PC2NS3
11-14th September
Sønderborg, Denmark

CATRIN
Czech Advanced Technology and Research Institute

Unleashing the Power: Superior Properties of Fluorographene-Derived Materials for Energy Storage Applications

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VSB TECHNICAL UNIVERSITY OF OSTRAVA
IT4INNOVATIONS NATIONAL SUPERCOMPUTING CENTER

CATRIN
Czech Advanced Technology Research Institute

the Olomouc city

lonely planet
The hidden gems of Europe ...

Olomouc and the Olomouc Region in Europe

Czech Advanced Technology and Research Institute

CATRIN
Czech Advanced Technology Research Institute

Palacký University Olomouc

Est. 1573
8 faculties
1 research unit (CATRIN)

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Czech Advanced Technology and Research Institute

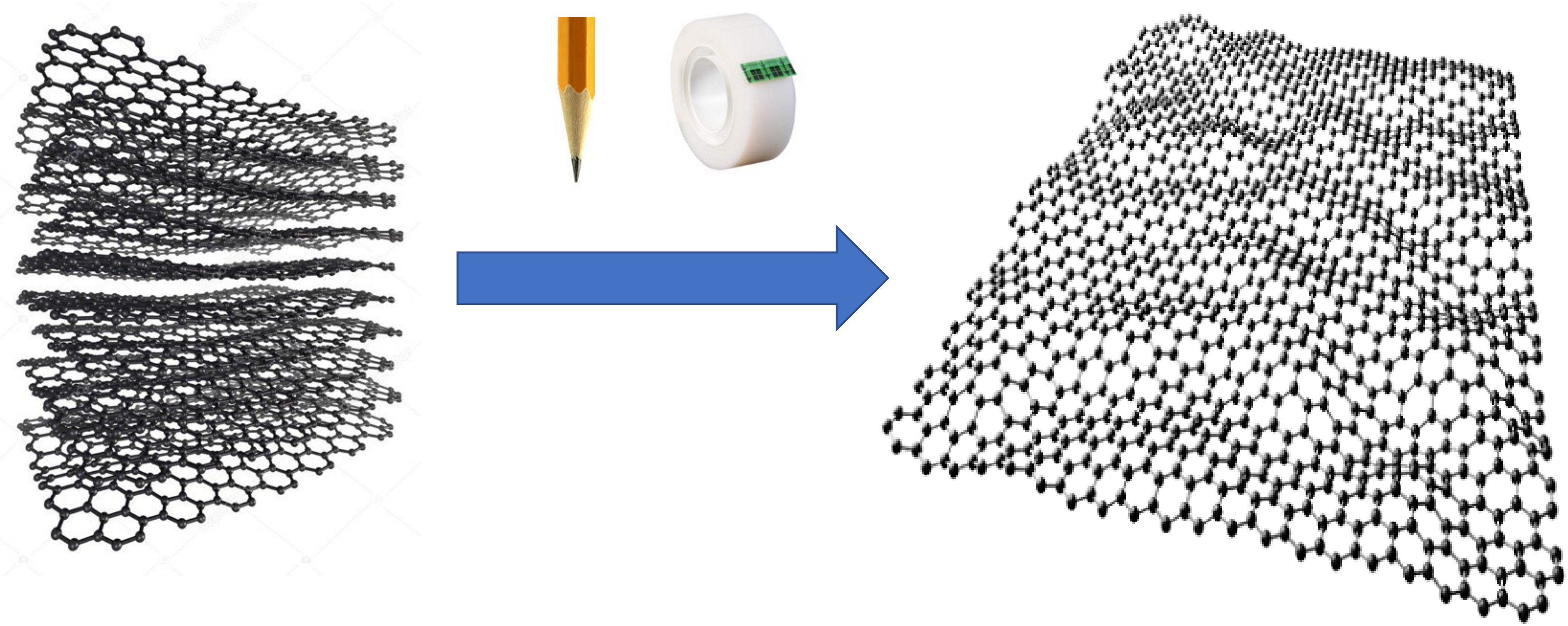
Est. 2021
(history from 2010)

CATRIN-RCPTM
Nanotechnologies, Chemistry

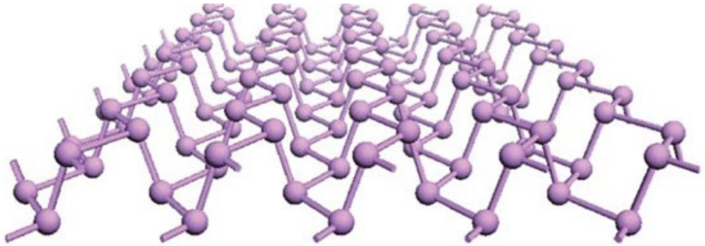
CATRIN-CRH
Biotechnologies, Agriculture

CATRIN-IMTM
Biomedicine

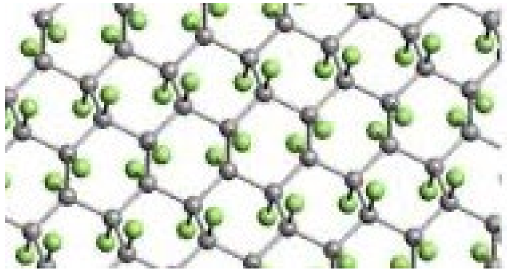
Graphene is 2D carbon material prepared by graphite exfoliation (Geim, Novoselov 2004)

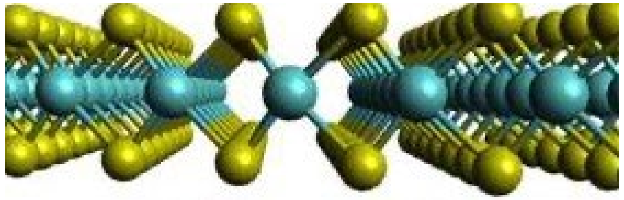


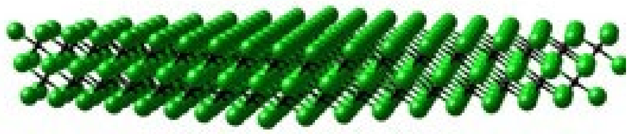
2D Materials

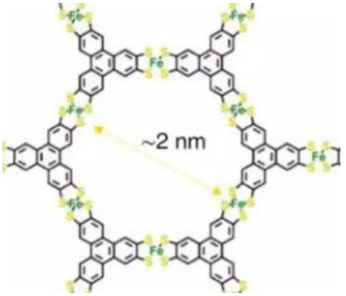


- Graphene - 2004 by Novoselov and Geim
- Wide family of 2D materials
  - One element
    - C: graphene, P: phosphorene, …
  - More elements
    - graphene derivatives – graphane (C_xH_x), fluorographene (C_xF_x), graphene oxide
    - graphene analogs – hBN
    - G-C_3N_4
    - MXenes (Ti_3C_2 …)
    - transition metal chalcogenides (MoS_2 …)
    - transition metal oxides and hydroxides (TiO_2, … $Ni(OH)_2$)
    - 2D zeolites
    - 2D MOFs, COFs







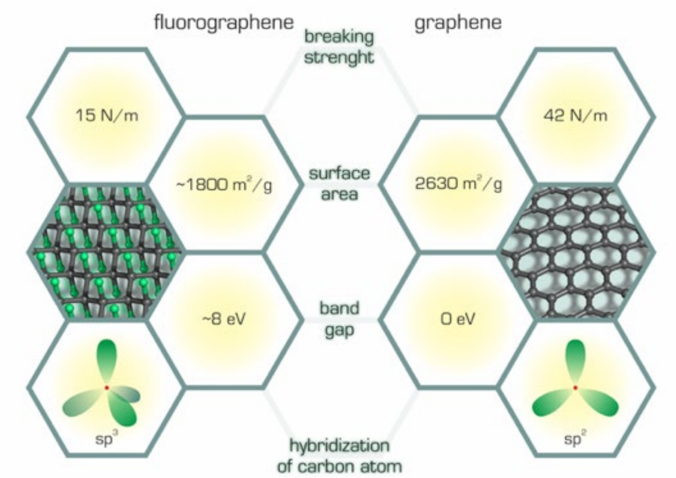


Fluorograhene (discovered in 2010)

