Graphene based printed micro-supercapacitors

… et al.

Alberto Ansaldo

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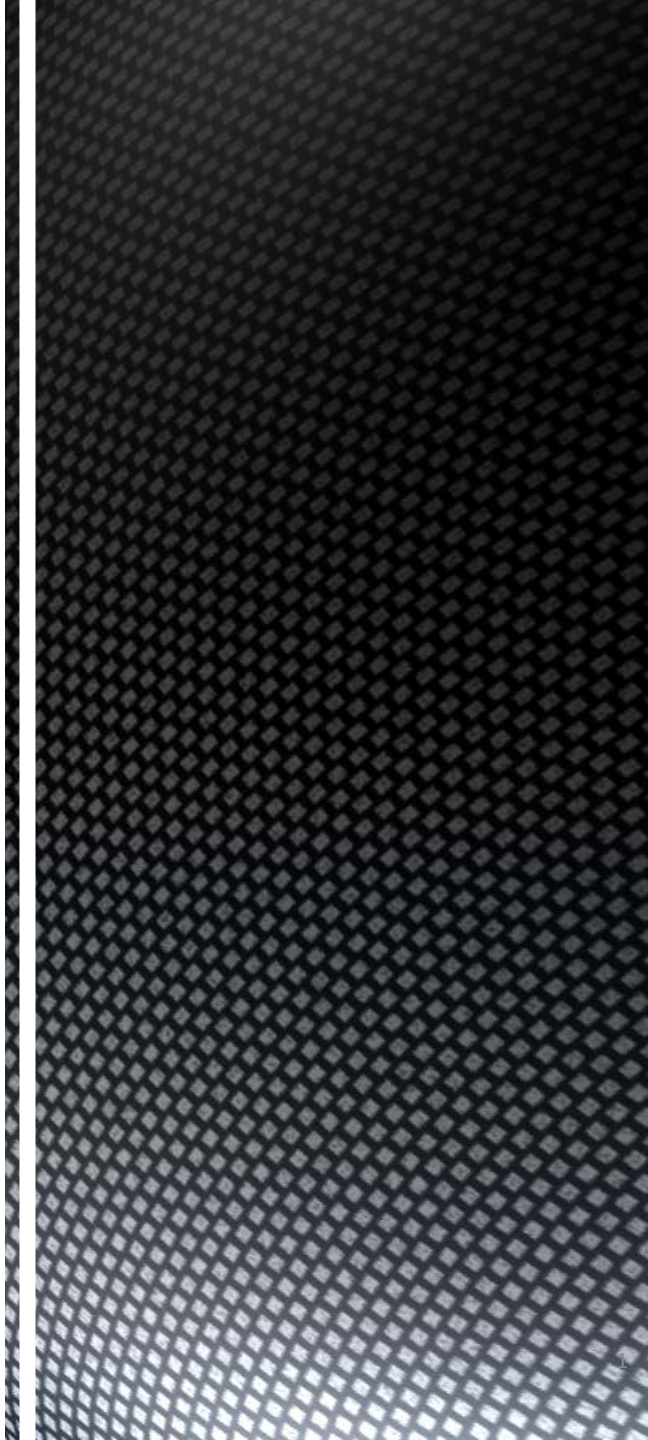
GRAPHENE LABS

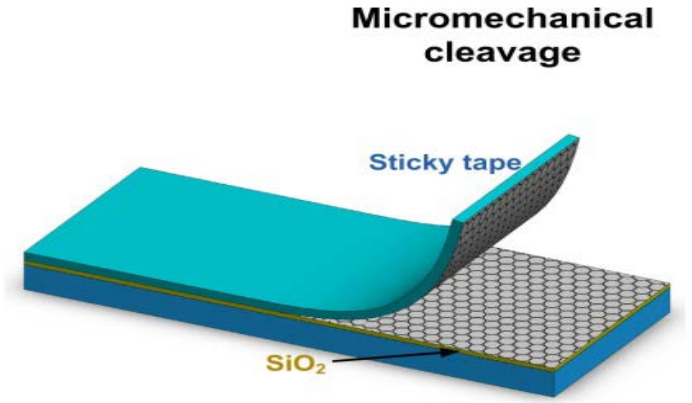


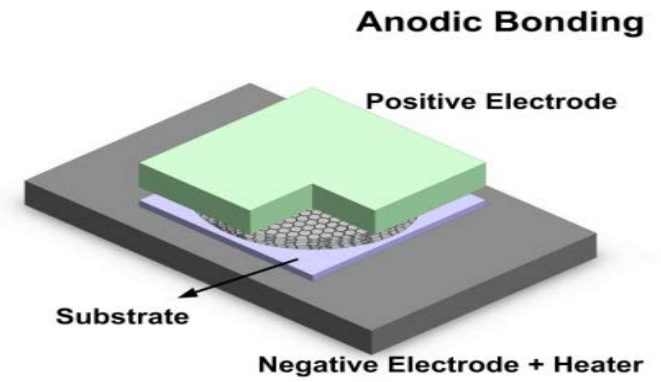
Outlook

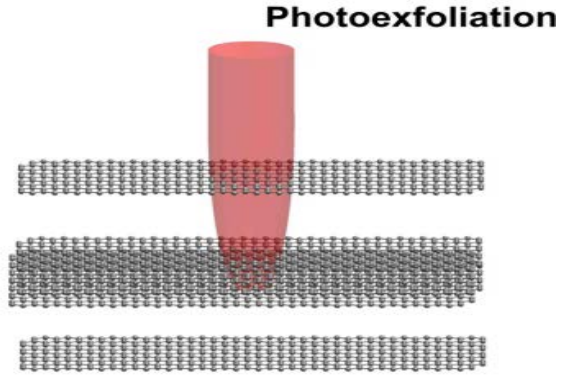
- Scalable graphene production:
  Wet-jet mill
- Printed micro super capacitors
- Towards large scale supercapacitors integration

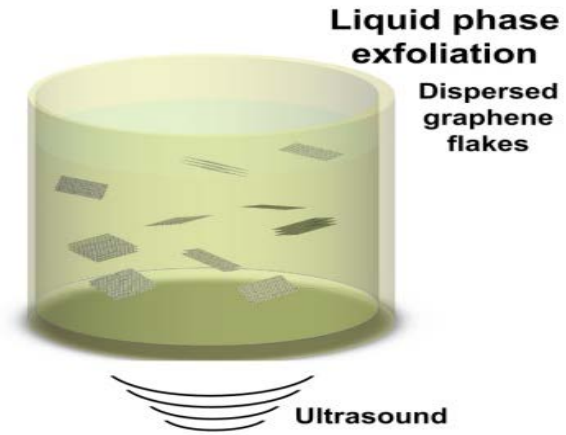
How to make Graphene?

