# Laser induced graphene microsupercapacitors


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ScuDo Scuola di Dottorato – Doctoral School
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## Research context and motivation

- In a world focused more and more on the IoT, the need of effective and portable energy storage devices is critical. **Laser induced graphene supercapacitors** have been under the spotlight for their **cheapness**, the **simplicity of the fabrication** and the possibility of a totally **green flexible device**.
- However, post fabrication treatments are required in order to obtain performances comparable with other developed devices.
- After doing so, it is possible exploit the laser writing technique in order to obtain an energy storage device that can be integrated with sustainable energy harvesters.

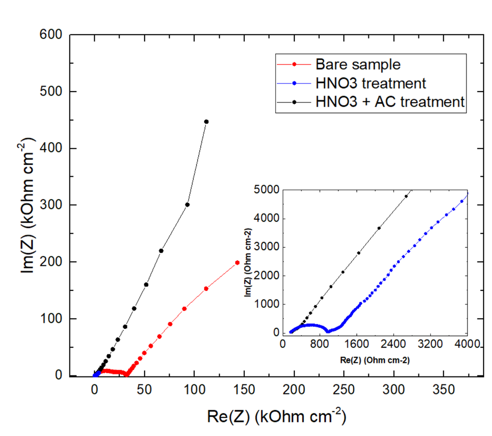
## Addressed research questions/problems

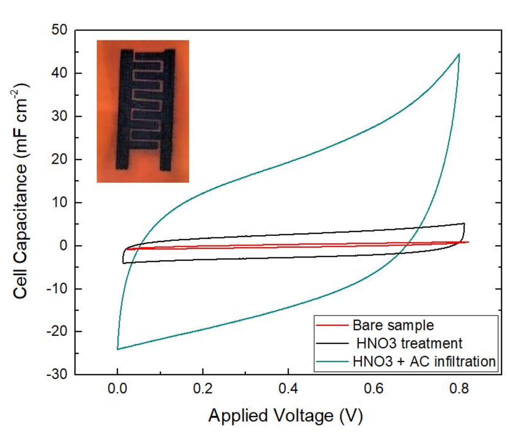
- Laser induce graphene (LIG) is a powerful technique. However, the fabricated supercapacitors are quite limited in terms of capacitance and conductivity. Therefore, one of the main topic of my research has been to improve those two parameters through **boosting of faradaic** and **non faradaic** contribute.
- This kind of supercapacitors are particularly appealing for the fabrication of flexible self-powered sensors or flexible integrated devices. Therefore, it has been tried to couple the devices with different energy harvesters such as **dye sensitized solar cells**, **piezoelectric membranes** and **hydrogel-based sensors**.

## Novel contributions

- **Boosting of electrical double layer capacitance in LIG supercapacitors.**

The incubation in nitric acid makes the surface more hydrophilic, while the infiltration of activated carbons and carbon black allows much higher capacitance and a lower equivalent series resistance.