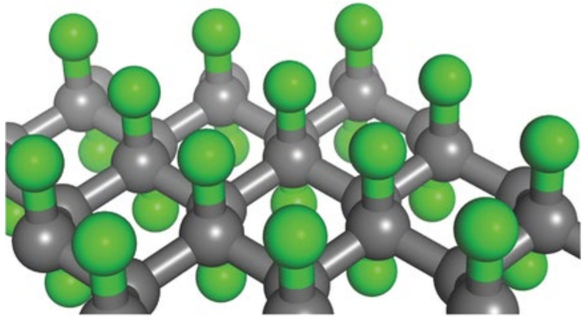
Mechanical exfoliation of graphite fluoride
Nair RR *et al.* Small 6, 2877 (2010)

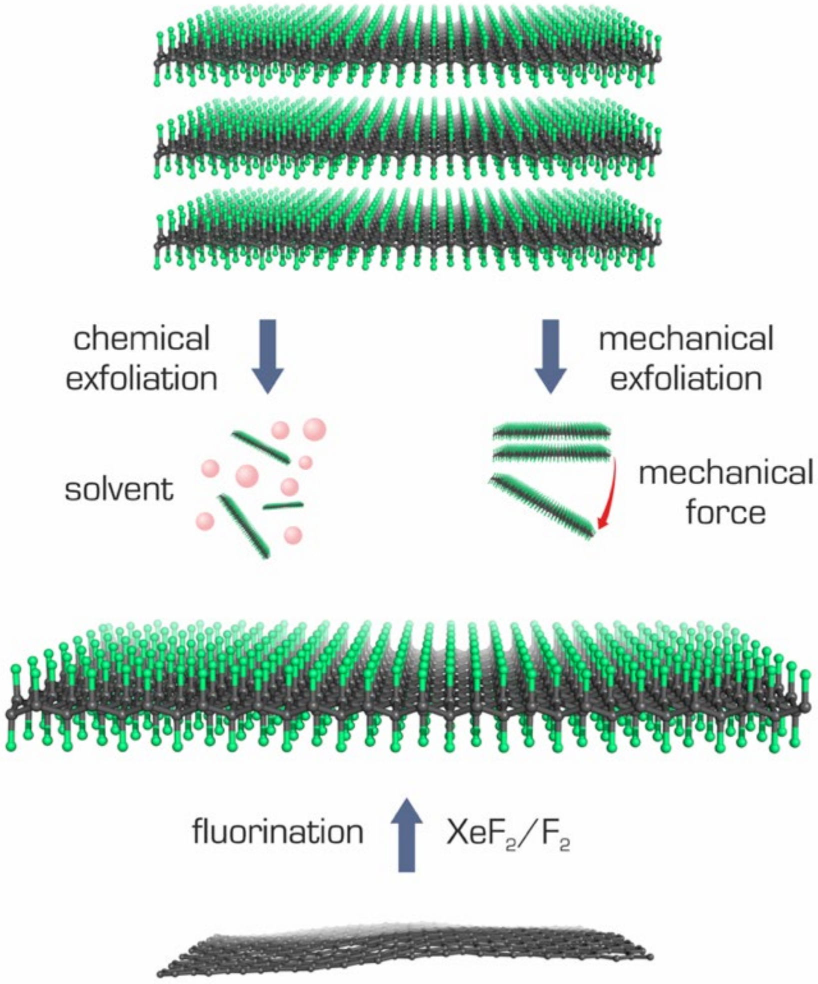
Chemical exfoliation of graphite fluoride
Zbořil R *et al.* Small 6, 2885 (2010)

Fluorination of graphene
Robinson JT *et al.* Nano Letters 10, 3001 (2010)
Cheng SH *et al.* PRB 81, 205435 (2010)



$C_1F_{1(1.1)}$





ACS Nano 7, 6434, 2013
Appl. Mater. Today, 9, 60, 2017

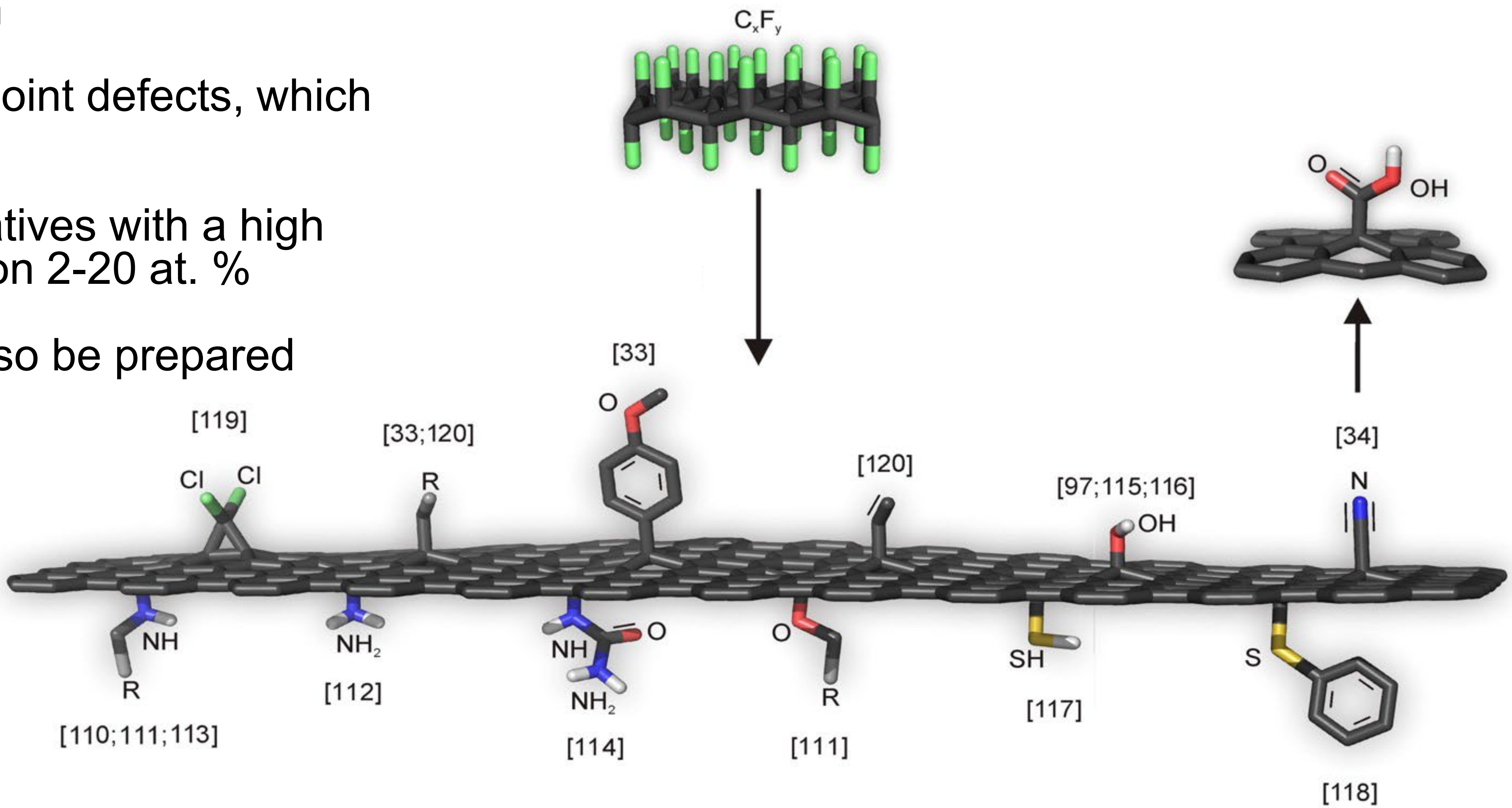
Fluorograhene reacts at mild conditions

elimination + substitution

reaction is triggered by point defects, which behave like el-philes

leads to graphene derivatives with a high degree of functionalization 2-20 at. %

doped graphenes can also be prepared



Nanoscale 10, 4696, 2018
J. Phys. Chem. Lett. 9, 3580, 2018
ACS Sustainable Chem. Eng., 8, 4764, 2020