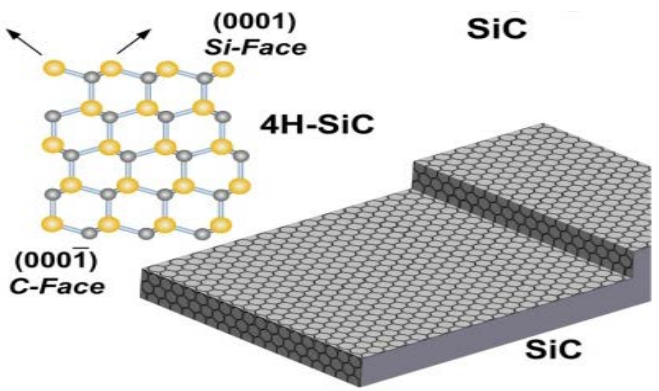
GRAPHENE FLAGSHIP

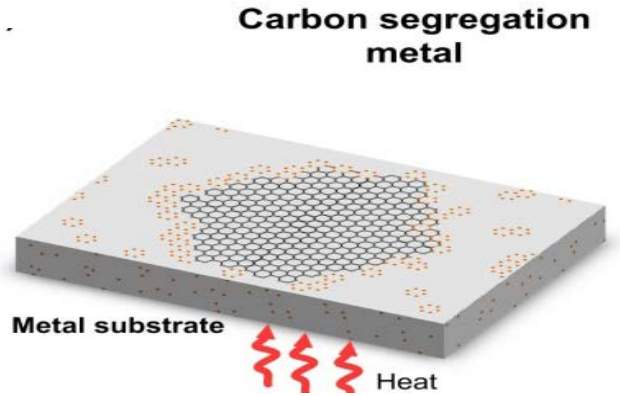


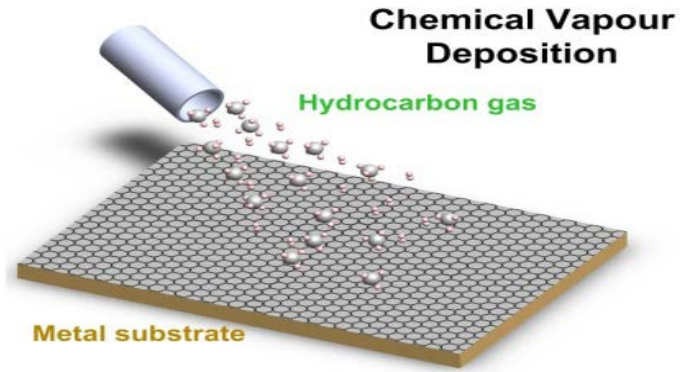


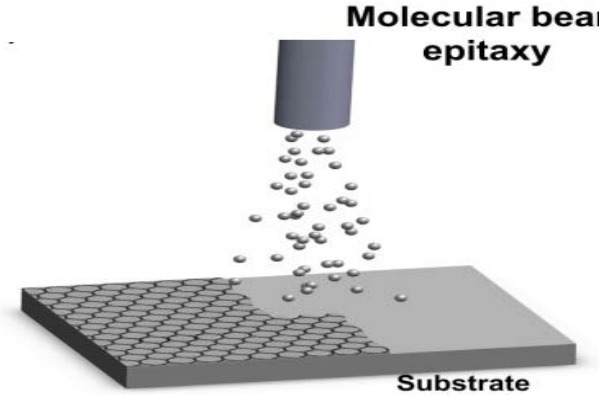


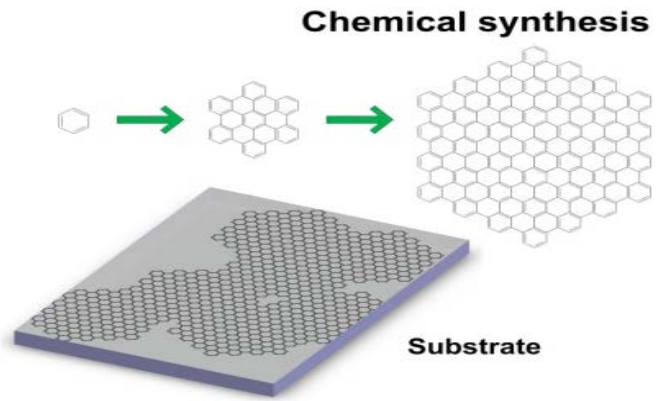












F. Bonaccorso, et al., Materials Today. 12, 584 (2012)

How to make Graphene?

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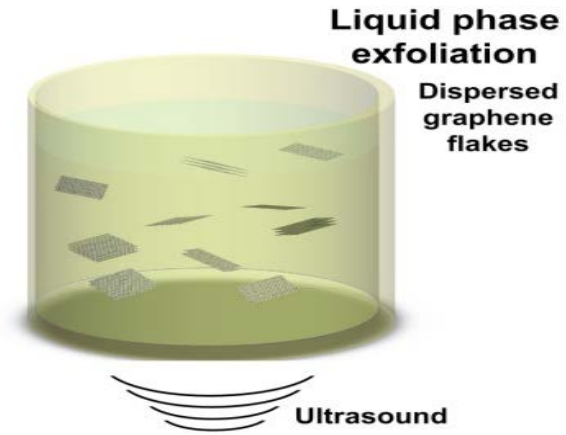

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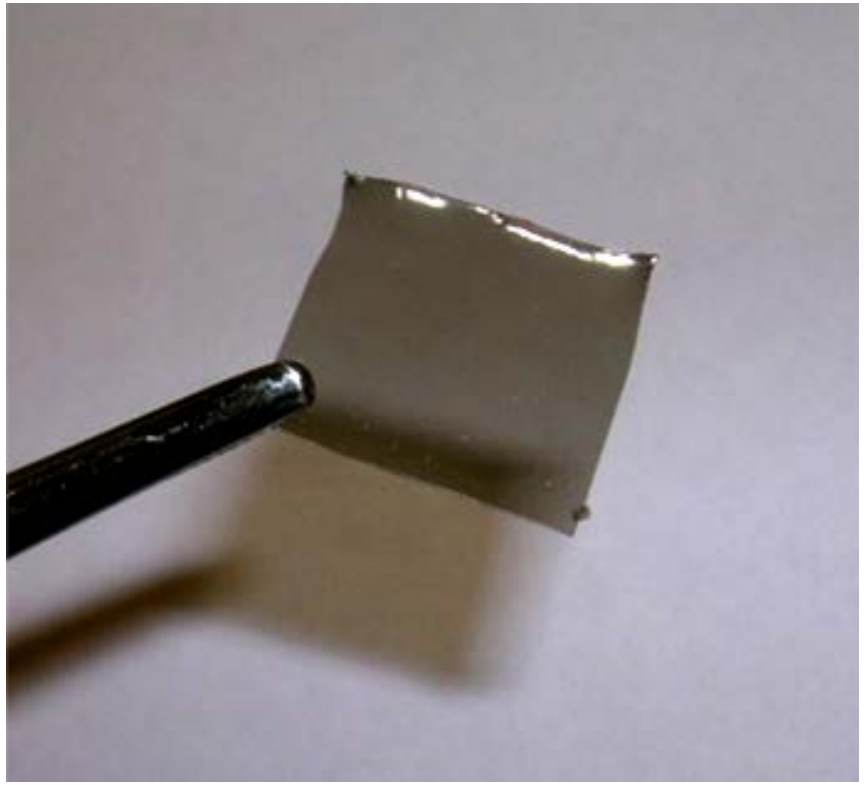
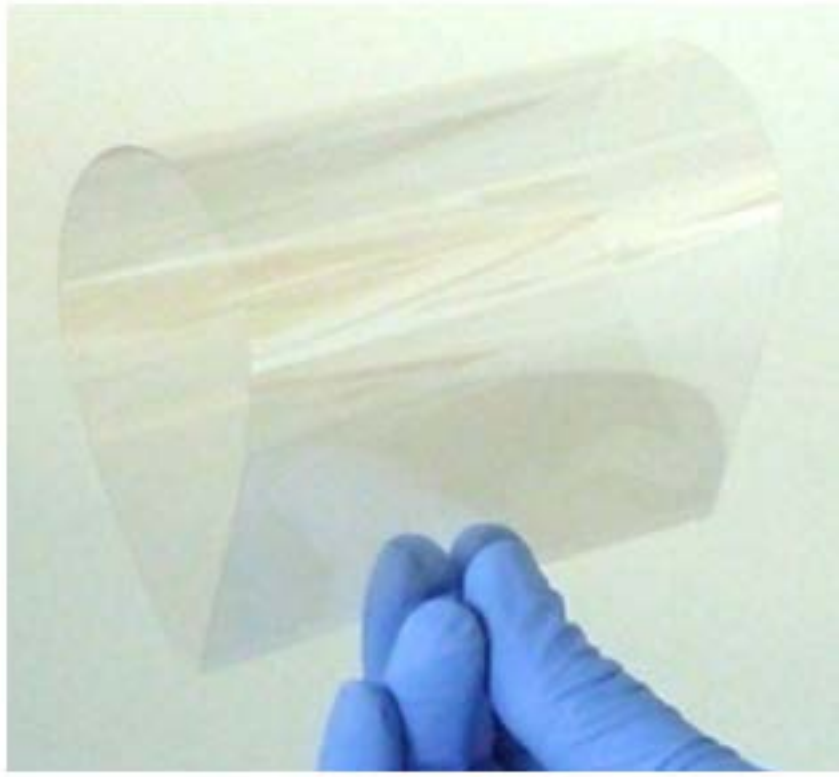
Solution Processing

