SHORT TERM SCIENTIFIC MISSION (STSM) SCIENTIFIC REPORT

This report is submitted for approval by the STSM applicant to the STSM coordinator

Action number: CA17107 – context
STSM title: Enhancement of electrical conductivity of reduced graphene oxide synthesized by thermal reduction
STSM start and end date: 15.11.2020 to 15.12.2020
Grantee name: Siamak Eqtesadi

PURPOSE OF THE STSM:

The use of e-textiles and their integration into clothing have been faced several challenges which are hindering commercialization of these products in important sectors like medicine, sport and military.

Graphene and its derivatives have unique features offering great promise for many applications including e-textiles or smart wearable due to its outstanding electrical, mechanical, and thermal properties and its ability to act as a very good platform for both transistors and sensors. Reduced graphene oxide (rGO) is a form of graphene that can be produced in scalable quantities from graphene oxide (GO) through a reduction process. The most commonly used commercial method to fabricate large quantities of graphene derivatives is based on the Hummers method. Graphite oxide can be readily exfoliated into single/few-layer GO sheets, and then GO will be converted to graphene through reduction. The reduction methods of GO are mainly categorized into chemical reduction and thermal reduction. Typical chemical reduction of GO often requires strong reductants which are hazardous or toxic. Other chemical reduction methods, such as green reductants are not applicable for industrial-scale production. Therefore, thermal reduction remains as main synthesis route for production of rGO in large quantities. In thermal reduction, the quality of GO as well as various reduction process parameters play a critical role in obtaining rGOs with properties needed for final application.

The main goal of this work is synthesis and characterization of highly conductive rGOs obtained from GOs with different degree of oxidation.

DESCRIPTION OF WORK CARRIED OUT DURING THE STSMS

The work done can be summarized as follow:

1- ***Synthesis of GOs****:* The GO is synthesized by proprietary methods at Abalonyx's production facility by the oxidation of graphite into graphite oxide followed by the exfoliation of this graphitic oxide into

GO. The GO possess a monolayer or just a few stacked layers, while graphite oxide contains a greater number of stacked layers. Degree of oxidation was changed through different parameters involved such as amount of oxidizing agent, temperature, reaction time and initial graphite particle size. Two GOs with 85% and 100% of oxidation degree were selected as the initial materials for the synthesis of rGOs. These two GO has been denoted as GO85 and GO 100,respectively.

2- ***Synthesis of rGOs****:* The synthesized GOs were thermally reduced to obtain rGOs. For this purpose, two different senarios were hired. In the first approach, GO powder is partly reduced by applying fast heating or flash pyrolysis in air at low temperatures (~200-400°C). This process is reproducible and partly automated. The rGOs obtained by flah pyrolysis of GO 85 and GO100 are denoted as GO85FP and GO100 FP, respectively. In the second approach, the GO85FP and GO100 FP, which are partially reduced GOs, were heated in a vacuum furnace with a constant heating rate at high temperatures (800-1200°C) for 1 h. The obtained rGOs were denoted as GO85FP Ann and GO100 FP Ann. The vacuum furnace is shown in Figure 1.

Fig 1. The vacuum furnace used for almost fully reduction of GO.

3- ***Characterization of the materials:*** In a collaboration with Servicios de apoyo a la investigación (SAIUEx), different characterizations such as XRD, XPS, FTIR, Raman, BET and electrical measurements were done to evaluate the characteristics of synthesized GOs and rGOs