Appl. Mater. Today, 9, 60, 2017
[refs therein]

Applications explored in our lab for graphene-derivatives

erc erc erc erc

Catalysis

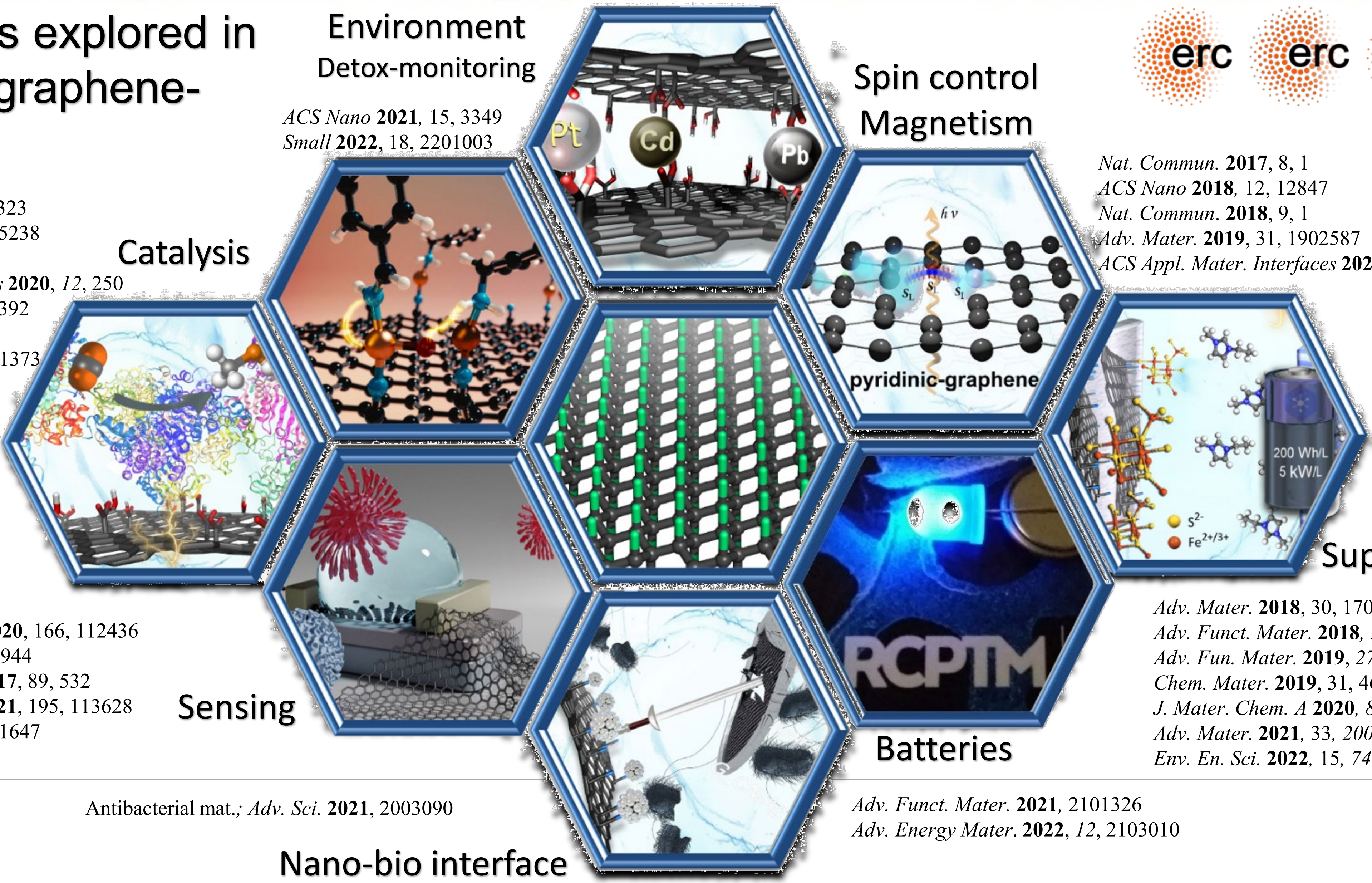
Adv. Mater. **2019**, 31, 1900323
Green Chemistry **2019**, 21, 5238
Chem. Sci. **2019**, 10, 9438
ACS Appl. Mater. Interfaces **2020**, *12*, 250
Adv. Mater. Int. **2021**, 2001392
Small **2021**, 17, 2006477
Nature Commun. **2023**, 14, 1373

Environment
Detox-monitoring

ACS Nano **2021**, 15, 3349
Small **2022**, 18, 2201003

Spin control
Magnetism

Nat. Commun. **2017**, 8, 1
ACS Nano **2018**, 12, 12847
Nat. Commun. **2018**, 9, 1
Adv. Mater. **2019**, 31, 1902587
ACS Appl. Mater. Interfaces **2020** 12, 34074, 2020



Supercaps

Adv. Mater. **2018**, 30, 1705789
Adv. Funct. Mater. **2018**, *28, 1801111*
Adv. Fun. Mater. **2019**, *27*, 1906998
Chem. Mater. **2019**, 31, 4698
J. Mater. Chem. A **2020**, *8, 25716*
Adv. Mater. **2021**, 33, *2004560*
Env. En. Sci. **2022**, 15, *740*

Sensing

Biosens. Bioelectron, **2020**, 166, 112436
ACS Omega **2019**, 4, 19944
Biosens. Bioelecron. **2017**, 89, 532
Biosens. Bioelecron. **2021**, 195, 113628
Green Chem. **2023**, 25, 1647
Small **2023**, in press

Batteries

Adv. Funct. Mater. **2021**, 2101326
Adv. Energy Mater. **2022**, *12*, 2103010

Nano-bio interface

Antibacterial mat.; *Adv. Sci.* **2021**, 2003090

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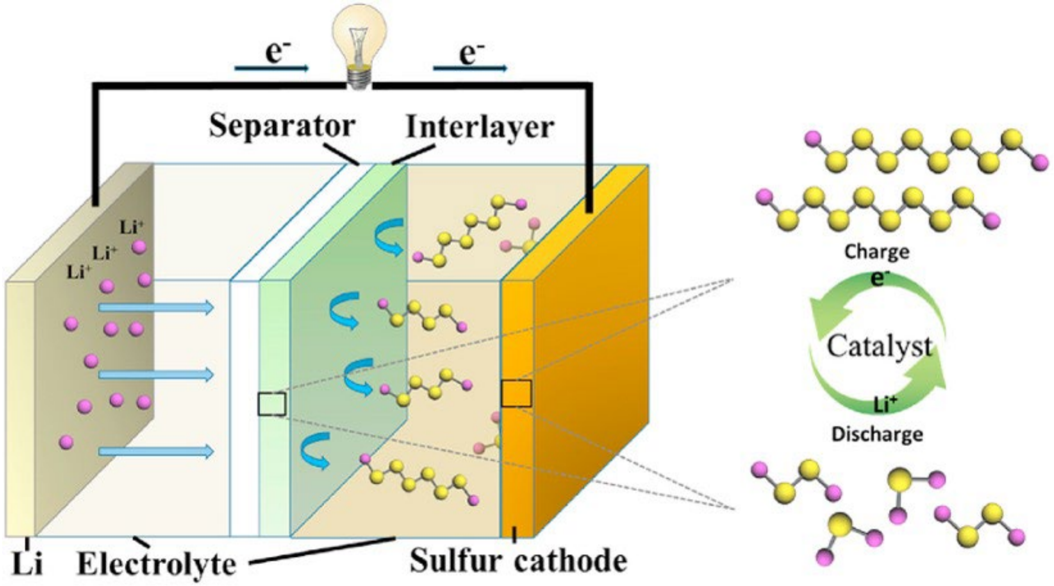
Sulphurized Graphene as Cathode for LSB