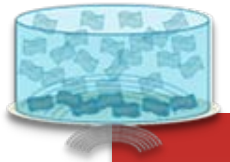
Dispersions and inks



Polymer composites



Liquid Phase Exfoliation

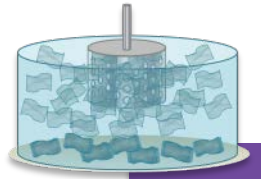


Ultrasonication

- Widely applicable
- High concentration achievable
- Widely used on labscale
- Scalability not demonstrated
- Low production rate, poor reproducibility

Ball Milling

- Scalable
- Slow in planetary ball mills
- Demonstrated for a few materials
- Process optimization needs further considerations, especially for new materials



Shear exfoliation

- Scalable
- Highest production rates
- Concentration lower than for ultrasonication at equal process time
- Exfoliation quality appears lower than for ultrasonication

Bonaccorso et al. Adv. Mater. 28, 6136-6166 (2016)

The first challenge

Goal

- produce large **quantities** of high **quality** 2D crystals

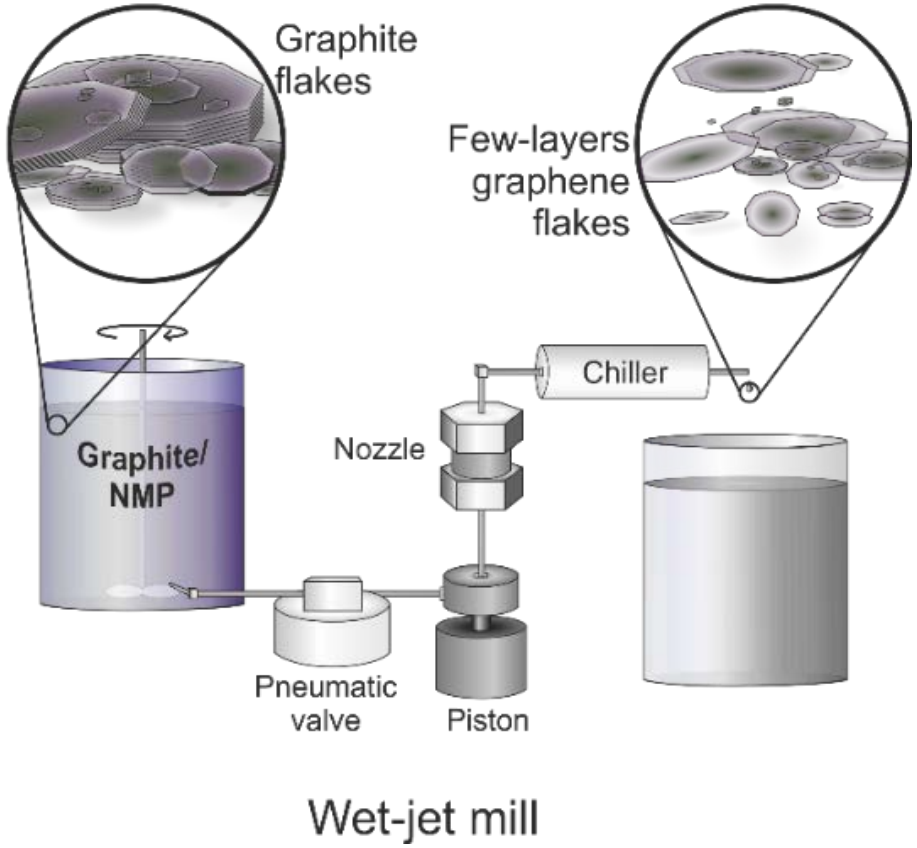
Quality

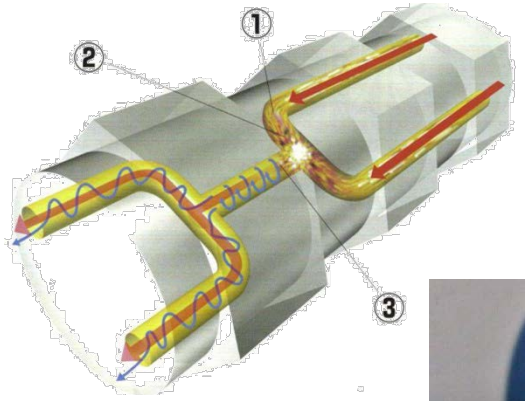
- known reproducible composition that does not change with time