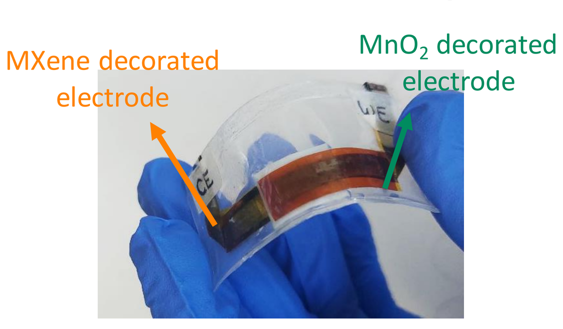



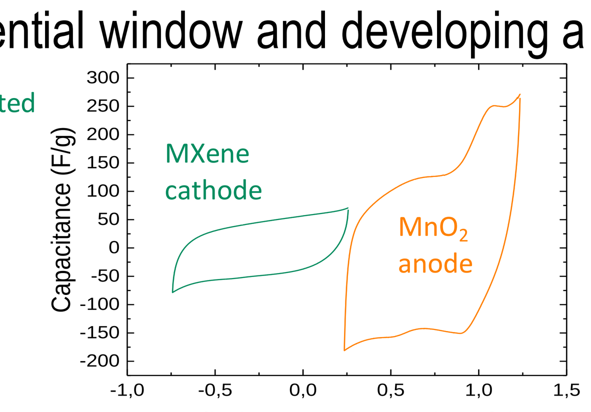

| ESR | Capacitance |
|---|---|
| 100 Ω/cm² | 20.7 mF/cm² |

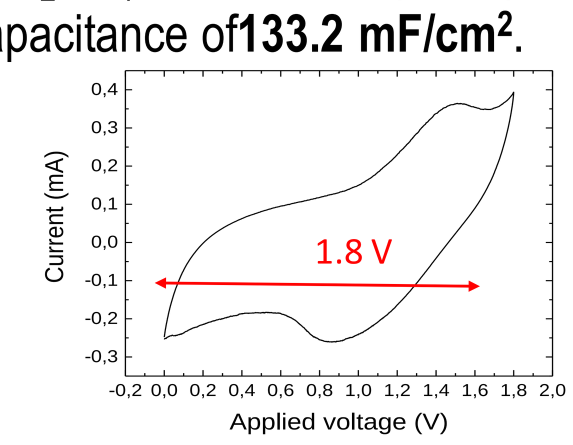
- **Decoration through electrodeposition.**

Another way to improve the performances has been to decorate one LIG electrode with manganese oxide and the other with MXene.

The results have been quite satisfying, allowing to obtain a $Na_2SO_4$ 1M based supercapacitor able to work in a **1.8 V** potential window and developing a capacitance of**133.2 mF/cm²**.



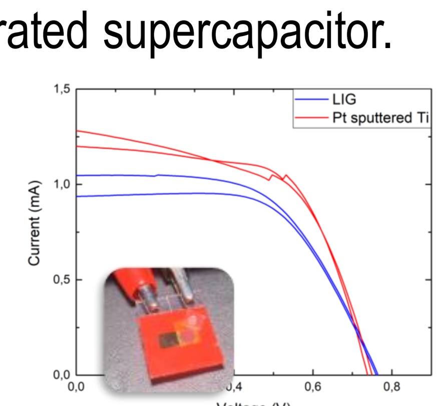



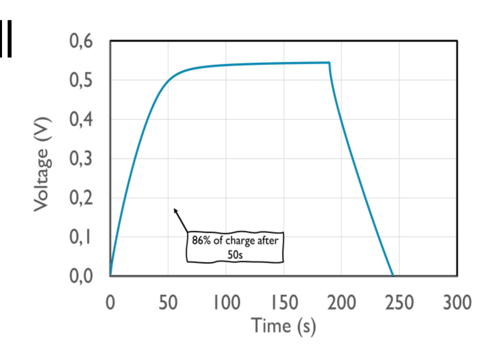

- **Integration with dye sensitized solar cells (DSSC).**

A DSSC has been fabricated using LIG as counter electrode. Then, it has been integrated with a laser written integrated supercapacitor.

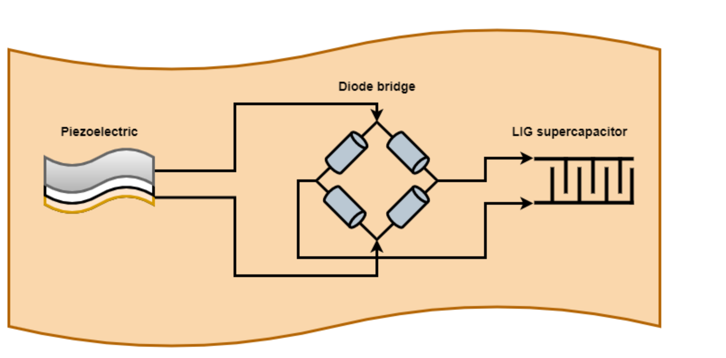
| | LIG | FTO |
|---|---|---|
| $J_{sc}$(mA/cm²) | 14.9 | 13.1 |
| Voc (V) | 0.64 | 0.64 |
| Fill factor | 0.43 | 0.51 |
| η | 4.13 | 4.21 |



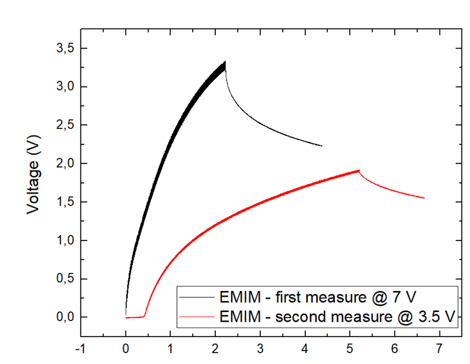

The LIG-based cell has been able to charge the LIG supercapacitor in reasonable time.