... just a short detour

Lithium-Sulfur Batteries (LSB)

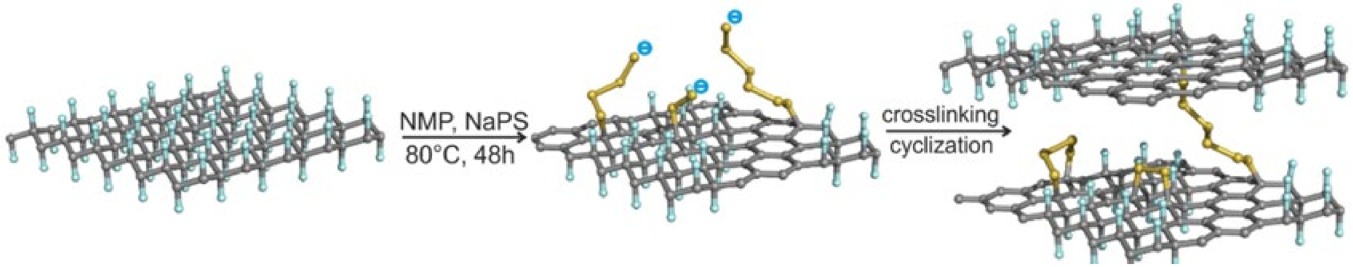
- a promising alternative for energy storage
- high theoretical capacity (1672 mAh g^{-1}) and specific energy (2600 Wh kg^{-1})
- sulfur is environmentally friendly and a key byproduct of the petroleum industry
- several bottlenecks hamper the practical development of the LSBs
    - sulfur's poor conductivity
    - large volume change
    - "shuttling effect" of lithium polysulfides (PSs), formed during the charge/discharge process. The dissolution of Li-PSs into the liquid electrolyte leads to low Coulombic effciency, poor sulfur utilization, fast capacity fading, and other parasitic reactions with the Li anode.

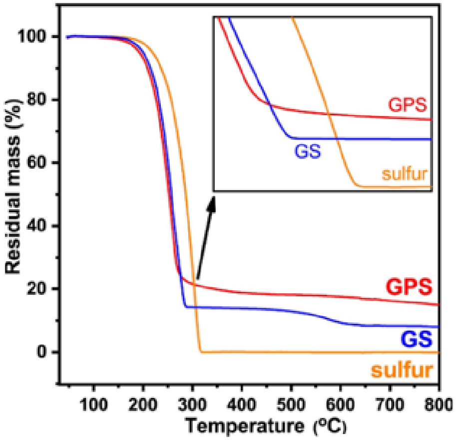


From: Energy Storage Materials 20, 55-70, 2019

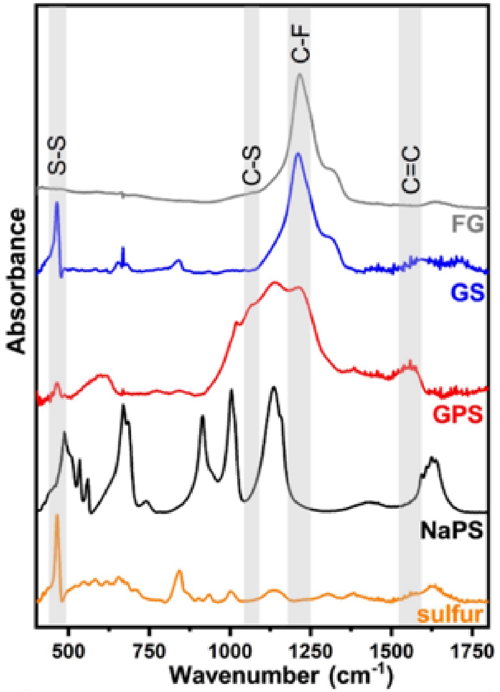
Background and characterization

- **highly and covalently sulfurized graphene cathode**
- **exploiting the nucleophilicity of polysulfide anions and the electrophilic centers in fluorographene**
- **Sulfur chains are immobilized by covalent bonding to graphene**





Sulfur loading ~80 wt. %

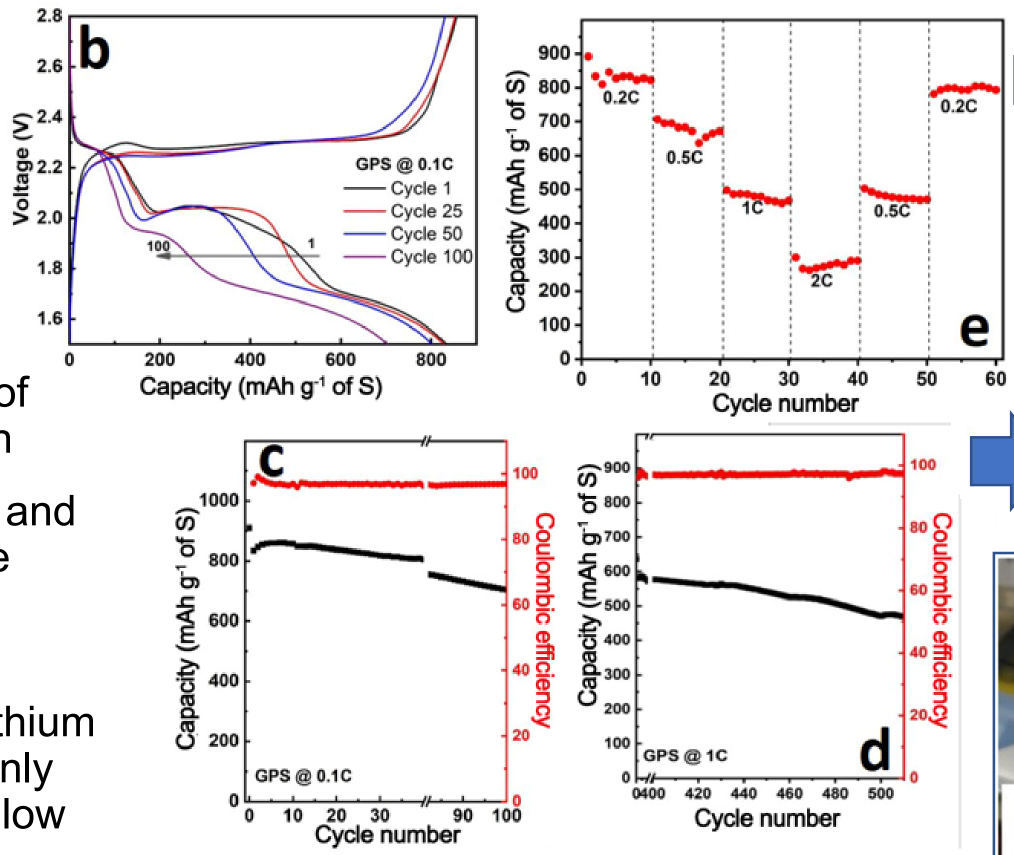


GPS: C–F at ~1200 cm^{-1} decreased (i.e., defluorination) 1580 cm^{-1} band emerged (graphene lattice formation).
The new band at ~1150 cm^{-1} demonstrates the development of covalent C–S bonds.

