produce inks using environmentally friendly solvents. These inks are deposited onto flexible substrates and further processed for the development of flexible electronic devices. Additionally, the use of perovskite active layers in high-performing solar cells and moisture energy generators (MEGs) has been explored.

In this context, various ink formulations and printing techniques have been developed for flexible, wearable, and self-powered sensors, as well as bio-compatible electrodes for real-time health monitoring devices. These projects have involved the use of advanced equipment for screen printing, ink formulation, and sample testing.

Oxide inks, produced using solution combustion synthesis (SCS), have been optimized for different deposition methods such as flexographic printing, inkjet printing, and slot die coating. These inks are versatile and adaptable for electronic applications such as thin-film transistors (TFTs), sensors, and optoelectronic devices. The continuous optimization of GRM and oxide inks has led to significant progress in the development of flexible electronics and energy storage solutions.

1.1. HMU

HMU follows several chemical synthesis protocols to produce a variety of bulk Graphene Related Materials (GRMs) from pure graphite (Figure 1). The properties and applications of prepared GRMs vary depending on the chemical composition and structure. HMU then uses an ultrasonic probe to produce GRM inks from the synthesized bulk materials through liquid-phase exfoliation (LPE). Depending on the chemical composition of the GRM, several solvents may be utilized for ink preparation, with priority being given to non-toxic and environmentally friendly solvents. HMU has deposited prepared Graphene Oxide (GO) inks onto flexible Polyethylene terephthalate (PET) substrates via custom-made automated spray coater. The resulting GO films were sent to Empa, Swiss Federal Laboratories for Materials Science and Technology to undergo e-beam lithography and laser-patterning for

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robust nanophotonic and flexible electronic devices in harsh environments. HMU has used mixed halide perovskite as active layers in high-performing solar cells. Their rich dynamics enabled by coupled ionic and electronic degrees of freedom have led to the demonstration of optoelectronic memristors [1]. GO and RGO inks prepared at HMU via LPE have been forwarded to FZJ for HSP measurements. Aqueous GO inks are prepared via LPE and used to fabricate moisture energy generators (MEGs) which can be tuned to produce different levels of output depending on the electrode surface area and the humidity level [2]. Water-based GO, RGO and GO-PEDOT:PSS are currently being formulated at HMU and deposited via inkjet-printing on flexible substrates at ICN2 to produce improved MEG devices. Another study at HMU also investigated the possibility that organic–Inorganic Halide Perovskites (OIHP) deployed across an inverted solar cell geometry might generate electricity [3].

Preparation of graphene related material (GRM) Inks and Films

Bulk GRM powders are prepared following chemical protocols from pure bulk graphite powder. Graphite oxide is prepared via chemical oxidation of graphite following a modified Hummers' method [2,4]. Reduced Graphite Oxide is prepared via chemical reduction of Graphite Oxide using reducing agents such as Hydroiodic Acid (HI) or L-Ascorbic Acid (L-AA or Vitamin C) [4,5]. The synthesised Graphite Oxide and Reduced Graphite Oxide powders are characterized via X-ray Photoelectron Spectroscopy (XPS), Attenuated Total Reflectance Infrared (ATR-IR), Raman spectroscopy as shown in Figure 2, to evaluate their chemical makeup, ensure successful chemical oxidation or reduction and measure their oxygen content. The synthesis of RGO from GO using L-Ascorbic Acid is outlined in Figure 1.

