

**Finest High-quality Natural and
synthetic polymer substrates and fibers
innovative plasma treatments for
fashion
MUSA Project- Spoke 5 Fashion**

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Summary

- State of the art
- Fabrication of Graphene Oxide
- Characterization techniques
- Results
- Plasma treatment on Polymers
- Deposition of GO on Polymers
- Discussion
- Future Aspects

Motivation

- Textiles going beyond clothing, actively contributing to well-being and comfort.
- Reshaping textiles through nanoscale surface modifications and plasma treatment.
- Introducing GO, rGO, and rGOQD's coatings to adapt textiles to diverse applications (UV protection, antistatic, antibacterial, thermoregulating, photoluminescent finishes, improvement of mechanical properties, flexible supercapacitors, sensors) *Nascimento et al. 2021[1]*.
- Revolutionize **antibacterial** and **comfortable** (thermoregulating) textiles for clothing, paving the way for applications in healthcare, sportswear, and beyond.

State of the Art

Innovation in Textile Industry: Weaving the future

- ❑ "Traditional textiles face challenges—limited durability, suboptimal wettability, and a lack of specialized functionalities. These challenges demand innovative solutions to propel textiles into the future.
- ❑ Plasma Treatment on textiles
- ❑ Coating on Textiles
- ❑ Different Textile materials respond uniquely depending on structures.

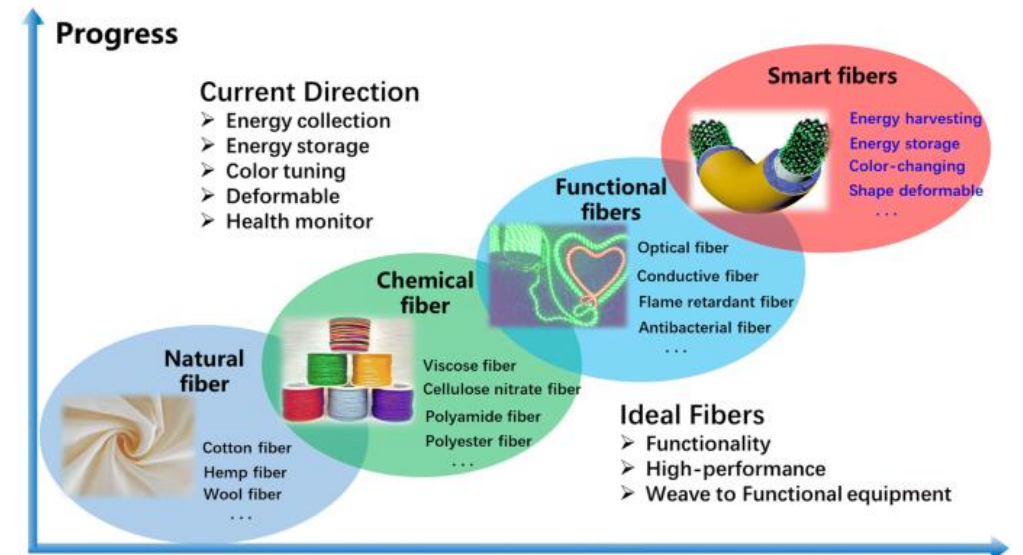


Fig 1. Innovation in textile industry

State of the Art

Graphene Oxide (GO), rGO, rGO-QD's: As a coating material

- Graphene Oxide, formerly called graphitic oxide, is a compound of carbon, oxygen, and hydrogen, obtained by treating graphite with strong oxidizers
- Structurally, GO can be visualized as a graphene sheet with its basal plane decorated by oxygen-containing groups.
- GO can be reduced to acquire rGO. Reduction eliminates the majority of the carbonyl, carboxyl, hydroxyl, and epoxy groups on the GO sheets

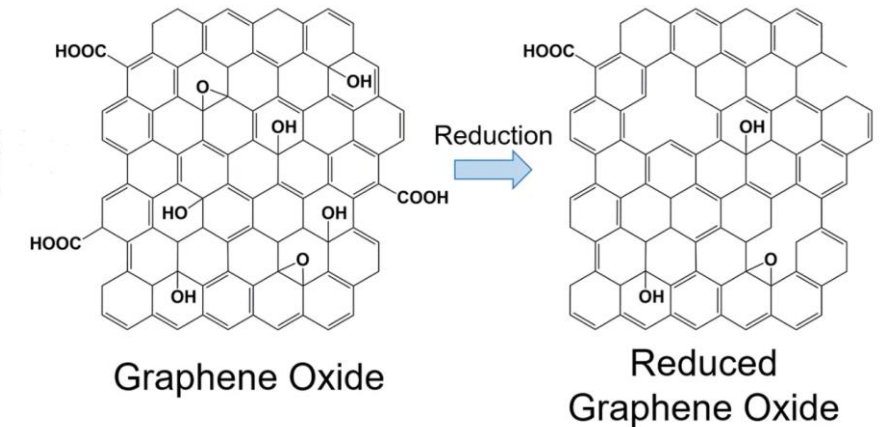


Fig 2. Structure of GO and rGO

State of the Art

Graphene Oxide (GO), rGO, rGQD's: As a coating material

- rGO-QDs, as a new type of zero-dimension quantum dot, have become one of the hottest interests compared to graphene form due to their unique properties originating from the quantum confinement effect
- rGO-QDs have non-toxicity, chemical stability, excellent photostability and biocompatibility

State of the Art

Methods:

- Modified Humers Method ---- for fabrication of GO
- Simple Dipping Method ----- for deposition