Tantis et al. Adv. Funct. Mater. ***2021****, 2101326*

Electrochemical performance of the graphene-polysulfide cathode

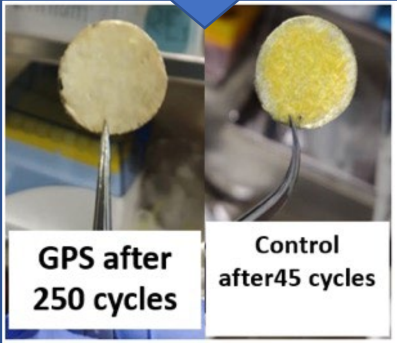
High electrochemical reversibility for more than 50 cycles at 0.1 C (167 mA g^{-1})



Good rate capability for both high and low specific currents

Outstanding stability for high and low specific currents
reduced shuttling-effect

- ✓ Alkylhalide-like and elegant chemistry of fluorinated carbon matrices exploitation
- ✓ Effective pathway for the development and study of previously unexplored cathode materials for LSBs.
- ✓ Electrochemical cycling of the sulfurized-graphene material against lithium exhibited top-rated performance with only **5 wt. %** of conductive additives and at low temperature of **25 °C**



Glass fiber separator after cycling showing the dissolution of sulfur at the control material

Supported by ERC PoC

EP 3978431
Tantis et al. Adv. Funct. Mater. ***2021****, 2101326*

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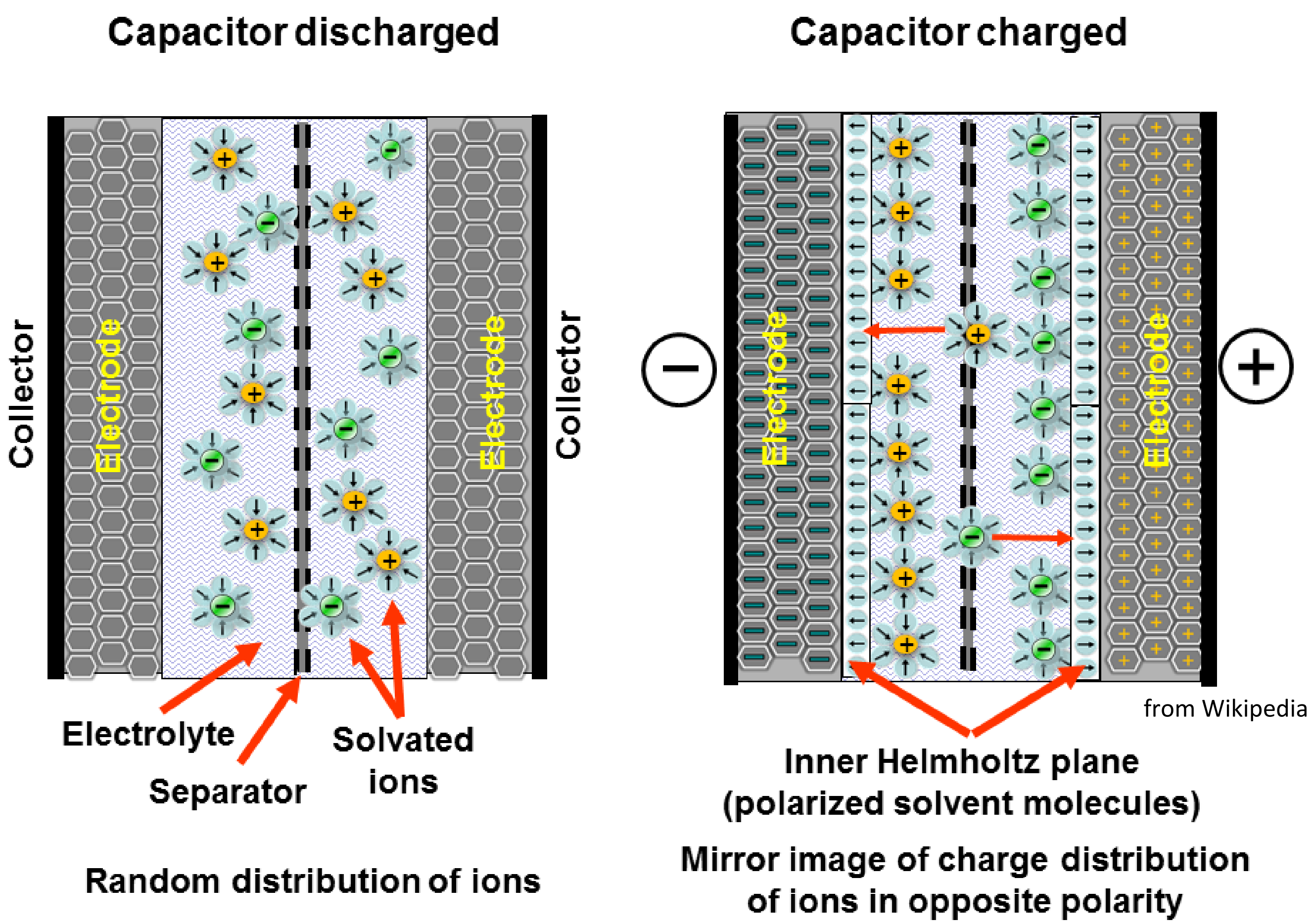
N-doped Graphene as A Supercapacitor Electrode Material

Supercapacitor

Energy storage mechanism is a physical process of ion accumulation on electrode material + electrolyte ion separation

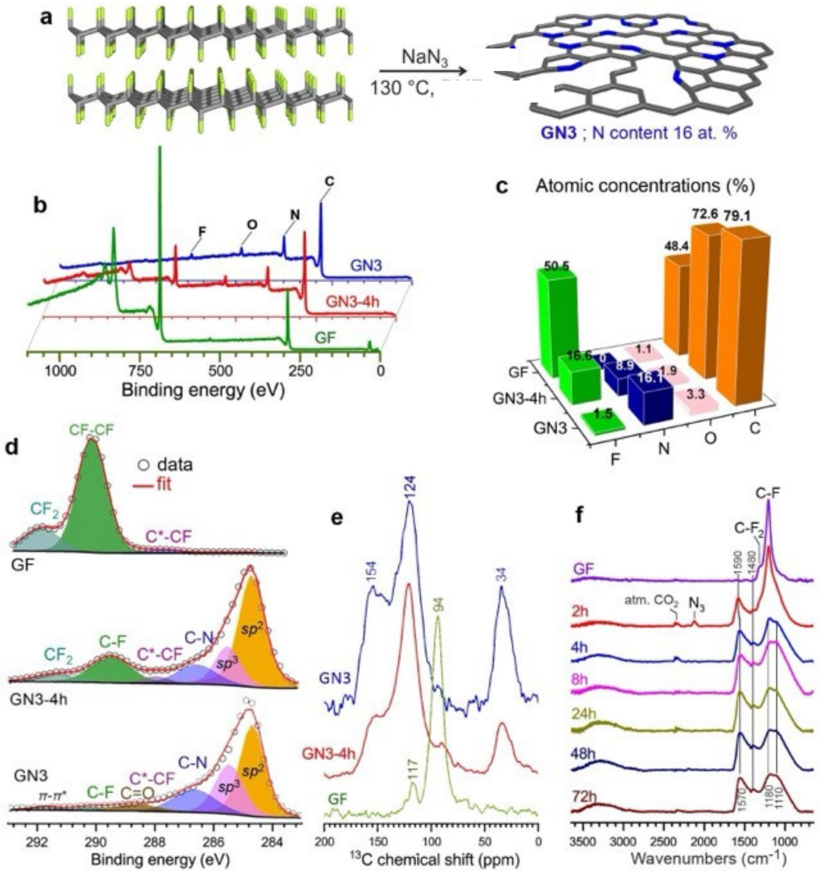
Quick and reversible charging/discharging

Applications: requiring many rapid charge/discharge cycles (circuit protection, combined with batteries for recuperation etc.)