DESCRIPTION OF THE MAIN RESULTS OBTAINED

1- Characterization of GOs

1-1 FTIR

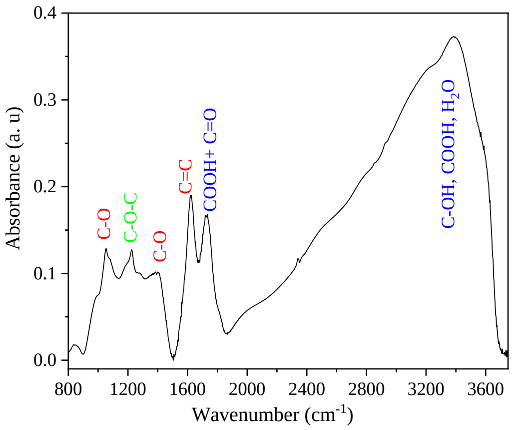

Fig. 2 IR spectra for GO100

C-O	Ethers	800-1200 cm^{-1}
C-O-C	Epoxides	1230-1330 cm^{-1}
C=C	sp^2 carbon	1550-1650 cm^{-1}
COOH	Carboxyls	1700-1900
C=O	Ketones (Carbonyls)	1650-1850 cm^{-1}
C-OH	Hydroxyls	3000-3700 cm^{-1}

Generally, the modified Hummer's method leads to strong infrared absorbance associated with the C-O/COOH and C-OH regions of multilayered GO with a sharp peak at 3000-3700 cm^{-1} due to larger hydroxyl, carboxyl, and water contribution (Fig.2). The shapes and widths of the bands give information about the concentration of each oxygen species specific to each sample under consideration.

1-2- XRD

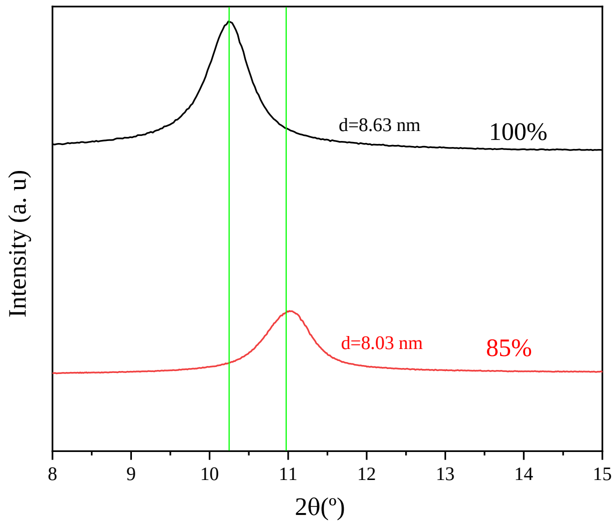

Fig. 3 The XRD patterns for GO85 and GO100.

The XRD patterns of GOs with 85% and 100% are shown in Fig. 3 confirming the successful conversion of graphite to GO by emergence of an intense peak at ~ $2\theta = 11°$.
Increasing the oxidation degree from 85% to 100% results in a clear shift to smaller angels due to oxidation and intercalation of more oxygenated groups in GO layers resulting in bigger interlayer spacing (d).

2- Characterization of rGOs

2-1- FTIR

The IR spectra for different rGOs obtained from GO85 and GO100 are shown in Fig. 4.

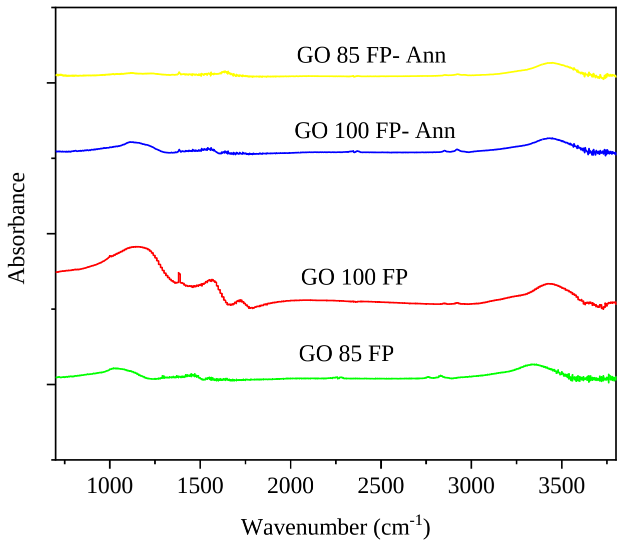

Fig. 4 IR spectra for indicated rGOs.

In comparison with IR spectra for GO100 (Fig. 2), it can be seen that:

- The intensity of OH peak is mostly reduced for all rGOs.
- For GO 100 FP, the C=O is partially reduced since it is not completely removed and still observable however in the case of GO 85 FP the removal of C=O is more pronounced. Some new C-O can be formed around 800-1200cm^{-1}.
- For GO 100 FP Ann and GO 85 FP Ann samples, most of the remained O groups has been already removed and only a slight contribution of OH an and C-O can be detected.