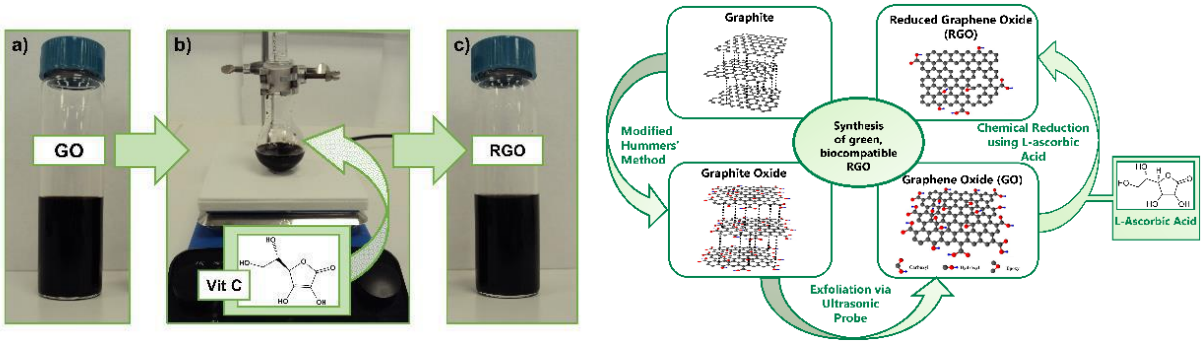

Figure 1. (Left) Chemical reaction of GO with L-Ascorbic Acid (VitC) to prepare RGO in an aqueous environment. (Right) Summary of methodology for RGO(VitC) synthesis from pure graphite

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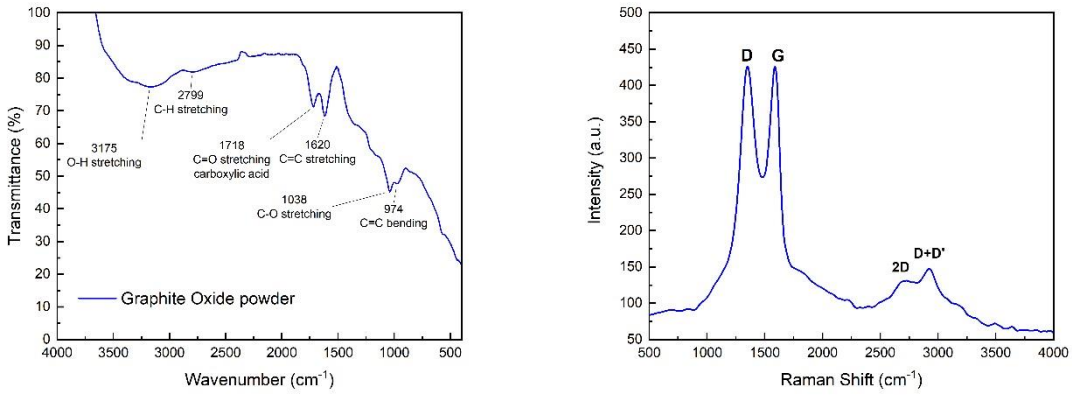

Figure 2. (Left) ATR-IR and (right) Raman spectrum of Graphite Oxide powder prepared via modified Hummers' method at HMU.

All GRM inks are prepared from the respective bulk materials via LPE using an ultrasonication probe Hielscher UP200Ht (200W, 26kHz, at 100% amplitude). Various solvents may be used depending on the chemical composition of the GRM, e.g. graphene oxide (GO) is readily dispersed in water owing to the high content in oxygen functional groups, whereas reduced graphene oxide (RGO (HI) is more easily dispersed in non-polar solvents such as o-Dichlorobenzene (o-DCB). A typical LPE preparation of GO in water is performed with 1 h ultrasonication at (200W, 26kHz, at 100% amplitude). Centrifugation (9000 rpm/5 min) is utilised to remove any unexfoliated particles and/or aggregates and ensure the supernatant, which is the final GRM ink, is uniform. Additives such as surfactants and polymers may be included to tune the rheological properties of the prepared inks. This allows for the inks to be modified to suit different deposition methods and ultimately assists in better film formulation upon deposition. GRM inks are continuously being optimised by tuning the LPE parameters, solvent and additive selection, rheological properties, material concentration, etc. This allows HMU to modify their inks to fit various film deposition methods, thus adapting them to be incorporated into more types of electrical, optoelectronic, energy and sensing devices.