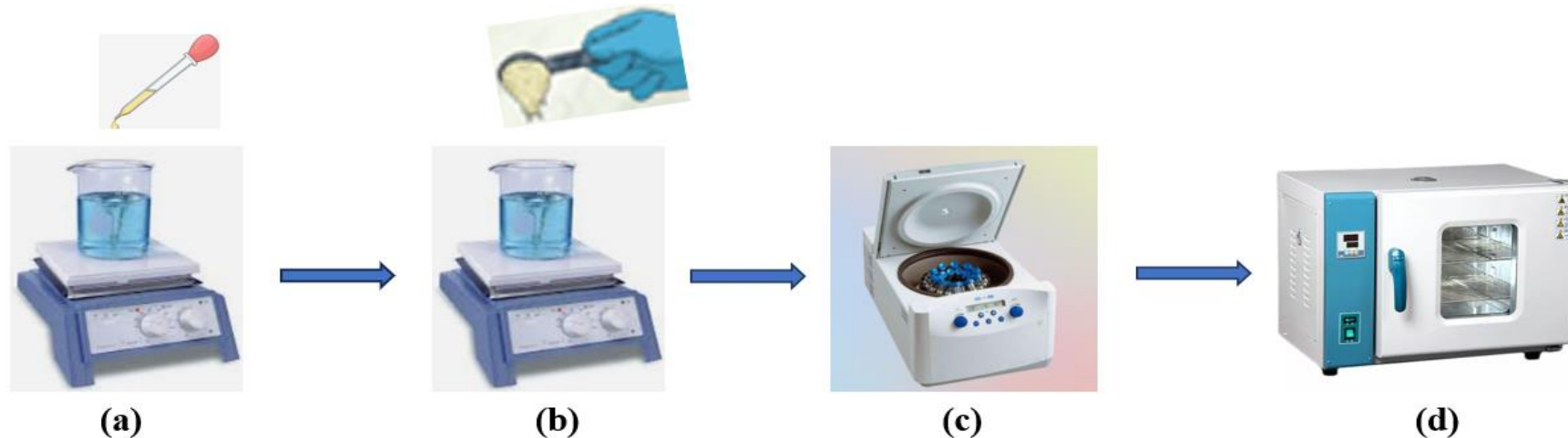


Fig. 3 Modified Humers Method (a) Stirring condition (b) Stirring condition adding powders (c) Centrifugation (d) Drying in Oven

Fabrication of Graphene Oxide

- ❑ Modified Humers Method *Zaaba. et.al 2017*[2]
- ❑ 27 ml of sulfuric acid (H_2SO_4) and 3 ml of phosphoric acid (H_3PO_4) (volume ratio 9:1) were mixed and stirred for several minutes.
- ❑ 0.225 g of graphite powder was added into the mixing solution under stirring condition
- ❑ 1.32 g of potassium permanganate ($KMnO_4$) was then added slowly into the solution.
- ❑ Stirred for 6 hours until the solution became dark green.
- ❑ To eliminate excess $KMnO_4$, 0.675 ml of hydrogen peroxide (H_2O_2) was dropped slowly and stirred for 10 minutes
- ❑ 10 ml of hydrochloric acid (HCl) and 30 ml of deionized water (DIW) were added and centrifuged 3 times each for 10 minutes
- ❑ The washed GO solution was dried using the oven at 90 °C for 24 hours to produce the powder of GO



At Stirring condition



The solution became dark green



GO after drying



Fabricated GO at weight balance

Fabrication of Graphene Oxide

- ❑ Prepared 4 batches of Graphene Oxide
- ❑ Each batch contains 4 days of fabrication.

Table 1: Weight and characterizations done of fabricated graphene oxide

	1	2	3	4
gram	0.290	0.220	0.295	0.246
XRD	✓	✓		
RAMAN	✓	✓		
SEM	✓	✓		



Characterization Techniques

**RAMAN
SPECTROSCOPY**



**For Structural and
Molecular Vibrations**

**X-RAY
SPECTROSCOPY**



**For Structural
Analysis**

**SCANNING
ELECTRON
MICROSCOPE**



**For Morphological
Analysis**

* Raman and XRD characterization was done by the collaboration of Material Science Department of Milano Bicocca and SEM was done by the collaboration of the Centre of Microscopy.

Results

Raman Spectroscopy of GO

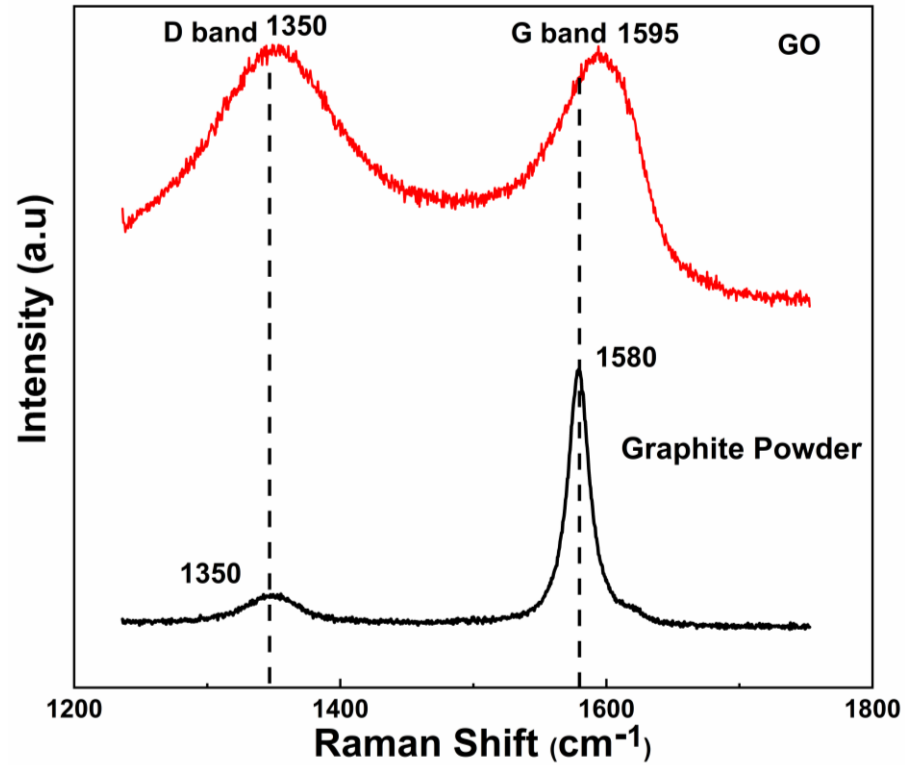


Fig. 4 Raman of Fabricated Graphene Oxide and Graphite Powder

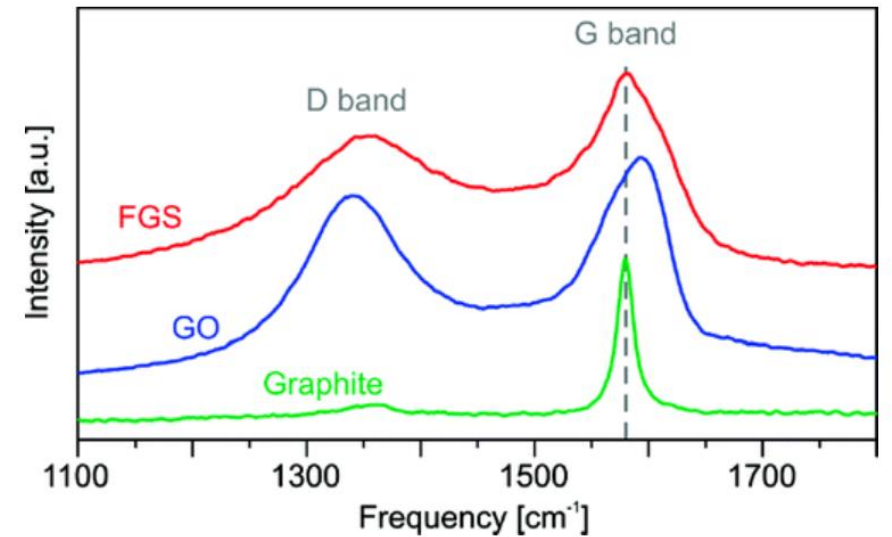
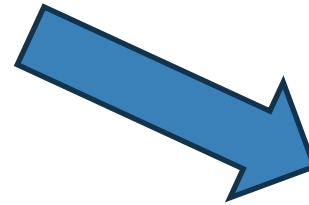