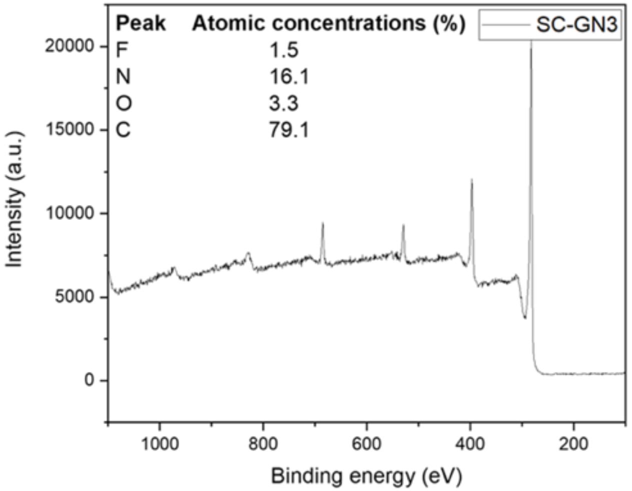


Operational principle of electrostatic double-layer capacitors (EDLCs)

SC-GN3 synthesis via chemistry of fluorographene



Reaction scheme, XPS, MS-NMR, and FTIR characterization of SC-GN3.

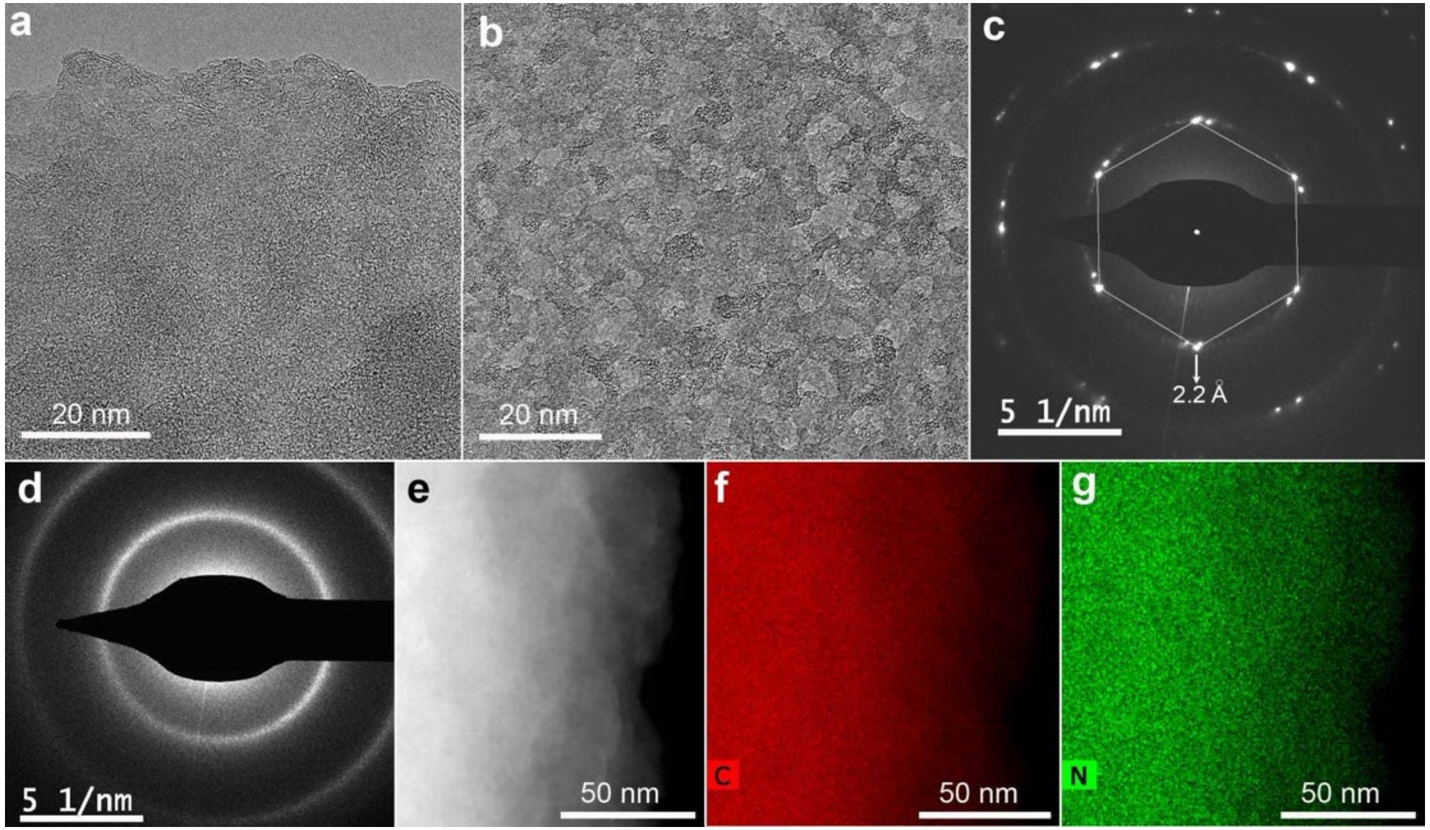


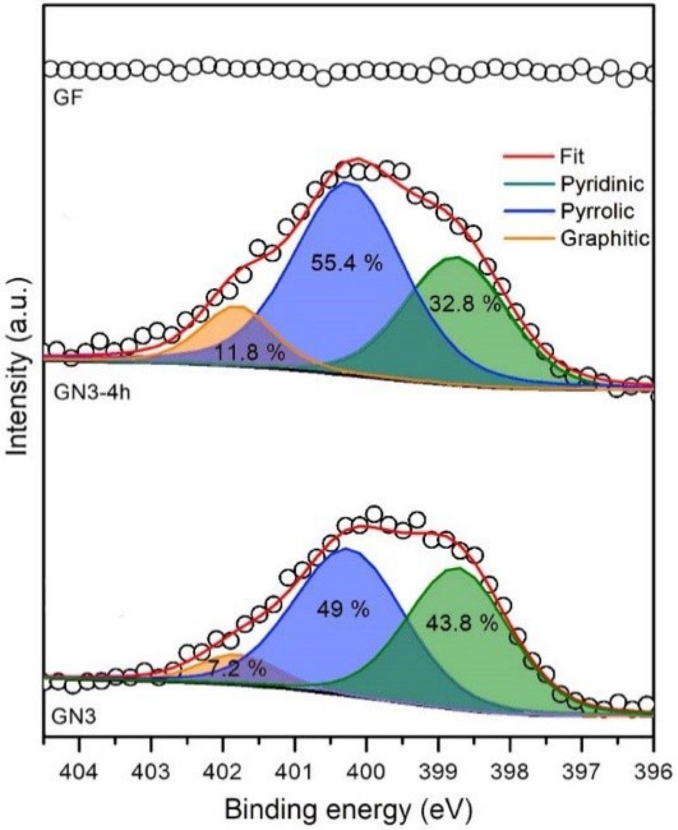
SC-GN3 powder and example of 50 g packing of purified product.

SC-GN3 material is highly N-doped (16 at. %) graphene-related material synthesized from graphite fluoride via wet chemistry in one step.

After synthesis purification steps are needed.