Quantity

- the methodology used can be scaled up without affecting the **quality**

Wet Jet Mill working principle

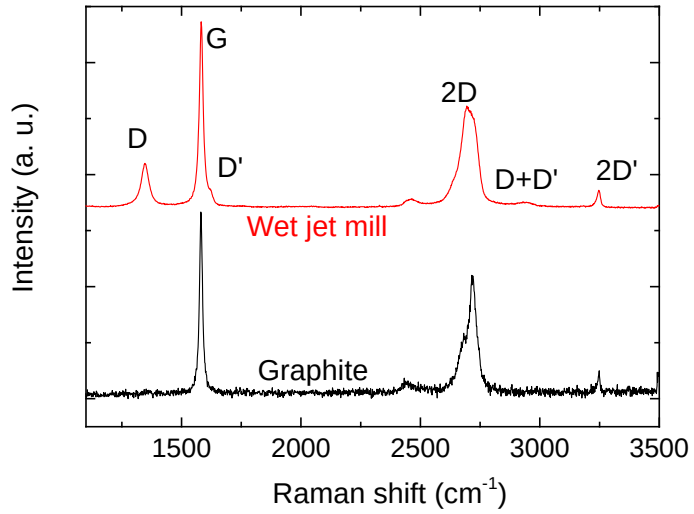




A.E. Del Rio Castillo et al., Mater. Horiz. 5, 890, 2018

Graphene ink characterization

Raman



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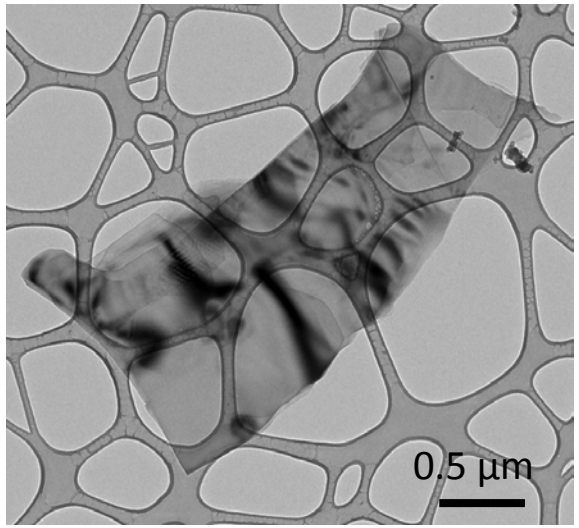
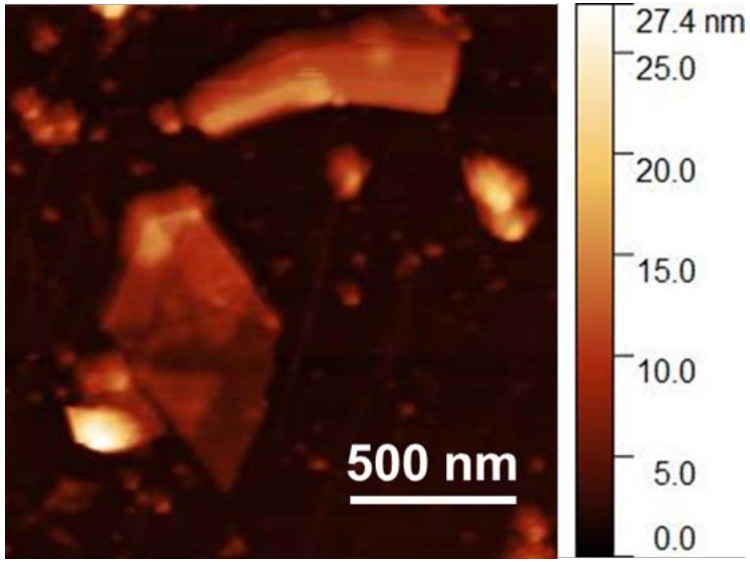


AFM



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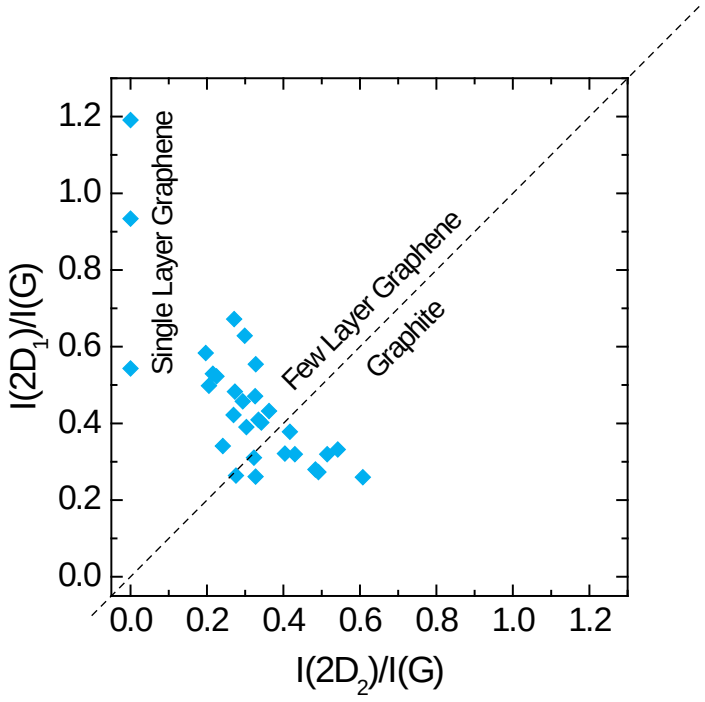

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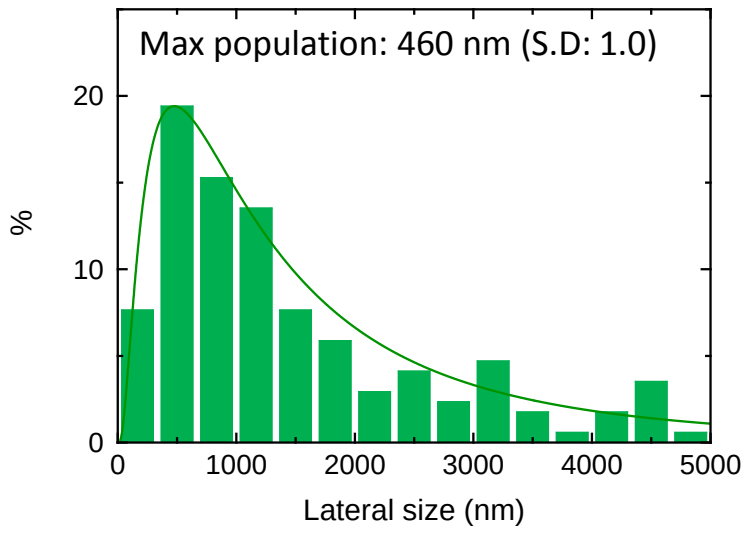

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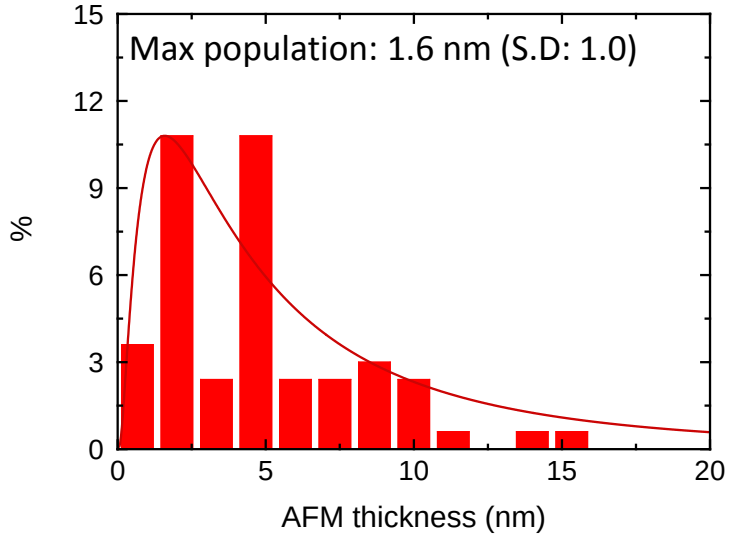


A.E. Del Rio Castillo et al., Mater. Horiz. 5, 890, 2018

The second challenge: Sustainability

- The best performing solvent is NMP
- High boiling point: difficult to remove

- NMP is included in the ECHA's **Candidate List of substances of very high concern for Authorisation**
  https://echa.europa.eu/candidate-list-obligations

- The use of NMP can have a huge economic impact on the final applications (safety, pollution, restrictions)

We can limit the use of NMP to the exfoliation step by:

- Solvent exchange (e.g., NMP to Ethanol)
- Graphene powder

A Capasso, et al, Solid State Communications 224, 53-63 (2015)

Wet Jet Mill Graphene Powder in short

1) Wet Jet Milling **3) Freeze drying** **2) Solvent Exchange**

Current production capacity

We can produce **2 litres** per hour

of graphene ink ≈**10g/L** in different solvents

Post processing: concentration up to **180g/L**

Capacity:

8-10 litres per hour

We can produce **powder** **~**0.1Kg per day

Scaling-up production →

BE DIMENSIONAL

A spin off of IIT

Patent: IT 102015000077259 , WO/2017/089987

Large scale production of 2d crystals

Site for graphene production rate of 10 T/y

4200 m^2 area

Including:

Extrusion line

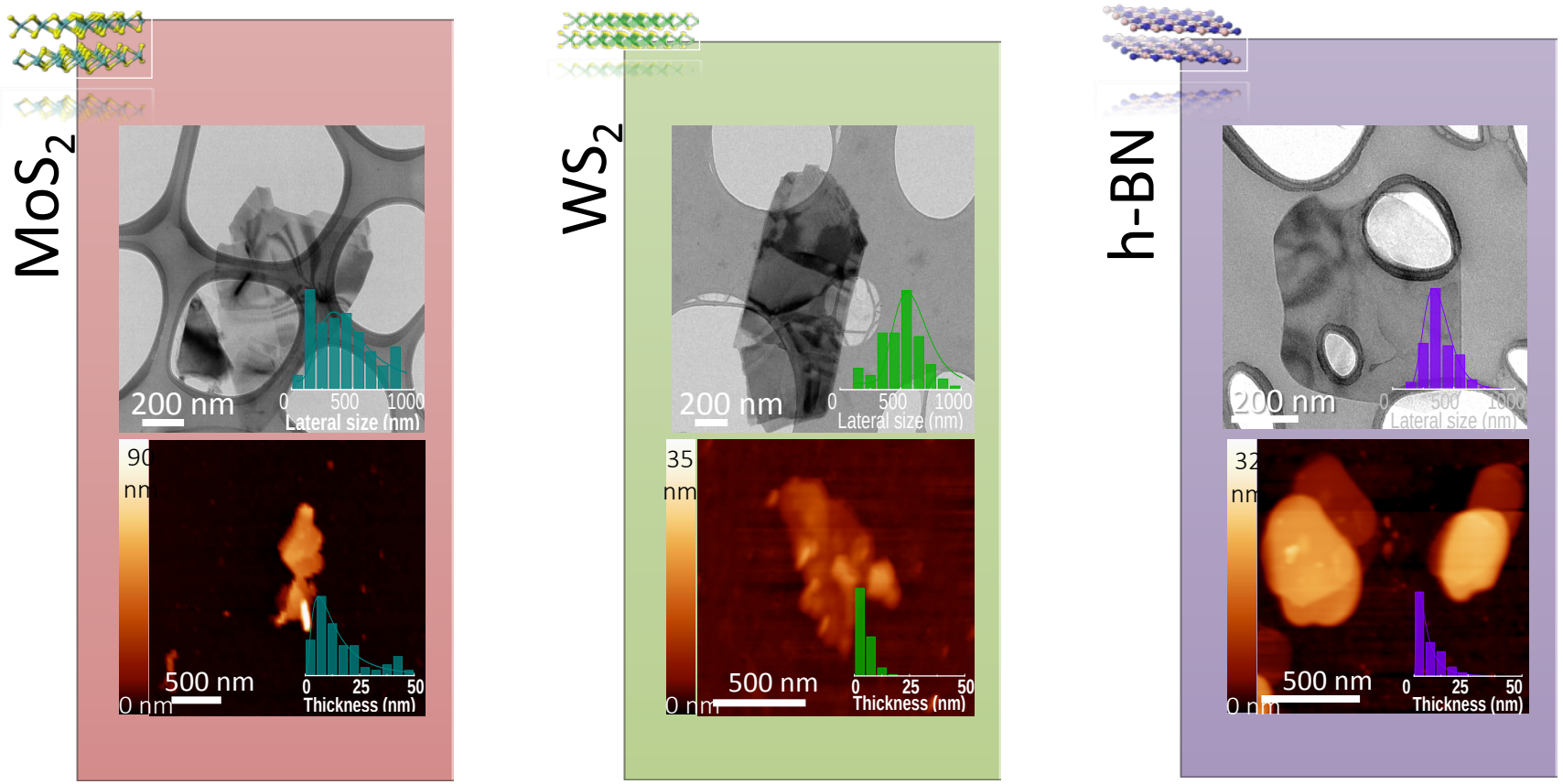
Injection moulding

Banbury mixer

Personnel: 18

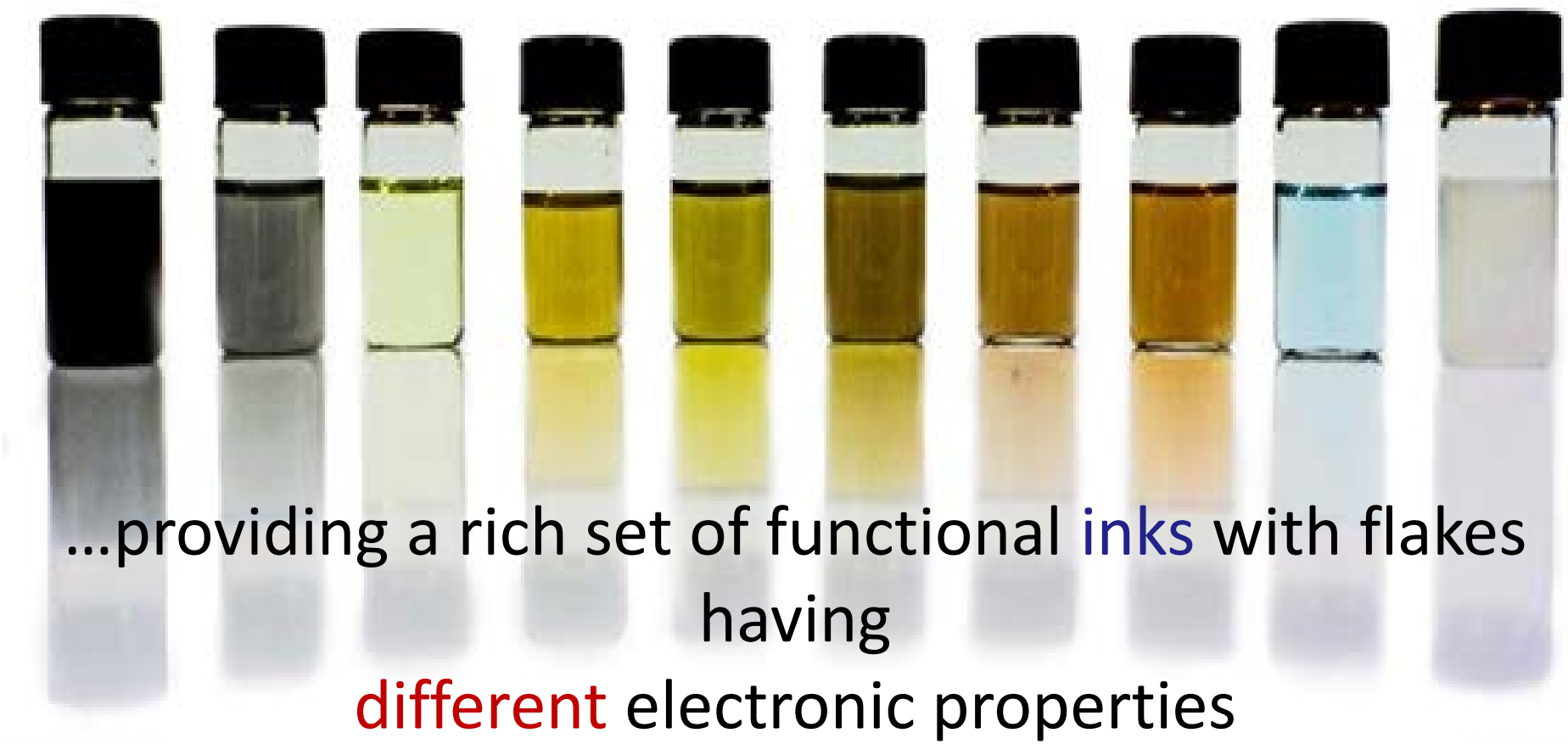
Planned personnel in 2019: ~30

Exfoliation of other layered crystals



A.E. Del Rio Castillo et al., Mater. Horiz. 5, 890, 2018

2D crystals-based inks

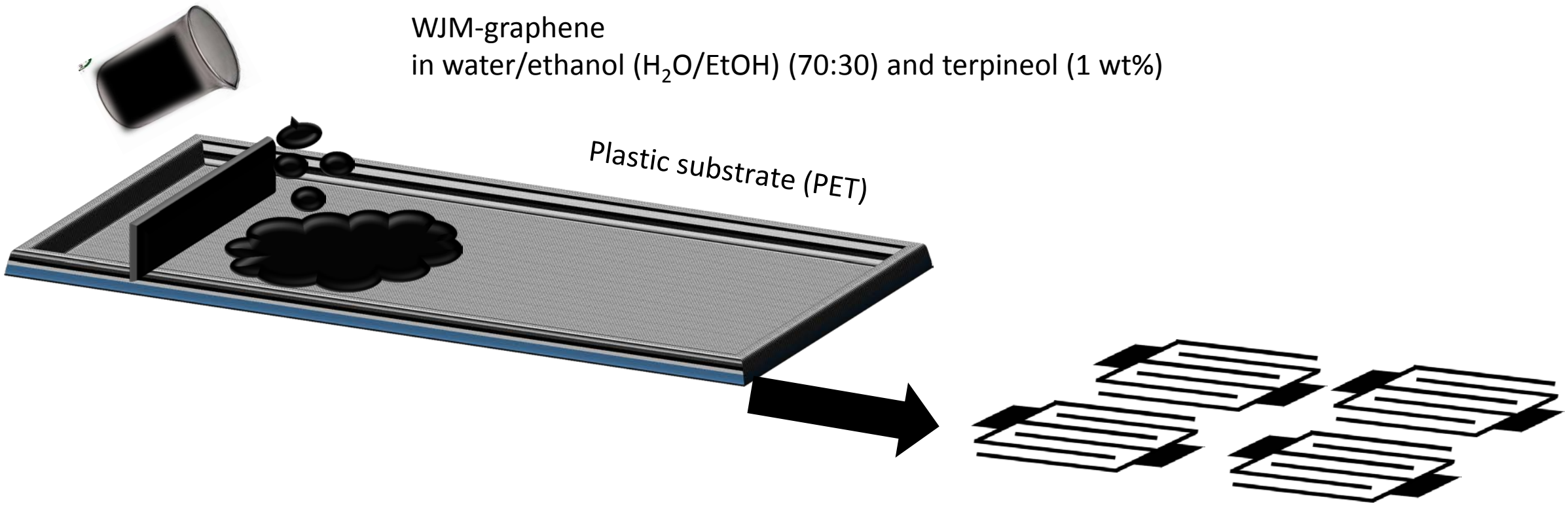


…providing a rich set of functional inks with flakes having