Fig. 5 Raman of Graphite Powder and Graphene Oxide in Literature. *Kudin et al. 2008* [2]

Results

X-ray Spectroscopy of GO

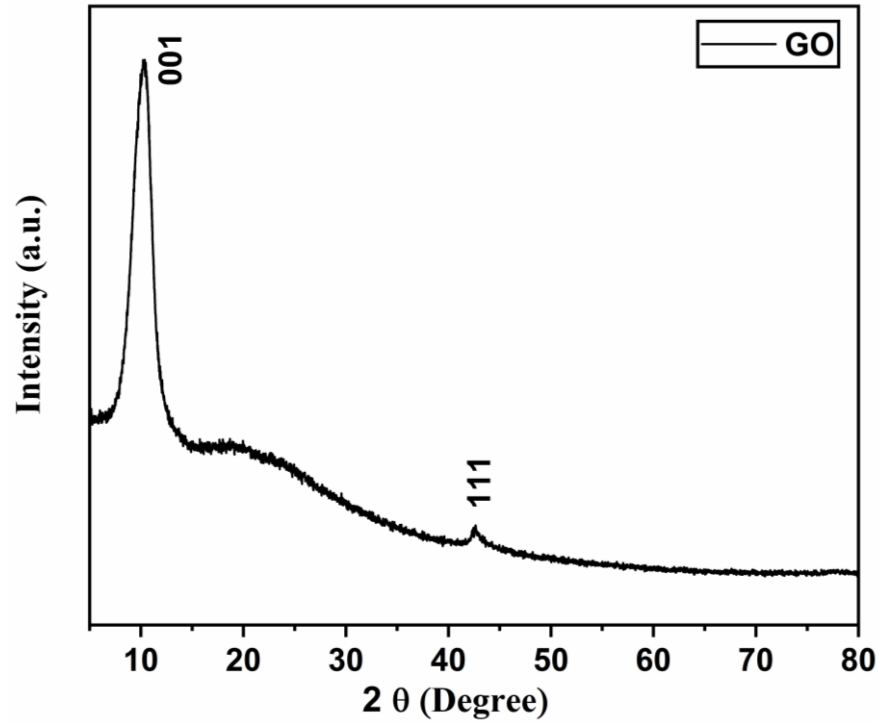


Fig. 6 XRD of Fabricated Graphene Oxide

Table 2: Crystallite size, lattice strains, and dislocation density calculation for GO

S.No	hkl	d-spacing (nm)	2θ(degrees)	FWHM	Crystallite size (nm)	Lattice Strain	Dislocation density
1	001	0.84	10.3	0.16	50.2	0.808	0.0003
2	111	0.21	42.6	0.1	92.7	0.111	0.0001

Average crystallite size = 71.45nm

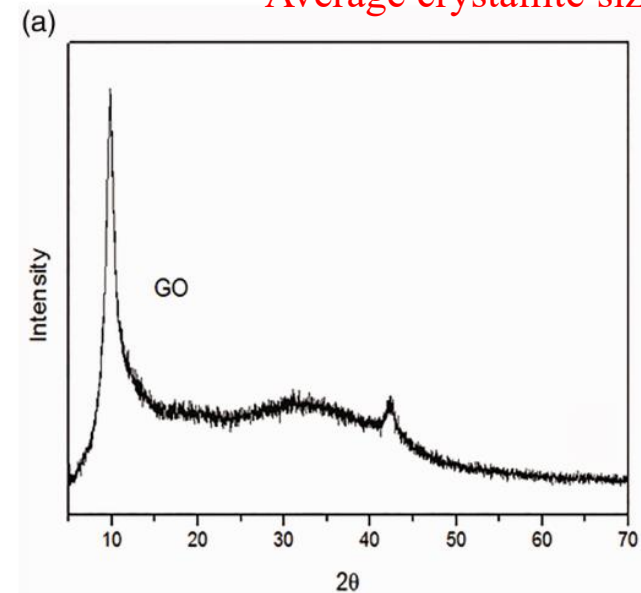
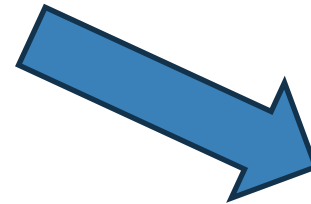