2-2- XRD

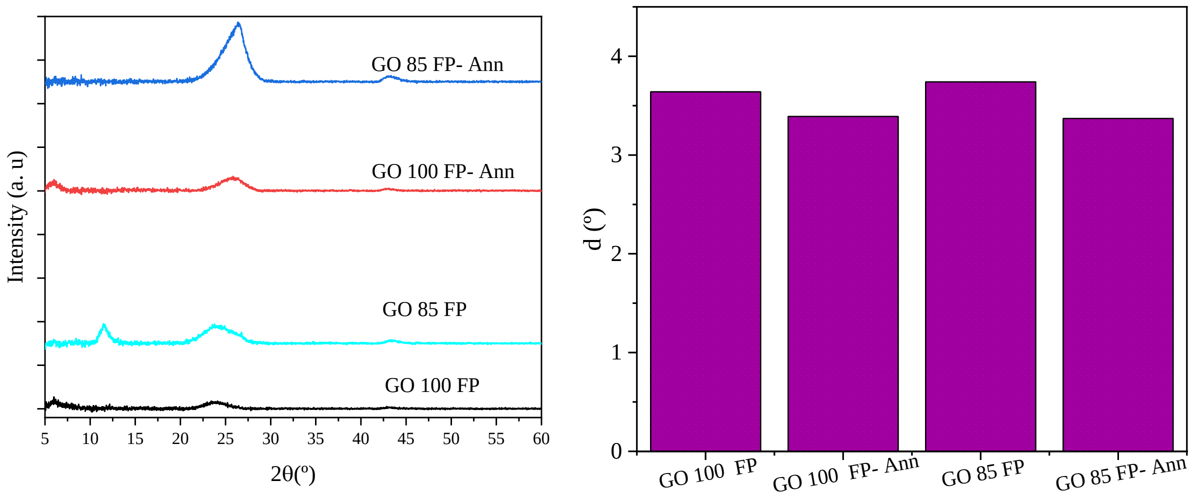

Fig. 5 XRD patterns for different rGOs as well as corresponding interlayer (d) spacing.

- After reduction of GOs to rGOs the main peak at ~ $2\theta = 11°$ is disappeared and a peak at ~ $2\theta = 24°$ appears.
- The interlayer spacing, d, can be used as a factor for discussing efficiency of oxidation/reduction processes. In the case of reduction, the decrease of d due to O removal is expected to happen by increasing reduction temperature.
- As it can be seen GO 100 FP has a smaller d spacing compared to GO 85 FP.
- After annealing under vacuum and at high temperatures the d is reduced furthure and both GO 100 FP Ann and GO 85 FP Ann both show almost the same d spacing.

2-3- Raman

The ratio of the intensities of the two bands (I_D/I_G) in Raman spectra could be used as a means to measure the defects present in the rGOs. The bigger the value of I_D/I_G is, the more disordered and defective rGO is.

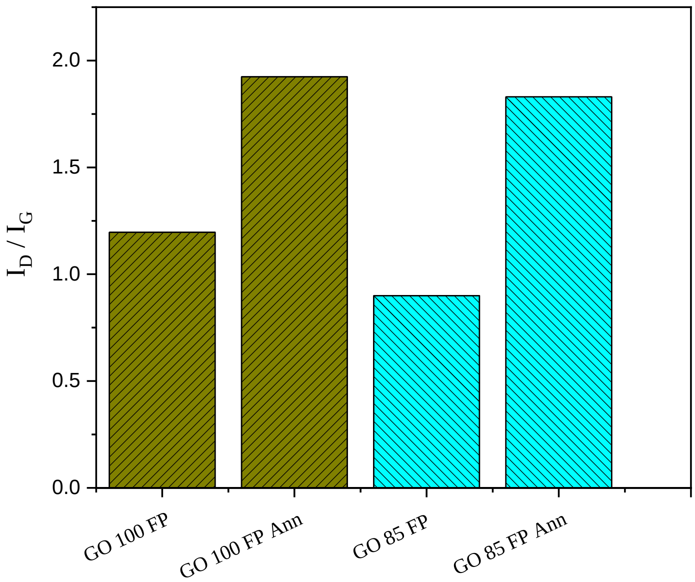

Fig. 6 The ratio of the intensities of the two bands (I_D/I_G) in Raman spectra

- Generally, I_D/I_G is increased due to C loss and defect formation.
- GO 85 FP and GO 85 FP Ann are less defective compared to GO 100 FP and GO 100 FP Ann.