GRM-based films are prepared from the respective GRM inks via spray coating using a commercial air gun. The ink is deposited on a rigid (e.g. glass) or a flexible (e.g. PET) substrate which is mildly heated to aid solvent removal and formulation of a solid thin film. The substrate undergoes O_2-plasma treatment in order to make the surface mor hydrophilic which promotes the creation of a uniform and continuous nanomaterial film. The optoelectronic properties of HMU's solid thin films are evaluated using Ambient

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Photoemission Spectroscopy (APS), four-point probe and Hall Effect measurements as well UV-Visible absorption spectroscopy. The surface topography and roughness are measured using Atomic Force Microscopy (AFM).

1.2. WUT

During the TA project no. 3651, carried out for IHTM, University of Belgrade, throughout 3 days of the visit, the printing pastes' samples prepared beforehand were printed manually (custom-made printing table) and automatically (Aurel C920). After curing (Memmert UF30 chamber heater), the samples were examined.

During the TA project no. 4009, carried out for Milija Sarajlic (IHTM, University of Belgrade, Serbia), the process of screen printing and paste preparation was implemented for flexible, wearable, self-powered sensor used as human respiration detector. Within the 5 days of project, we prepared: 4 aluminium-based pastes (60% aluminium on 10%PMMA, 55% aluminium + 5%MgO on 10%PMMA, 55% aluminium + 5%Al2O3 on 10%PMMA, 55% aluminium + 5%SiO2 on 10%PMMA), 3 pastes on oxides (25%MgO on 10%PMMA, 40%Al2O3 on 10%PMMA, 25%SiO2 on 10%PMMA) and 3 carbon pastes (12%GNP on 8%PMMA, 7%CNT on 8%PMMA, 25%Graphite + 5%CB on 8%PMMA - finally replaced with -25%Graphite+ 5%CB on LAROFLEX)
For preparation of the pastes we used:

- hotplate stirrers Heidolph MR Hei Tec,
- laboratory scales,
- three roll mill EXAKT 80E,
- Kakuhunter Planetary Mixer SK-350TII CE.

Then the bilayer structure was printed in 21 material configurations, on two substrates, using Aurel C920 screen printer and dried using PolEko dryer and Memmert chamber dryer. Then samples were subjected to further examination.

During the TA project no. 4001 carried out for Levidian Nanosystems Limited formulating screen printing ink/paste application for resistive heater application was done. Within the 10 days of project, we obtained graphene nanomaterials, which were used for the manufacture

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of screen printing pastes. The samples were prepared using Aurel C920 semi-automatic screen printer and subjected to further testing.

During the TA project no. 4083 (revised 4010) carried out for Kyoko Jansson, Noui Life (Sweden), flexible electrodes for non-invasive real-time bladder monitor were investigated. The project included designing and manufacturing the printing screens and preparation and characterization of samples. For the preparation of carbon-based pastes we used:

- EDAG PF-407A
- an experimental biodegradable composition.

The samples were printed using Aurel C920 semi-automatic screen-printer and then examined.

During the TA project no. 5826 carried out for Marta Corvo, Nova FCT (Portugal), 2D/3D CELL-PILs for tissue engineering were investigated. The preparation of the samples required using:

- hotplate stirrers Heidolph MR Hei Tec,
- laboratory scales,
- Kakuhunter Planetary Mixer SK-350TII CE.

This work included the design of three different patterns and adjusting the printing parameters for each of them. The printing process was carried out on CELLINK 3D bioprinter BIOX.

During the TA project no. 6497 carried out for Kyoko Jansson, Noui Life (Sweden), bio-compatible wet-state organic material for a sensitive sensor, was investigated. The project involved design, fabrication (with printing pastes including custom-made compositions), and characterization of the dry electrodes for further modifications. For the preparation of the samples we used:

- Kakuhunter SK-350T II planetary mixer
- AUREL C920 semi-automatic screen-printer,
- chamber dryer Memmert UF 55
- CO_2 cutting laser VLS 2.30.