Fig. 7 XRD of Graphene Oxide in Literature *Thy, et al. 2020[3]*

Results

Scanning electron microscope (SEM) of Graphite powder and GO

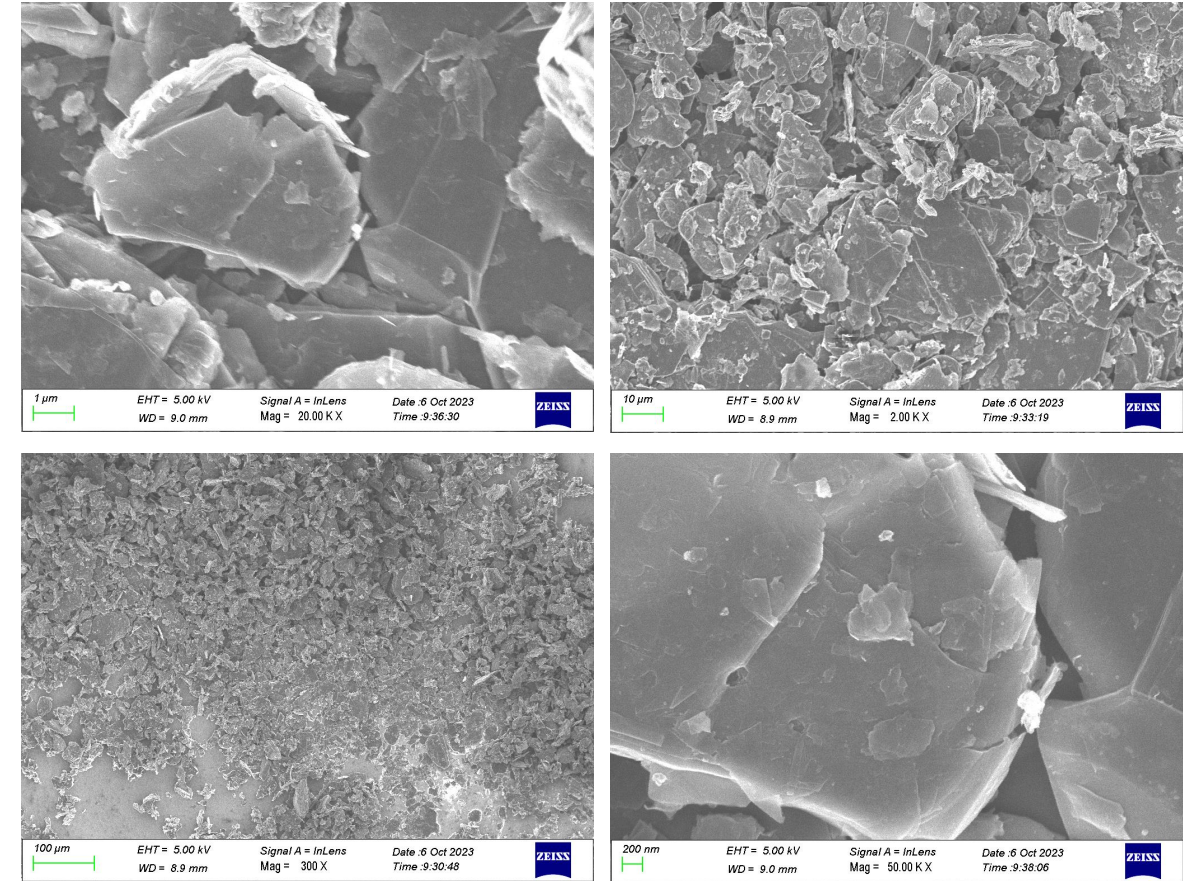
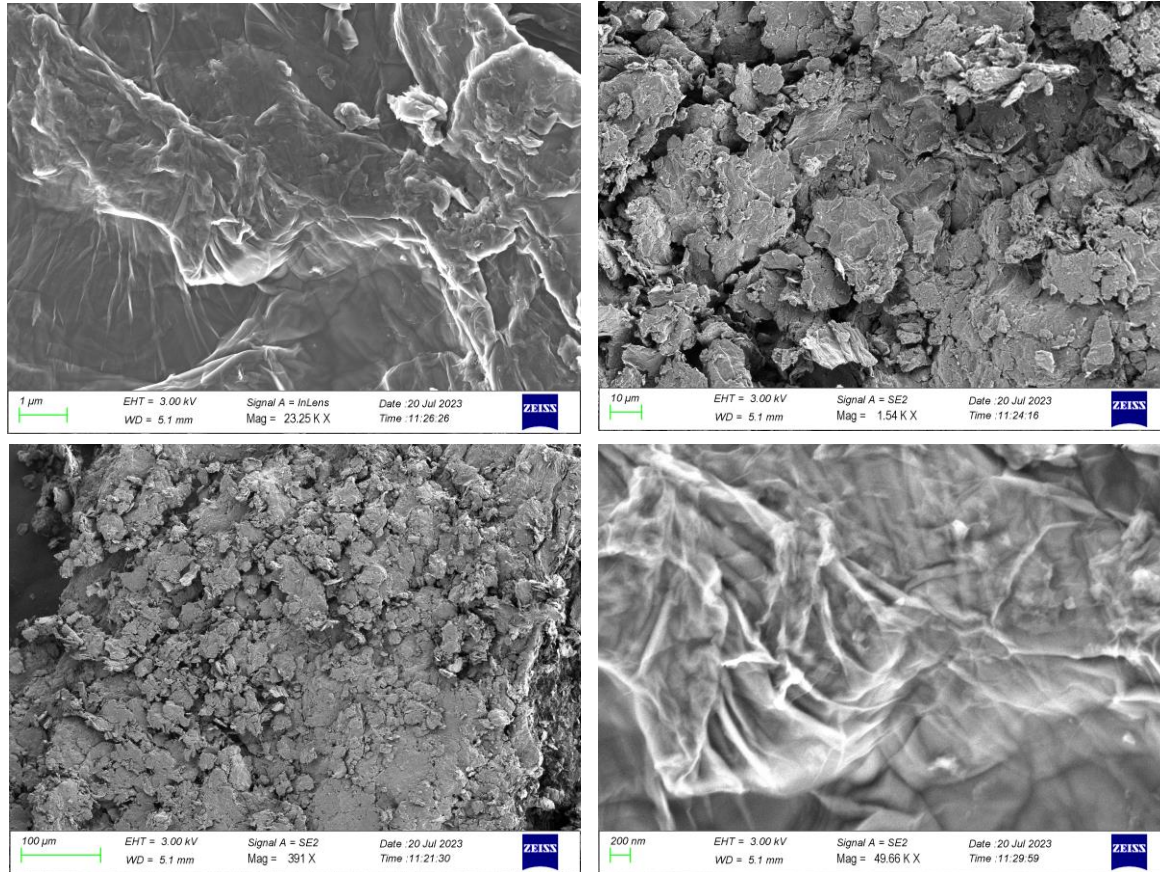


Fig. 8 SEM images of Graphene Oxide at 1 μm, 10 μm, 100 μm, and 200nm

Fig. 9 SEM images of Graphite Powder at 1 μm, 10 μm, 100 μm, and 200nm

Plasma Treatment Setup

- Plasma treatments were carried out to enhance surface area and change the wettability by **chemical etching**.
- On polymeric (PET, PP, Teflon, Polycaprolactone) fabrics