2-4- XPS

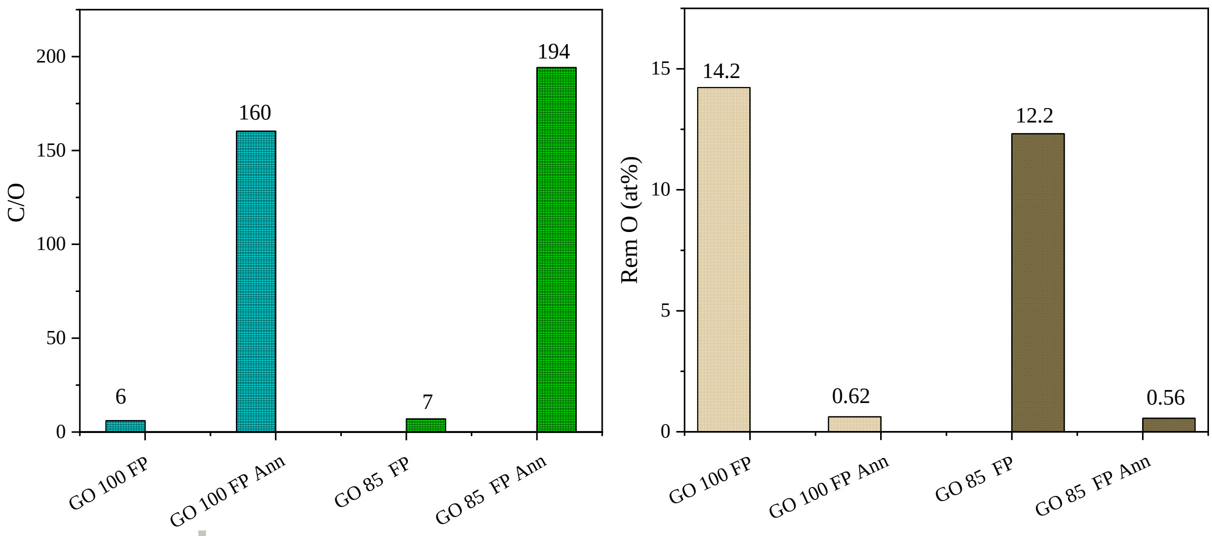

Fig. 7 The C/O ratio and Remained O in at% for four synthesized rGOs.

- The C/O ratio and remained O shown in Fig. 7 indicate that for obtaining rGOs with less than 1 at% remained O, They must be annealed at temperatures higher than 1000C.
- The removal of the last 1 at% remained O is so important and difficult.