different electronic properties

Screen-printed G/SWCNTs-based supercaps

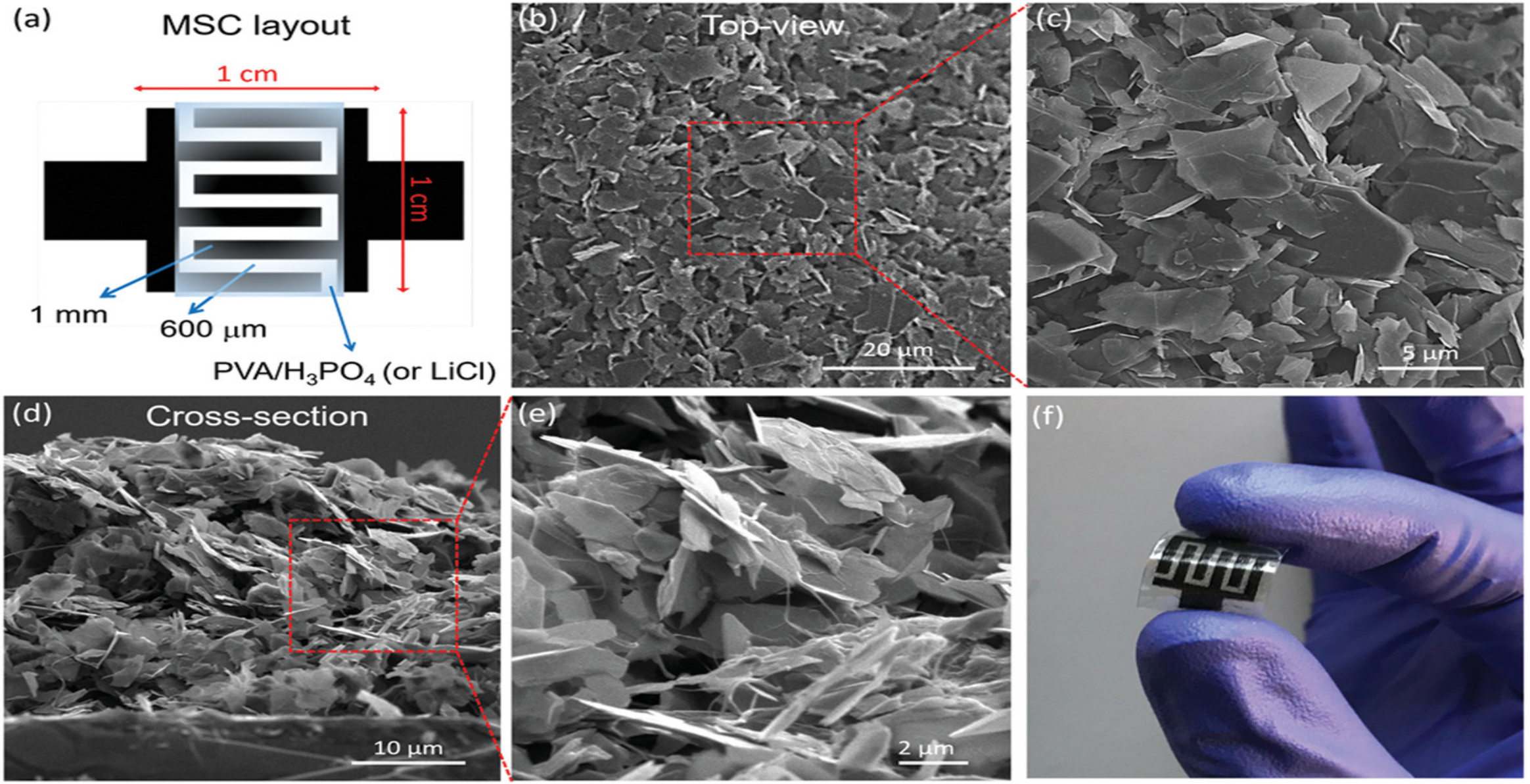
MICROSUPERCAPACITORS (MSCs) SCREEN PRINTING

WJM-graphene
in water/ethanol (H_2O/EtOH) (70:30) and terpineol (1 wt%)



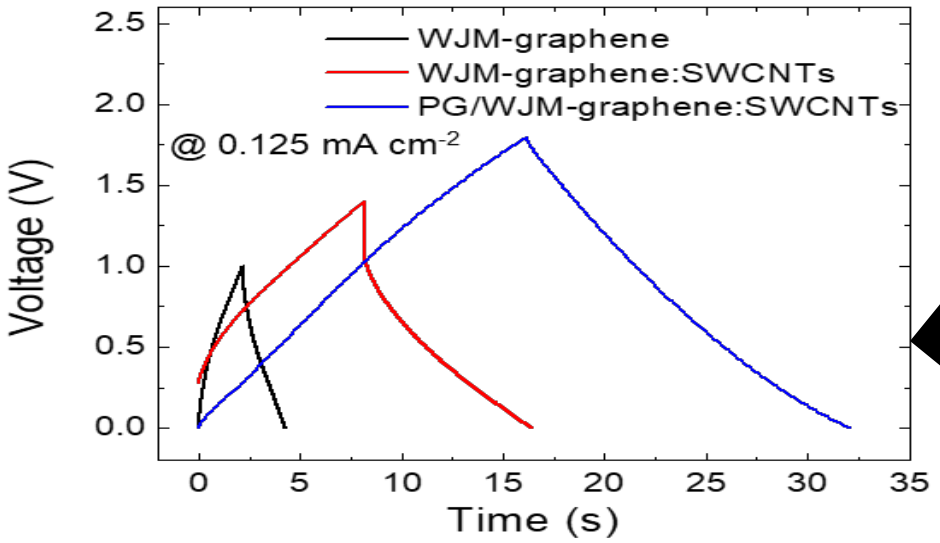
S. Bellani, et al., Adv. Funct. Mater. 2019, doi.org/10.1002/adfm.201807659