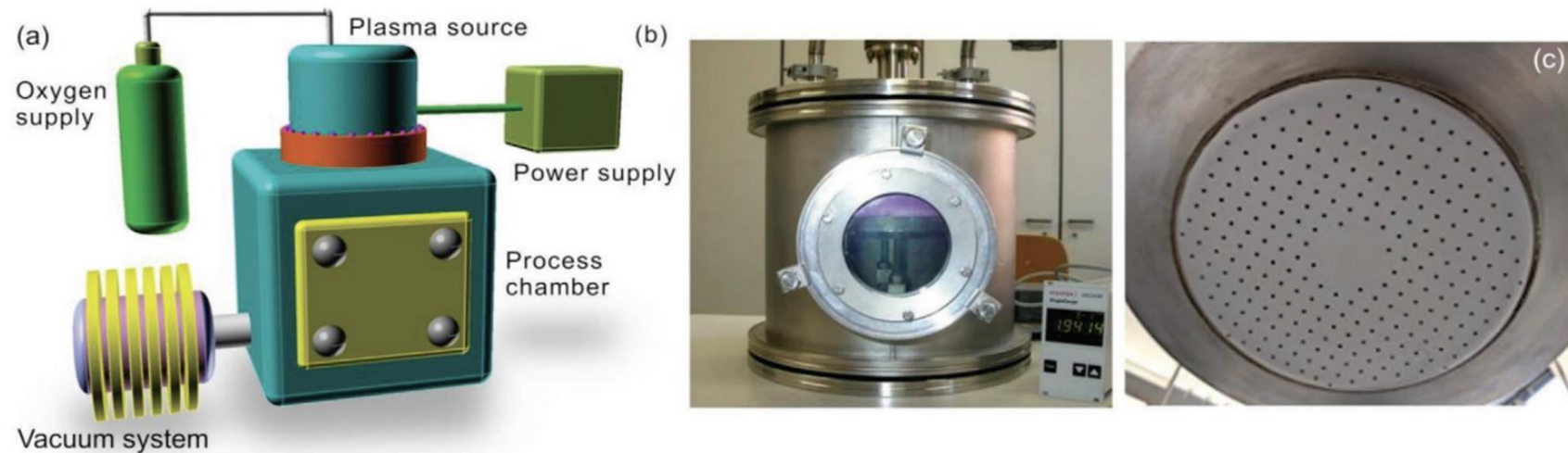


Fig. 8 a) General schematics of the experimental setup, b) photograph of the process chamber with ignited plasma and of the upper aluminum plate (upper electrode) with about c) 250 holes of 2 mm diameter spaced at a distance of 10 mm

Plasma Treatment on Polyethylene tereftalato (PET)

- The Oxygen-Plasma was performed by an inductively coupled generator with an output power of 100W at 13.56MHz.
- The Pressure was assessed by a vacuum gauge of 1.5×10^{-1} mbar.
- The samples were placed in the discharge chamber, at a distance from the antenna between 2 and 5 cm, and treated for 2 min up to 30 min.

SEM Results of Non-Treated and Plasma-Treated (PET)

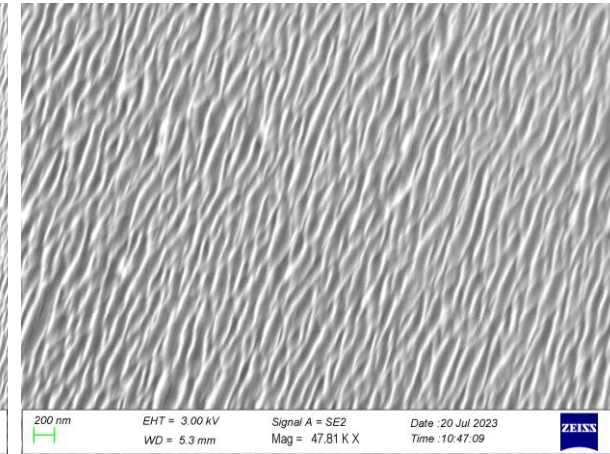
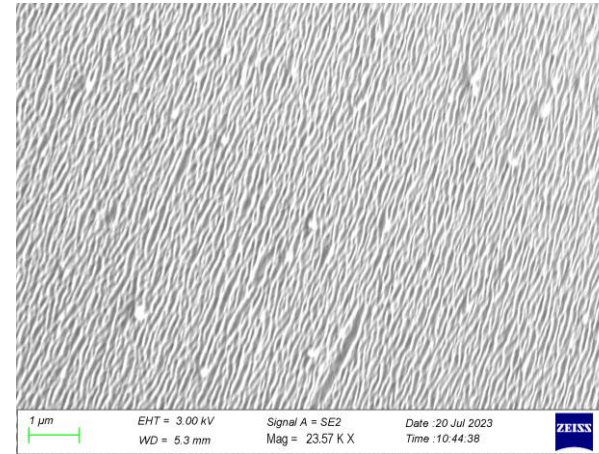
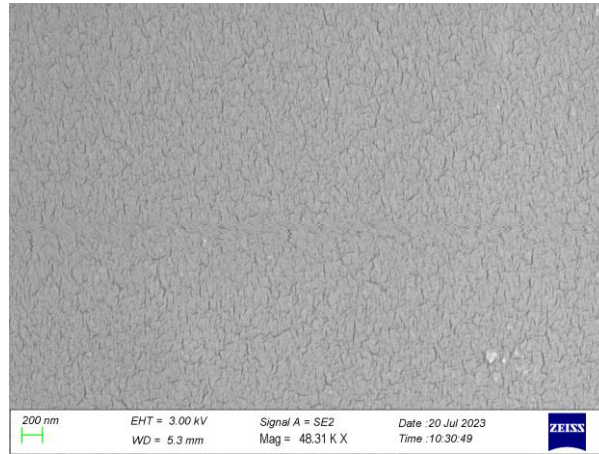
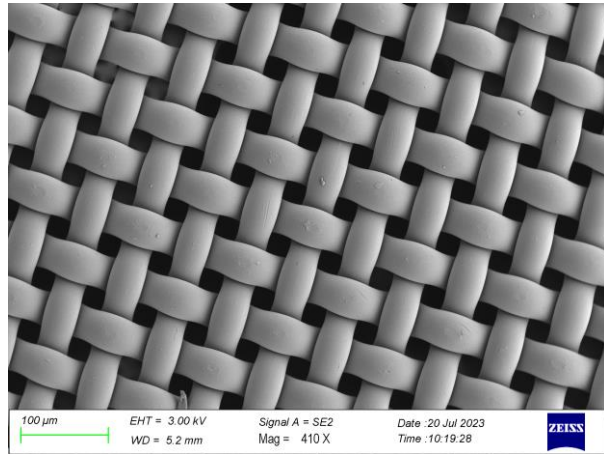