2-5- BET

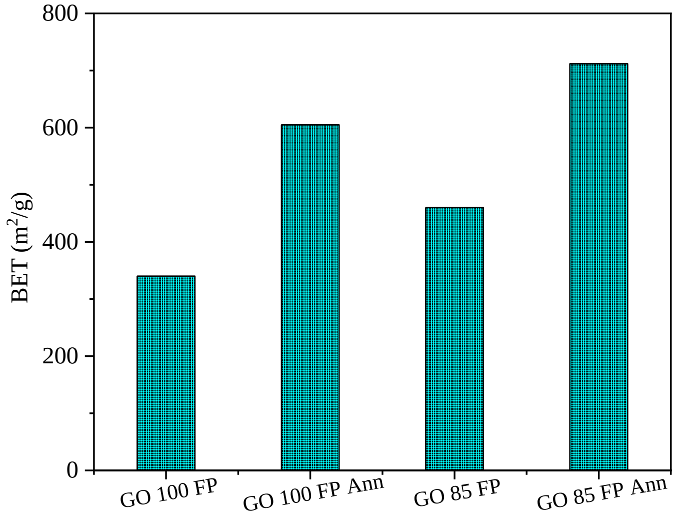

Fig. 8 The specific surface area obtained from BET analysis

- The specific surface area GO85 FP and GO100 FP was determined as around 320 m^2/g and 450 m^2/g, respectively.
- The annealing treatment of GO85 FP and GO100 FP increased the BET numbers to 600 m^2/g and 700 m^2/g for GO85 FP Ann and GO100 FP Ann, respectively.

2-6- Electrical Conductivity

- In the case of powder and porous materials such as graphene derivative materials, the determination of the electrical conductivity is rather complicated. Here, the electrical conductivity is studied under very low compression for different synthesized rGOs.

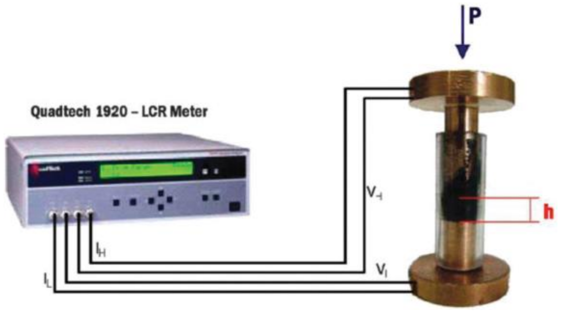

Fig. 9 Set up used for measuring the electrical conductivity of powdered materials under low /moderate compression [1]⁎.

⁎ A. Barroso-Bogeat et.al, Electrical conductivity of activated carbon–metal oxide nanocomposites under compression: a comparison study, Phys Chem Chem Phys. 2014 Dec 7;16(45):25161-75.

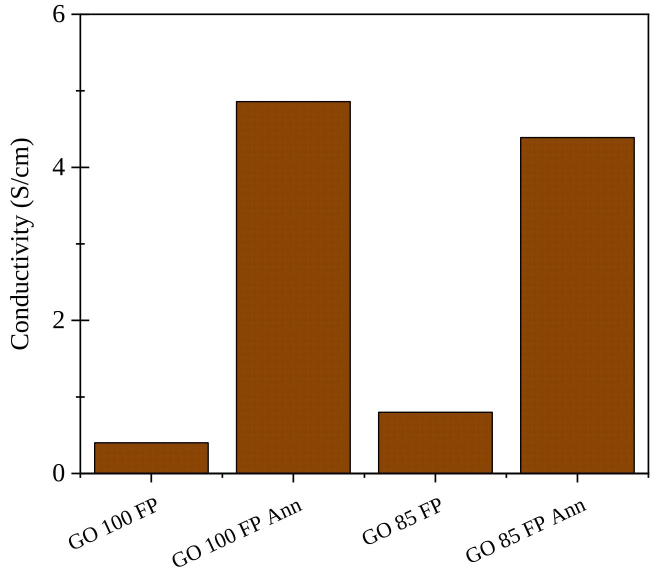

Fig. 10 Electrical conductivity of synthesized rGOs

- The electrical conductivity of GO 85FP and GO 100FP lay within the medium range conductivity and make it applicable for using in an ink recipe with aqueous solvents.
- The electrical conductivity of GO 85FP Ann and GO 100FP Ann are considered as rGOs with very high conductivity and hydrophobic. This characteristic may make it difficult for a good dispersion in aqous solvents used in ink printing.

3- Summary and conclusions

- Two types of GOs with 85% and 100% oxidation degree were synthesized and used as precurours for rGOs obtained by thermal reduction.
- The material were characterized microstructurally
- It was concluded that the level of defects present in graphene derivatives affects majorly on the electrical conductivity.

FUTURE COLLABORATIONS (if applicable)

- Abalonyx will be happy to provide free samples (limited quantities) for the COST members who are interested to work on graphene derivatives.
- The collaboration with Unex will be continued and also two of synthesized rGOs might be tested in ink development in order to validate functionality of rGO as an additive in printing.