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1.3. UNOVA

UNOVA's work focused on the chemical synthesis of oxide inks for application as functional layers in electronic devices.

Semiconductor, conductor and dielectric inks have been by solution combustion synthesis (SCS). Solution combustion synthesis (SCS) is similar to sol-gel synthesis where the organic fuel is added to promote an exothermic combustion reaction between the metal oxide precursor and the added fuel, which allows the reaction itself to act as an energy source. This method was used to prepare thin films for electronics which require the deposition of materials onto flexible substrates, low temperature processing and large scale processability.

The produced inks are very versatile and can be easily tuned for different deposition techniques (spin-coating, flexoprinting, inkjet printing, aerosol jet printing and slot die coating) yielding uniform films for electronic devices as TFTs, diodes, PVD and sensors.

Preparation of oxide inks and films

The oxide SCS inks are obtained by dissolution the metal salt, preferably metal nitrate, and an organic fuel, such as urea, in an appropriate solvent (water/alcohol). The fuel can form stable complexes with metal ions which prevents selective precipitation of the metal ions in solution leading to enhanced uniformity in multicomponent oxides. The resulting oxide inks were stirred at room temperature until dissolution was complete, filtered and subsequently stored in cold (Figure 3).

The inks solvent (ethanol, 2-methoxyethanol, 1-methoxypropanol), concentration, viscosity and composition were varied to optimize the film properties. Characterization of the inks was performed by viscosity assessment, FTIR and TG-DSC.

UNOVA prepared AlO_x, Hf-doped InO_x (further details in D10.2), ZnO, SnO and ZTO inks (further details in D10.3, D10.5, D10.6).

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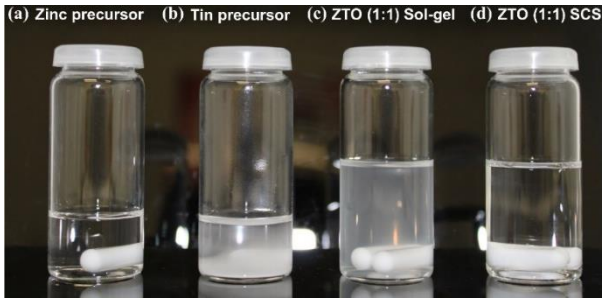

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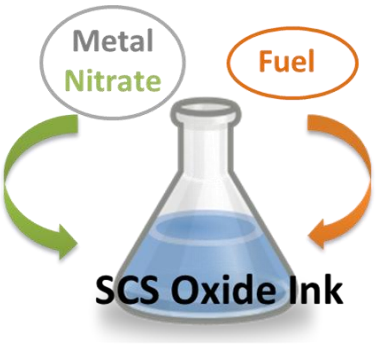

Figure 3. Photograph of the different inks mixed in 1-methoxypropanol (1-MP): (a) zinc precursor solution; (b) tin precursor solution; (c) ZTO (1:1) sol-gel precursor solution; (d) ZTO SCS precursor solution. e) Schematic representation of SCS oxide inks preparation.

ZTO semiconductor inks were further developed, and their properties tuned to allow deposition by different techniques. Increasing the ink's concentration and/or using additives allows for a controlled viscosity variation for both sol-gel and SCS ZTO precursors which is highly desirable for adaptation to different printing techniques and the adjustment of the thickness of deposited layers.

These ZTO inks were successfully optimized for flexographic printing (further details in D10.6) and inkjet printing at UNOVA (further details in D10.5).

ZTO and AlO_x inks were sent to WUT for aerosol jet printing deposition and to FZJ for slot die deposition. In both cases the layers were successfully deposited yielding smooth and uniform films (further details in D10.3).

FZJ produced OPVD devices by slot die coating, using ZnO, SnO and ZTO as hole transporting layer with ZTO films showing the most promising results (further details in D10.3).

Overall solution combustion synthesis-based oxide inks are very versatile and can be easily tuned for different deposition techniques with application in electronic devices.

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