Screen-printed G/SWCNTs-based supercaps

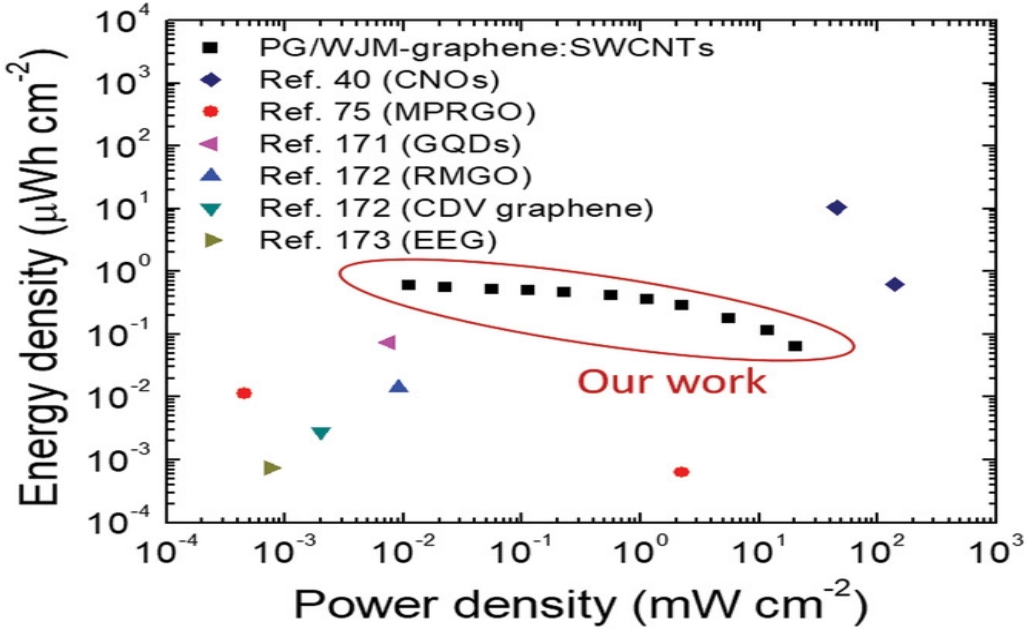


Screen-printed G/SWCNTs-based supercaps

Electrochemical characterization



High energy and power density compared to previous art...



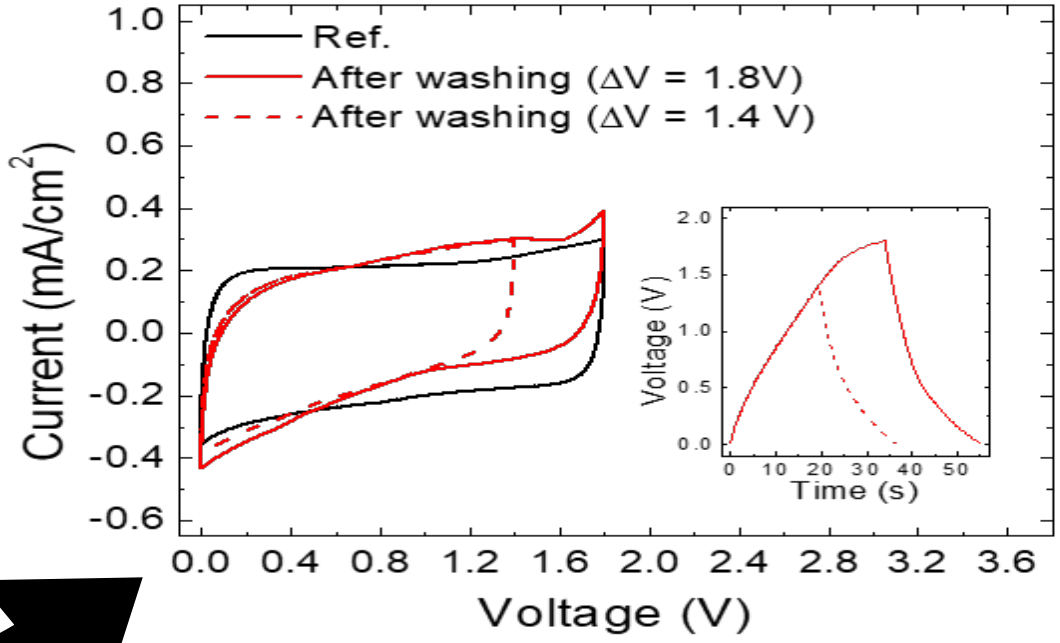
Screen-printed G/SWCNTs-based supercaps

Washability test

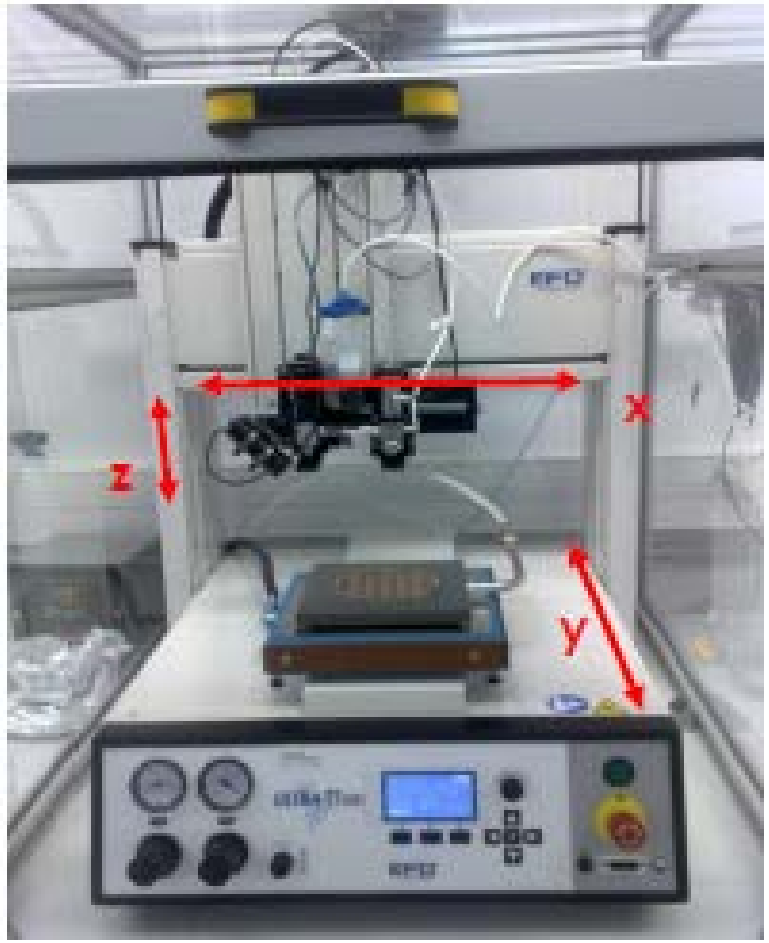
Garment integration

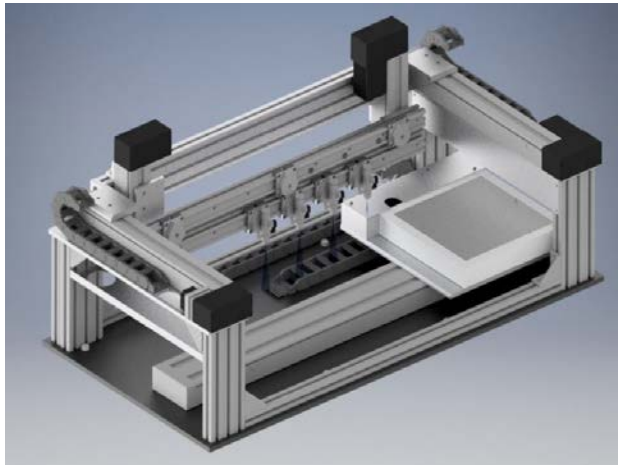
Laundry cycles

EC characterization after washing



Dynamic Spray Gun Deposition





Process advantages:

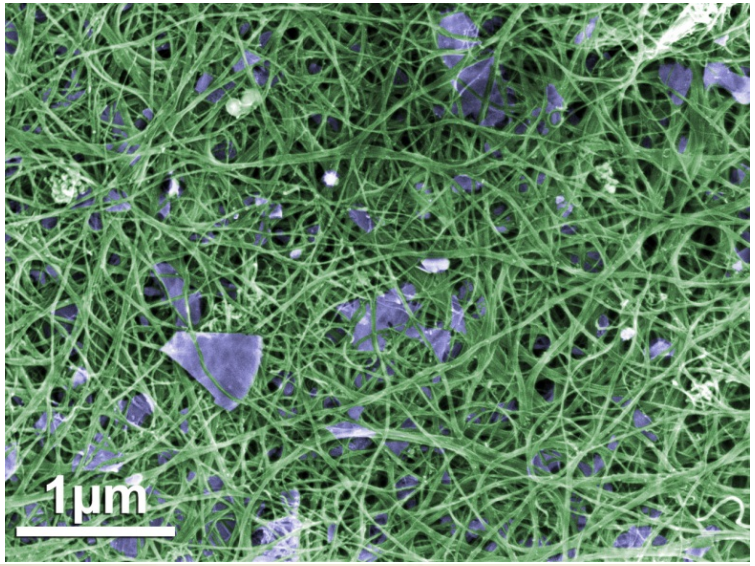
- Allow co-deposition of different carbon-based materials
- Film morphology can be monitored during deposition
- Scalable

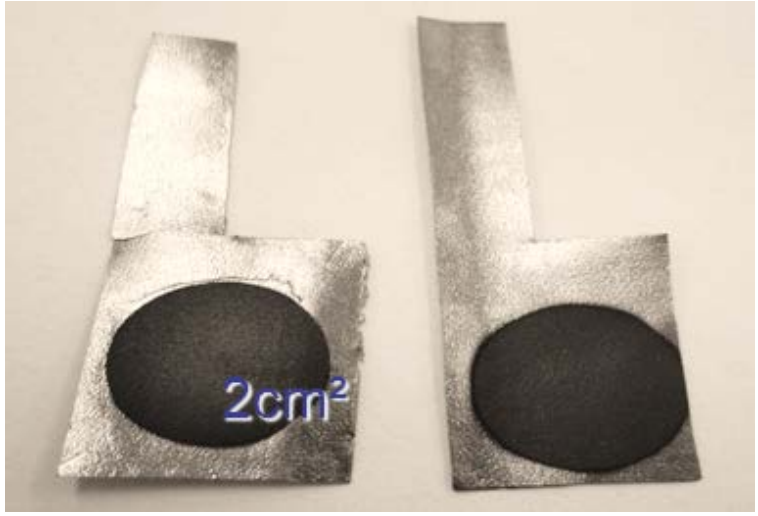
M-SOLV Limited

Graphene/CNT hybrid Supercapacitors

Dynamic Spray Gun Deposition

- Temperature >200 °C
- Collector Graphite paper
- Electrodes area $2cm^2$
- Deposited hybrid 1.15mg
- Electrolyte aqueous 3M $LiNO_3$

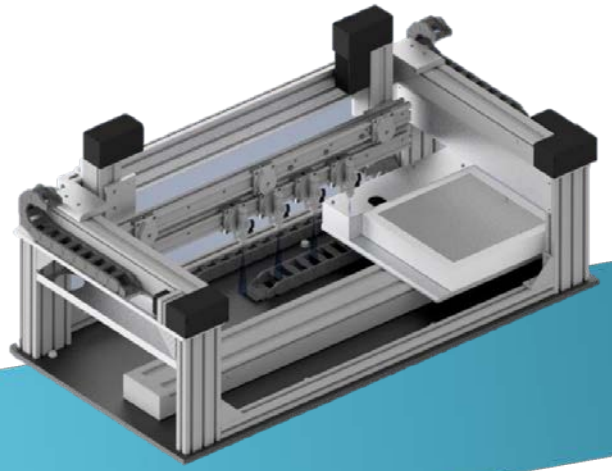




A. Ansaldo et al. *ChemNanoMat* **3**, 436 (2017)

Spray-coated graphene based supercaps

GRAPHENE-BASED ACTIVE MATERIAL INKS



DYNAMIC SPRAY COATING DEPOSTION

60 F Pouch

Currently under patenting process

Spray-coated graphene/AC-based supercaps

- Temperature range: -40/+100 °c
- Energy denisty:
  - > 31.5 Wh/kg @150 kW/g
  - >12.5 Wh/kg @ 30000 kW/kg
- Maximum power density: > 80 kW/kg

60 F Pouch

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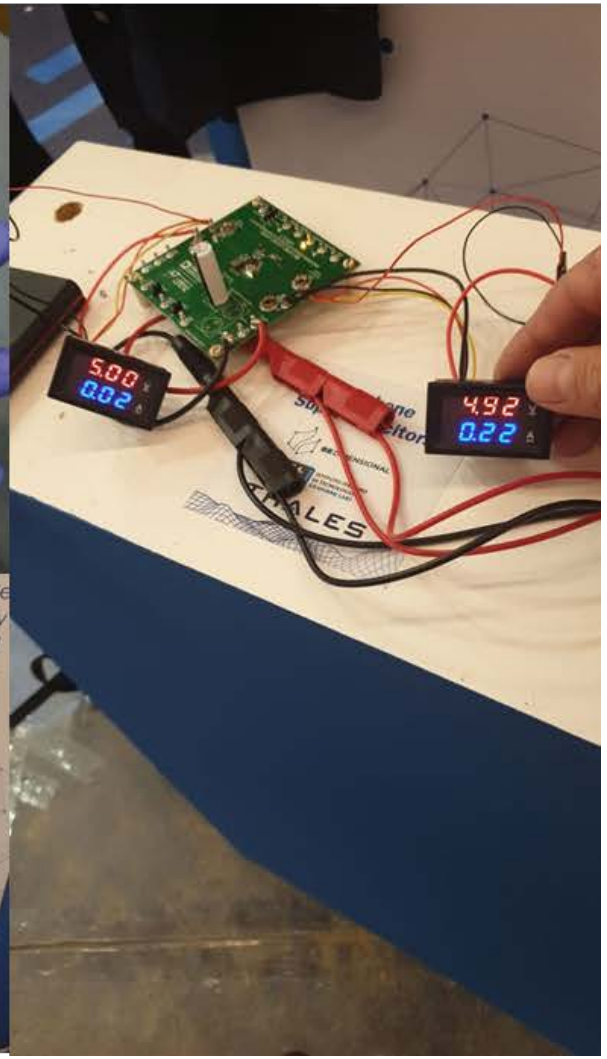
THALES

GRAPHENE FLAGSHIP

@World Mobile Congress 2019, Barcelona (E)



Acknowlegments

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