Fig 9. SEM images of non-treated PET Fabric at a) 100 μm b) 200nm

Fig 10. SEM images of 2mint Plasma-treated PET Fabric at a) 1 μm b) 200nm

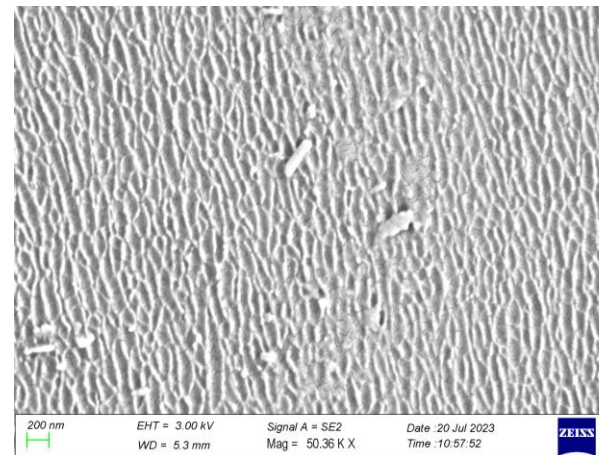
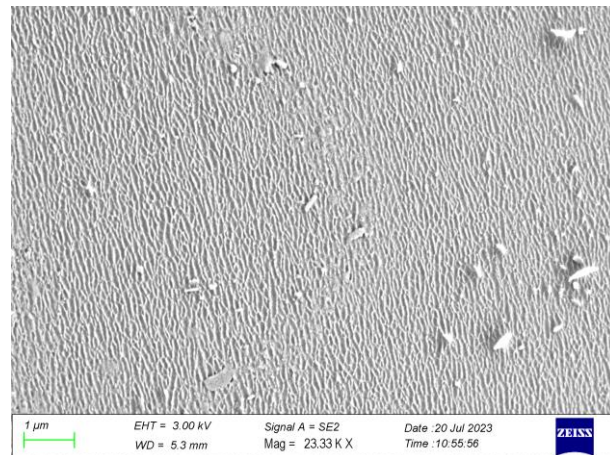


Fig 11. SEM images of 4mint Plasma-treated PET Fabric at a) 1 μm b) 200nm

Deposition of Graphite and GO on PET

- ❑ 0.5% of GO and Graphite Powder is dispersed in the DI water and it is sonicated for 60 min.
- ❑ The PET fabrics treated with plasma and non-treated are soaked in the solution of Graphite Powder and GO for 30 min
- ❑ Fabrics are dried in a hot air oven at 80 °C for 30 min.
- ❑ This process is repeated for several times to increase the adsorption of Graphite and GO.
- ❑ Finally, the fabrics are washed to remove any unattached Graphite Powder and GO.
- ❑ Dried again in an oven and kept in the desiccators



Fig. 12 Coated PET

Water Contact Measurements

Table 3: Weight of samples after deposition

Samples	Weight deposition ($W_2 - W_1$)	g/m^2
P(untreated) with Graphite Powder	1.6 mg	4
P4 with Graphite Powder	0.5mg	1.25
P(untreated) with Graphene Oxide	0.9mg	2.25
P4 with Graphene Oxide	0.9mg	2.25

Table 4: Water Contact Angle Measurement of Samples

Samples	Contact Angles	Standard Deviation
P (untreated)	113.4°	6.09
P2 (2 mins oxygen-plasma treated),	75.86°	7.60
P4 (4 mins oxygen-plasma treated),	< 5°	-
P (untreated) coated with Graphite Powder	91.5°	7.04
P4 coated with Graphite Powder	66.9°	4.79
P (untreated) coated with Graphene Oxide	26.7°	4.5
P4 coated with Graphene Oxide (GO)	57.9°	1.97

- In the case of plasma treatment the GO deposition did not change the wettability
- Plasma changes the **wettability** while graphene will provide **antibacterial, comfort, flexible supercapacitors, sensors, etc.**
- Next studies on GO **release** in time will be done.

SEM Results of Coating on PET Fabric

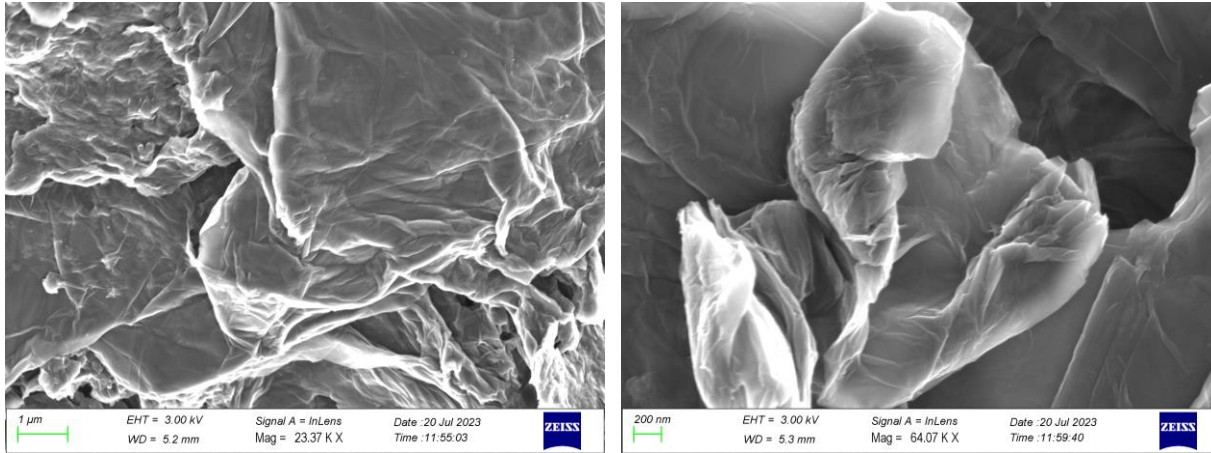


Fig 13. SEM images of non-treated PET Fabric coating with GO at a) 100 μm b) 200nm