Characterization of SC-GN3

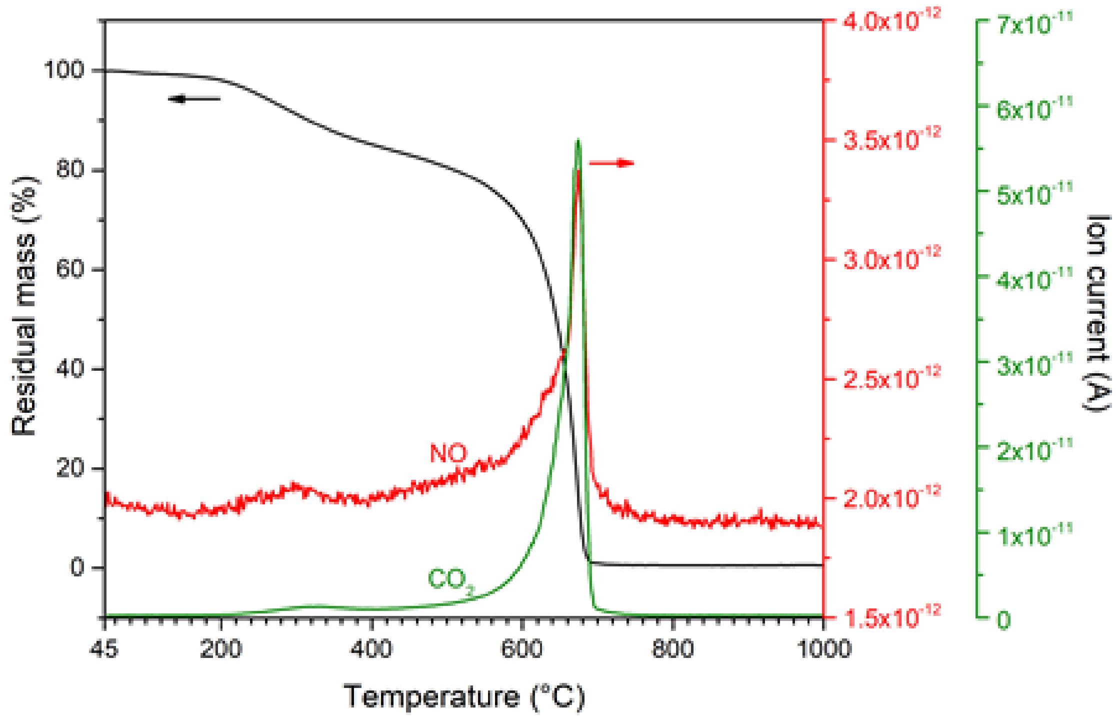


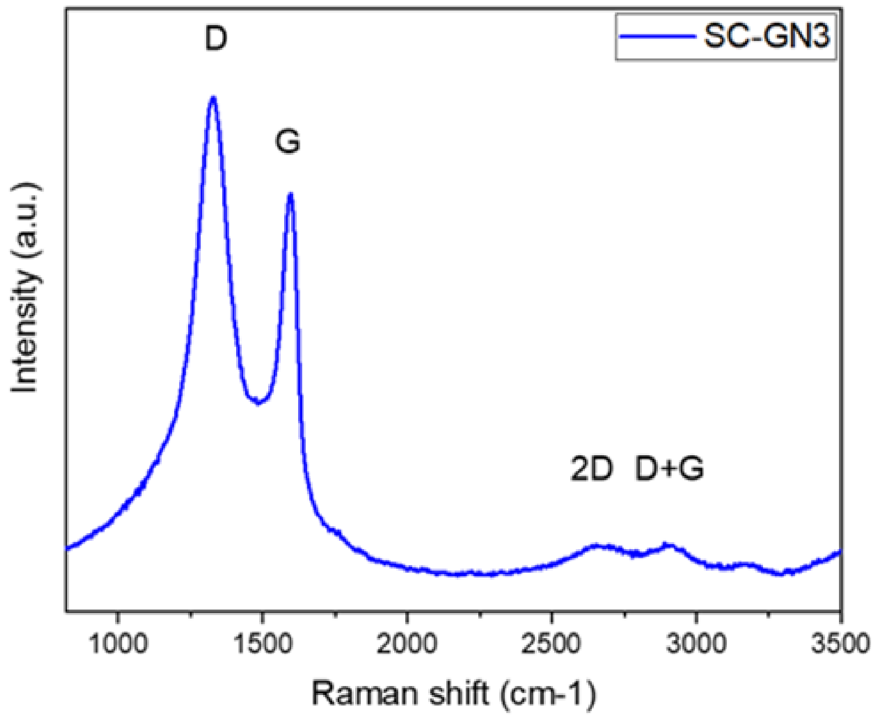


Homogeneous distribution of nitrogens in the lattice.

Chemical forms of nitrogens from HR XPS 1s N.

Characterization of SC-GN3

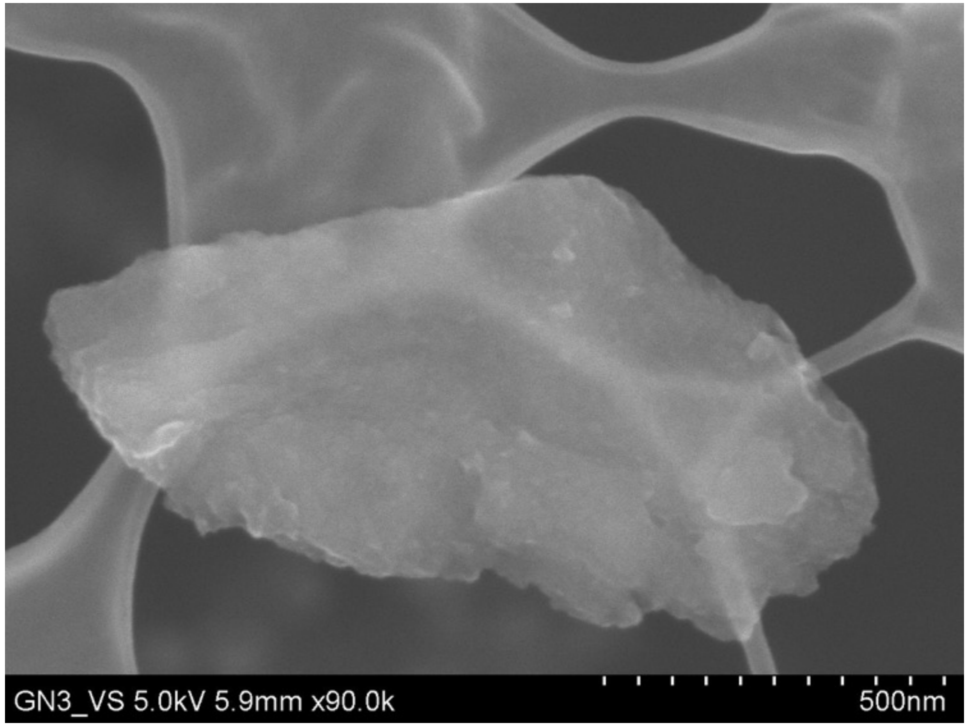




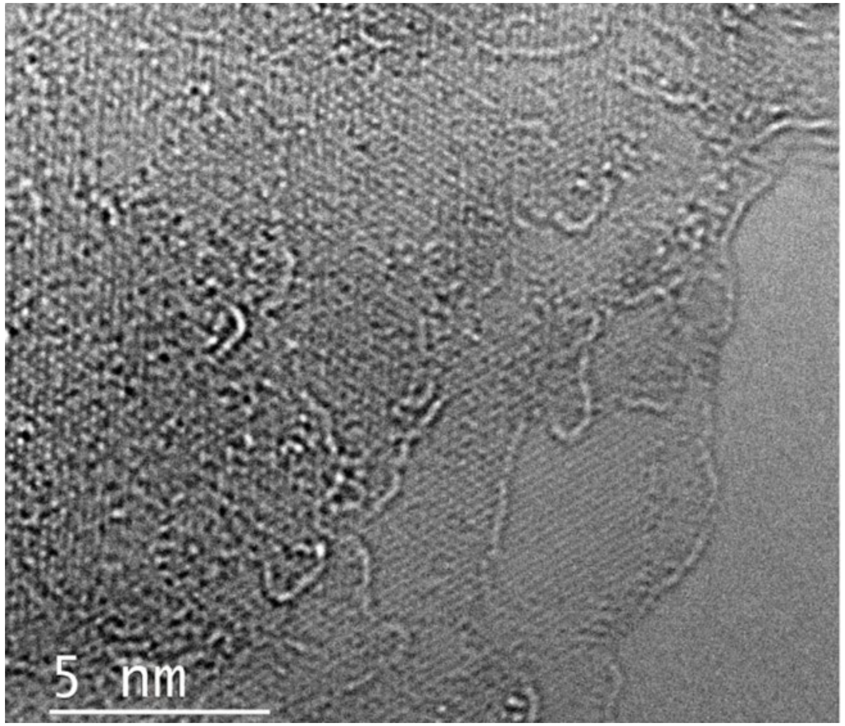
Thermal stability of SC-GN3 (with evolved gas analysis).