- **Integration with piezoelectric membrane.**




The P(VDF-TrFE)membrane generated **50 nW/cm²**

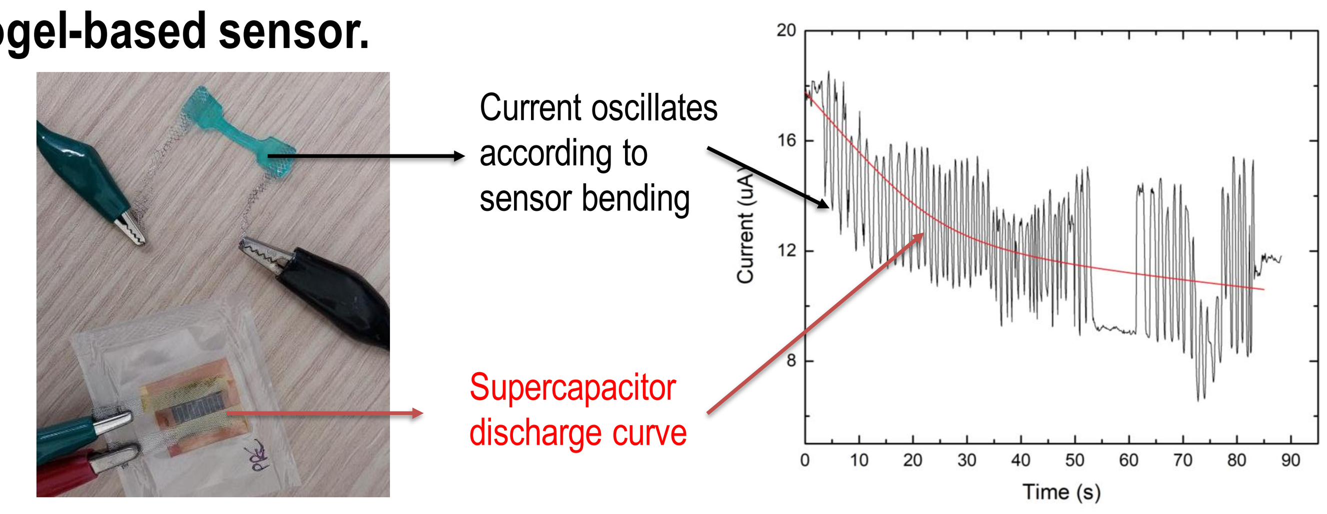



## Submitted and published works


- M. Reina, A. Scalia,G. Auxilia, M. Fontana, F. Bella, S. Ferrero, A. Lamberti, *"Boosting Electric Double Layer Capacitance in Laser-Induced Graphene-Based Supercapacitors"*, Advanced Sustainable Systems Vol.6, Issue 1, January 2022, 2100228


- **Self-powered hydrogel-based sensor.**

A strain/stress hydrogel sensor has been powered with a LIG SC using the same hydrogel as electrolyte.




## Adopted methodologies

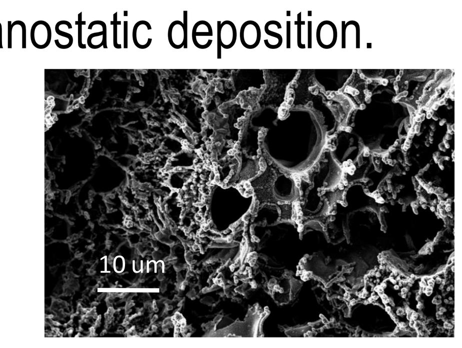
- **Infiltration of activated carbons:**

1 gram of mixture made **by 85% activated carbons** (surface area of 1666 m², a particle size of 10–30 μm), **10% carbon black** (C65) and **5% PVDF in** 5 mL of DMSO. The solution has been poured onto the LIG surface, then the sample has been put under vacuum in order to let the air out of the surface, infiltrating the powder.

- **Electrodeposition of $MnO_2$:**

Decoration with $MnO_2$ has been done through a galvanostatic deposition.

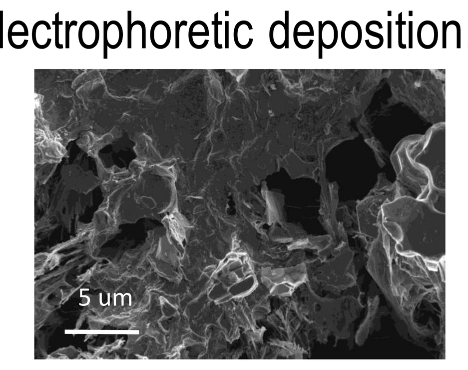
| Solution (in DI-Water) | 0.1 M Mn(CCOOH) 0.1 M Na2SO4 |
|---|---|
| Counter electrode | Platinum bar |
| Reference electrode | Ag/AgCl |
| Current applied | 1 mA/cm² up to 4 mA/cm² |