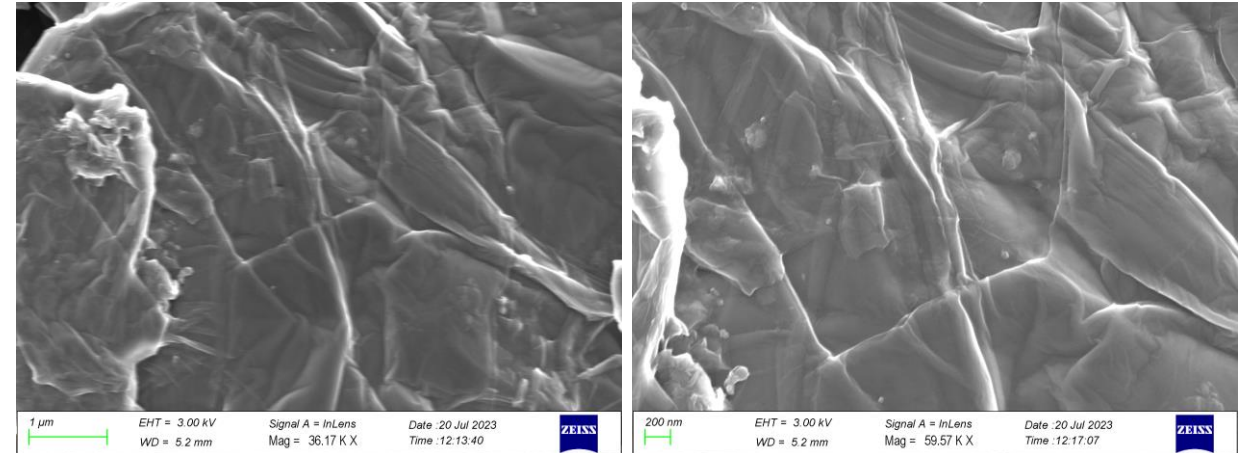


Fig 14. SEM images of 4min Plasma-treated PET Fabric coating with GO at a) 1 μm b) 200nm

The coating of GO on PET covers almost all the fabric surface due to the particle size of Graphene Oxide. Next studies to reduce the GO size.

Discussion

Sizing of GO

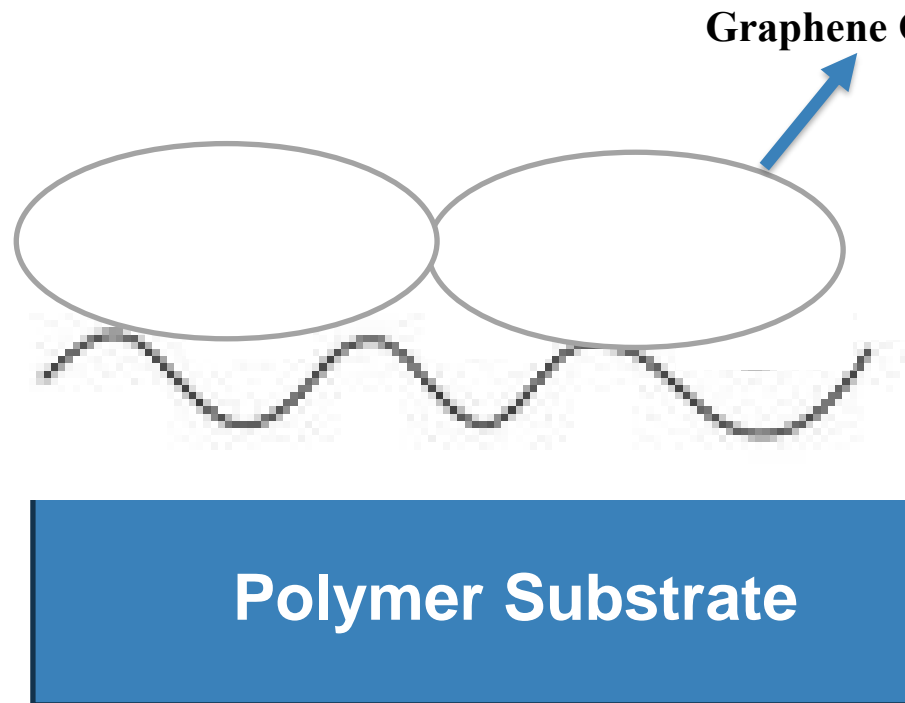


Fig 15. Our Coated case

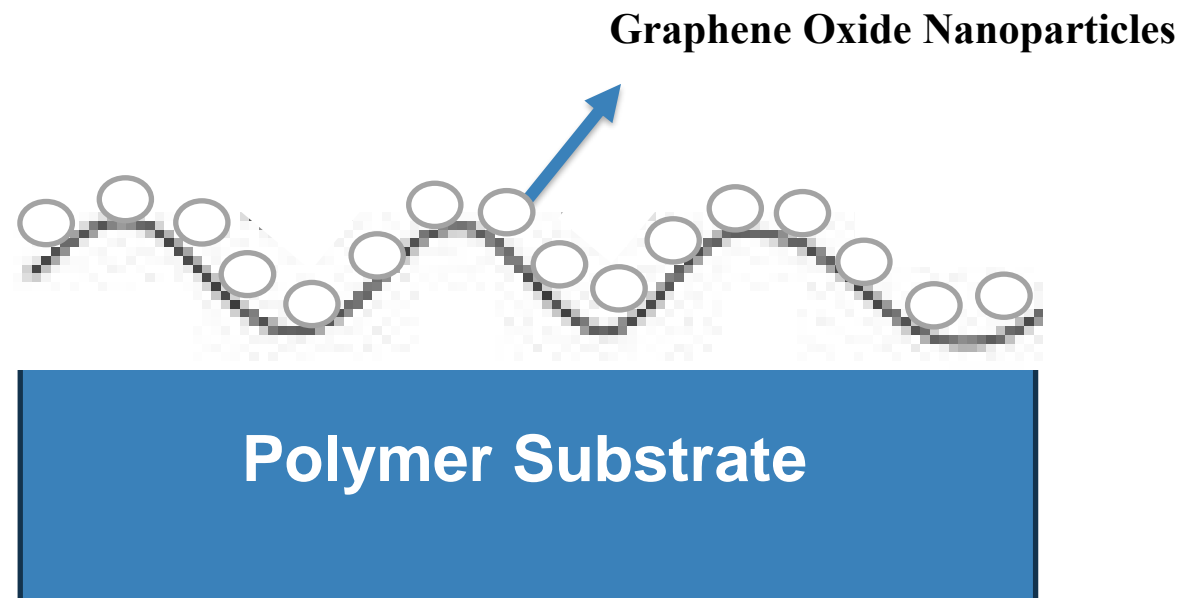


Fig 16. Required Coated case

Method to Reduce Particle Size

- Graphene Quantum Dots**
- I will use the hydrothermal method.
- For this I need a few things
 - Teflon-lined Autoclave
 - Dialysis bags
 - Microporus membranes
 - Some chemicals

Future Aspects 1

- In the Future Quantum dots will be used.
- Deposition of rGO QD's nanoparticles on different textile materials
- GO is an effective antibacterial agent. Antibacterial application will be used on rGO QDGO-coated textile materials

Future Aspects 2: plasma surface sizing

Study of Interaction of Plasma-Polymer by investigating the particle sizes in plasma gas and the polymer surface: correlation between surface roughness and the production of polymeric particles in plasma gas



Fig 17. Setup for Particle counter

Future Aspects 3: Review on graphene applied to textile

- Will work on a Review article on graphene-coated fabrics
- With the aspect of
 - Toxicity of Graphene Oxide
 - Coating methods
 - Substrate behaviours
 - Applications of GO coated fabrics

Conferences, Papers

- EPS 49th Plasma Physics Conference - **Poster**

- **Proceedings**: Tuning the surface wettability of graphene-coated polymeric substrates by plasma treatment, R.Maryam et al. 2023

- **Review article** on Development of medical masks: performance, properties, and prospects, Memon et al., 2023

Tuning the surface wettability of graphene-coated polymeric substrate by plasma treatment

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1. Introduction and Motivation

Non thermal plasma technology [1] progress is very clear, and easy method for modifying the surface of different material without changing their bulk properties. This is particularly advantageous for heat-sensitive polymers commonly used in textiles, as non-thermal plasmas can be applied without thermal damaging materials. Plasma processing includes partial or complete functional groups, deposition of inorganic or organic thin films and cleaning and etching. The different plasma processing can be subdivided into glow discharges, dielectric barrier discharges or inductively coupled plasmas [2]. By engineering the polymers surfaces. The adhesion and efficiency of a coating can be influenced by the surface kind of its wettability. In the treatment of plasma, the chemical composition^{3,4} and physical structure^{5,6} of a material's surface will change, which in turn can affect its ability to facilitate the adhesion of most coatings as well as non-specific interactions.

In the work polymers are plasma treated N_2 or CO_2 facilitate graphene coverage on their surfaces with the aim to control thermal properties such as thermal conductivity and heat transfer, in view of applications in the textile sector. In order to describe the experimental procedure the chemical treatment of polymers, is a reactive oxygen plasma, to enhance the surface wettability and the deposition of graphene on the polymeric surfaces. Scanning electron microscopy (SEM) on the polymeric surfaces for structural information. Atomic force microscopy (AFM) on the treated graphene and substrate wettability analysis prior and after the graphene deposition are performed.

2. Equipment set-up

Plasma treatment was carried out in hydrophobic the fabric. The experiment was performed on polyurethane (PU) fabric covered. The sample was cut into small pieces of 0.5×0.5 cm². The Oxygen Plasma was fed with an inductively coupled generator with an output power of 200W. The pressure was maintained by a vacuum pump of 1.5 - 10⁻³ Torr, and the power is supplied by a 15.75 MHz power generator. The sample was placed in the discharge tube and treated for 2 min and 4 min. SEM has been performed for sample to investigate the structure of the polymeric substrate. We used Zeiss SEM instrument for SEM analysis. SEM analysis, which allows sample observation at different magnifications. The hydrophobicity was measured after plasma treatment by determining the water contact angle by using a contact-angle measuring device for water. An apparatus equipped with TC software (CAM200) was used for taking measurements. For each sample, 3 measurements were taken by changing the position of the contact angle. The droplet was deposited on the surface of the sample. Seven samples were measured (F (non-treated), F1 (1 min oxygen plasma treated), and F4 (4 min oxygen plasma treated), P (non-treated) coated with Graphene powder, P4 (4 min with graphene powder, P (non-treated) with O2, P4 (4 min with O2).

3. Results

Raman spectroscopy was also performed on the Graphene powder and O2 to analyze the vibrational bands. The Raman spectrum of Graphene powder and O2 is shown in Fig. 5. The D and G band is observed in Fig. 3 at 1350 cm⁻¹ and 1500 cm⁻¹ respectively. While the D and G bands Fig. 5 is observed at 1350 cm⁻¹ and 1500 cm⁻¹ respectively. The intensity of D band of each spectrum is different. The ratio of graphene powder is 0.29 and for O2 is 0.6.

Figure 1: SEM images showing the morphology of the surface of the polymeric substrate (a) before and (b) after plasma treatment.

Figure 2: SEM images showing the morphology of the surface of the polymeric substrate (a) before and (b) after plasma treatment.

Figure 3: Raman spectra showing the intensity of the D and G bands for Graphene powder and O2.

Figure 4: SEM images showing the morphology of the surface of the polymeric substrate (a) before and (b) after plasma treatment.

Figure 5: SEM images showing the morphology of the surface of the polymeric substrate (a) before and (b) after plasma treatment.

Table 1 Weight of sample after deposition

Sample	Weight (g)	W/W
F (non-treated)	1.00	1.00
F1 (1 min oxygen plasma treated)	1.00	1.00
F4 (4 min oxygen plasma treated)	1.00	1.00
P (non-treated)	1.00	1.00
P4 (4 min with graphene powder)	1.00	1.00

Table 2 Water Contact Angle Measurements of Samples

Samples	Contact Angle	Wetted Area (%)
P (non-treated)	117.6	0.0
P4 (4 min oxygen plasma treated)	103.9	1.0
P (non-treated) coated with Graphene powder	7.3	99.3
F1 (1 min oxygen plasma treated)	101.7	7.04
F4 (4 min oxygen plasma treated)	65.9	47.91
P (non-treated) coated with Graphene powder	26.7	4.2
P4 (4 min with O2)	37.9	1.97

Figure 6: Water contact angle measurement of the sample F4 (4 min oxygen plasma treated).

Figure 7: Water contact angle measurement of the sample P4 (4 min with O2).

Figure 8: Water contact angle measurement of the sample P (non-treated) coated with Graphene powder.

Figure 9: Water contact angle measurement of the sample F1 (1 min oxygen plasma treated).

* European Physical Society * 49th Conference on Plasma Physics, 3-7 July, 2023

Courses

- ❑ Course: **“New lignin-based sustainable materials science and technological aspects”** Luca Zoia (DISAT), Ruggero Barni (DFO) and Carmen Canevali (SdM), **1CFU**
- ❑ Course: **“Masterclass in Big Data within Science and Industry”** Dr. Elena Cuoco, Dr. Matteo Bregonzio, **1 CFU**
- ❑ Course: **“Deep Learning for Physicists”** Professor Stefano Giagu. **2 CFU**

Thank you

References

- [1] Nascimento, J. H. O., Felipe, B. H. S., Dias, J. M. T. C., Souza, A. G. F., Júnior, A. P. S., Galvão, F. M. F., ... & Ahmad, A. (2021). Creating Smart and Functional Textile Materials with Graphene. *Nanomaterials and Nanotechnology: Biomedical, Environmental, and Industrial Applications*, 411-444.
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