- **Electrophoresis of MXene:**

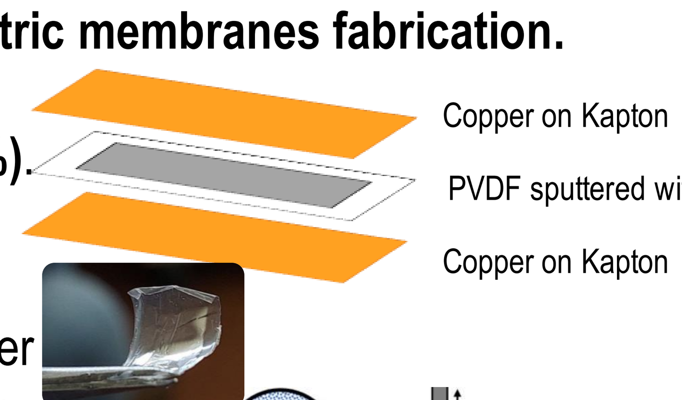
Decoration with MXenes has been done through an electrophoretic deposition.

| Solution (in DI-Water) | HF-etched Mxene 10 mg/ml |
|---|---|
| Counter electrode | Platinum bar |
| Reference electrode | Ag/AgCl |
| Potential applied | 8 V up to 20 V |



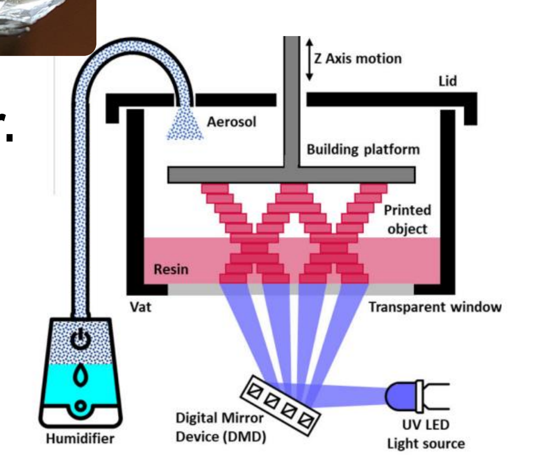

- **Spin coating of PVTF onto Kapton for piezoelectric membranes fabrication.**

Membranes have been derived by a commercial **P(VDF-TrFe)** dissolved **in methyl ethyl ketone (10w%)**. Then, the solution has been spincoated onto a layer of copper on kapton, at 1500 up to 3000 rpm. Then the device was assembled by adding another kapton-copper layer above the membrane. Layers are around 5-10 um.




- **Printing of NaCl-based hydrogel on LIG supercapacitor.**

The sensors have been fabricated through UV using the Asiga MAX printer. The same device has been used to deposit the polymer onto the LIG supercapacitor.




| Acrylic acid | PVA | DIW | PEGDA | Photoinitiator | DYE |
|---|---|---|---|---|---|
| 19.90% | 15.52% | 63.68% | 0.20% | 0.30% | 0.006% |

M.Caprioli et Al. «3D-printed self-healing hydrogels via Digital Light Processing»

## Future work

There is much room for improvements in all the projects carried out. Next steps will be:

- Improvements of the MXene electrodes in order to obtain a more performant supercapacitor.
- Integration of the whole DSSC-SC device in a single flexible packaging.
- Integration of the piezoelectric-SC device in a single flexible packaging.
- Poling of the PVTF membrane in order to enhance the generated power.
- Laser writing of supercapacitors in series in order to increase the discharge current that powers the hydrogel sensor.
- A collaboration with Tyndall Instute of Cork will start next year in order to obtain storage devices from LIG process onto cork substrates.

## List of attended classes

- 01QAAAA – Title of the course (Date, credits)
- 02UMBIY – Advanced elements of chemical engineering (28/6/2021, 50)
- 02UKHKI – Applied spectroscopic methods (10/6/2021, 50)
- 01LXBRW – Life Cycle Assessment (LCA) (13/7/2021, 33.33)
- 08IXTRV – Project management (5/9/2022, 6,67)
- 01RISRV Public speaking (28/1/2021, 6.67)
- 01LEXRP Strumenti e tecnologie per lo sviluppo del prodotto (7/6/2021, 33.33)
- 01QSXRU The measurement of electrical impedance (10/3/2021, 16.67)

Politecnico di Torino

PhD program in
**Electrical, Electronics and Communications Engineering**