Raman spectrum of SC-GN3.

Characterization of SC-GN3

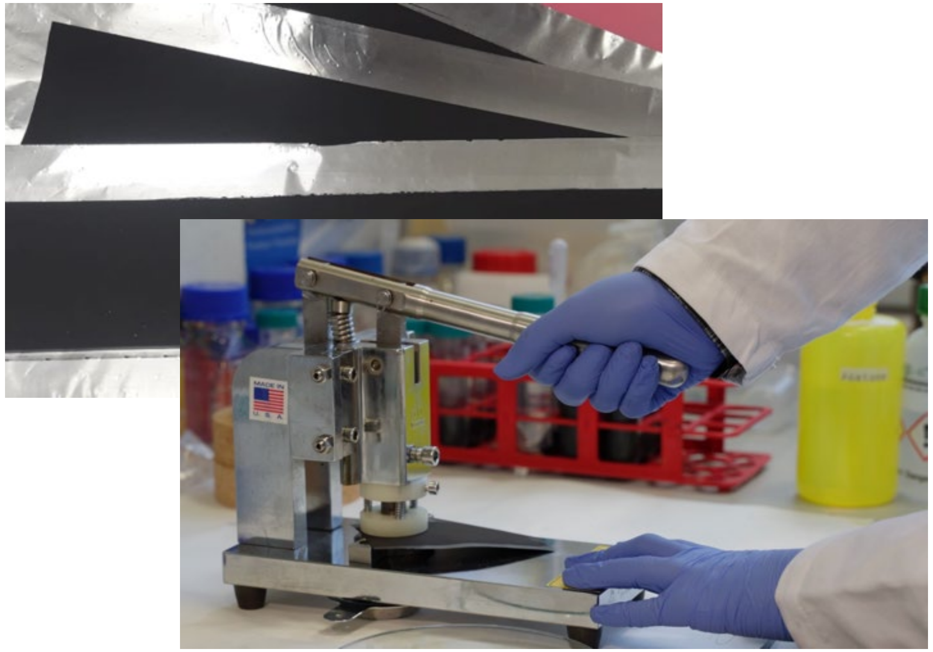


SEM image of N-doped graphene indicates on a few-layer structure.

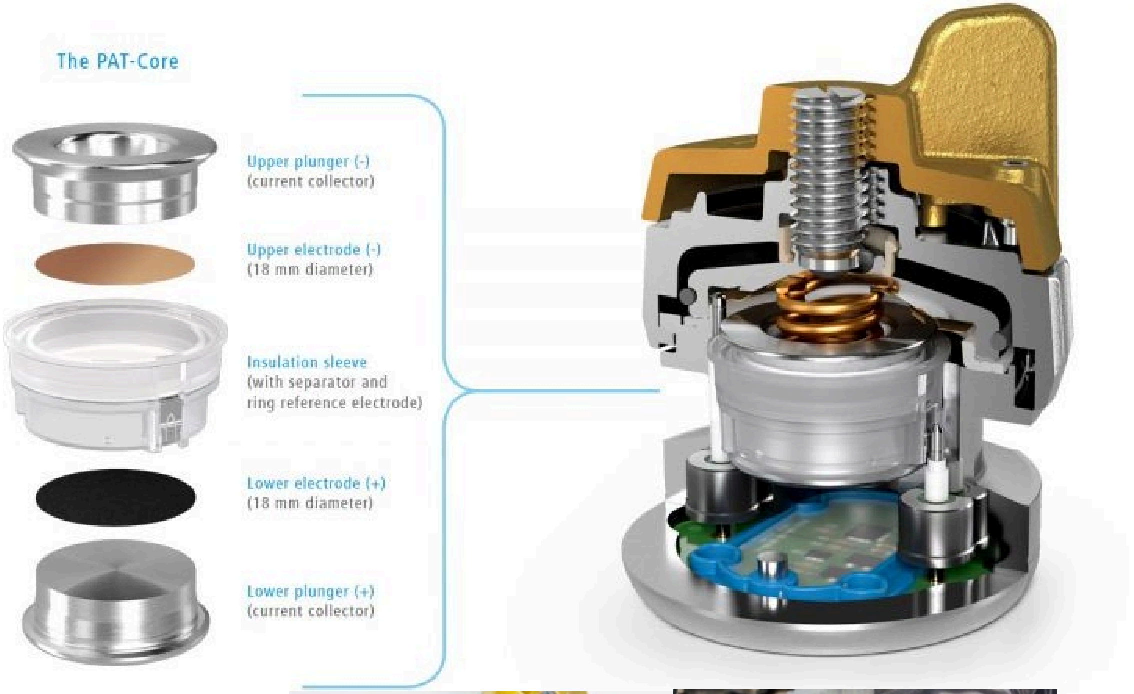


TEM image of N-doped graphene

SC-GN3 testing

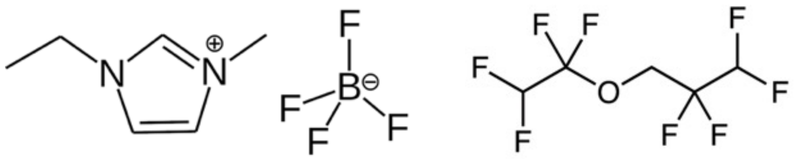


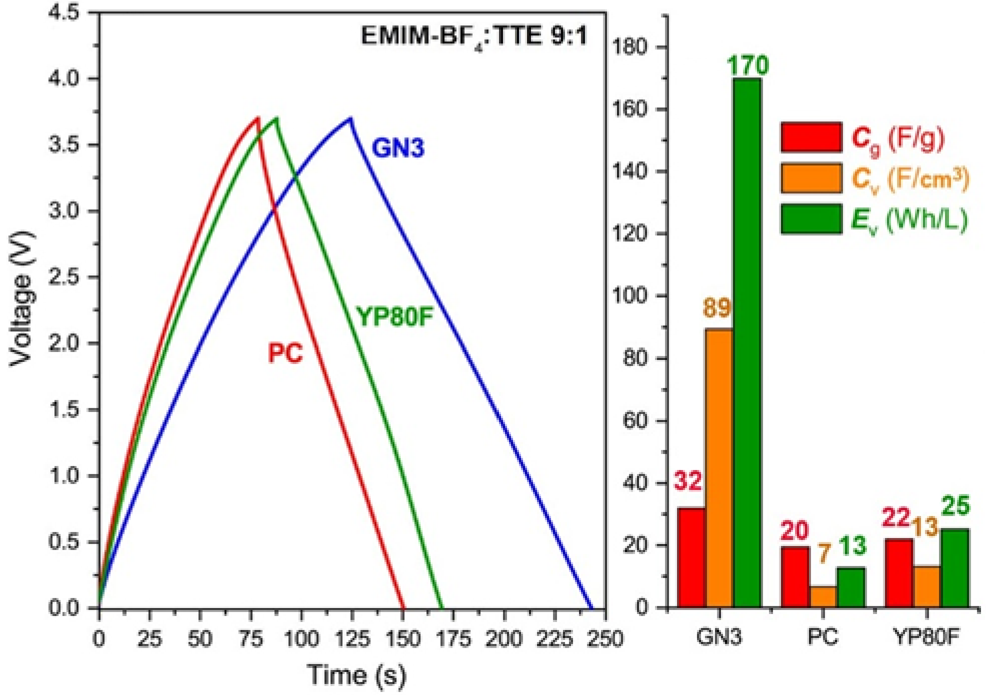
SC-GN3 is mixed with binder, electrodes are prepared.



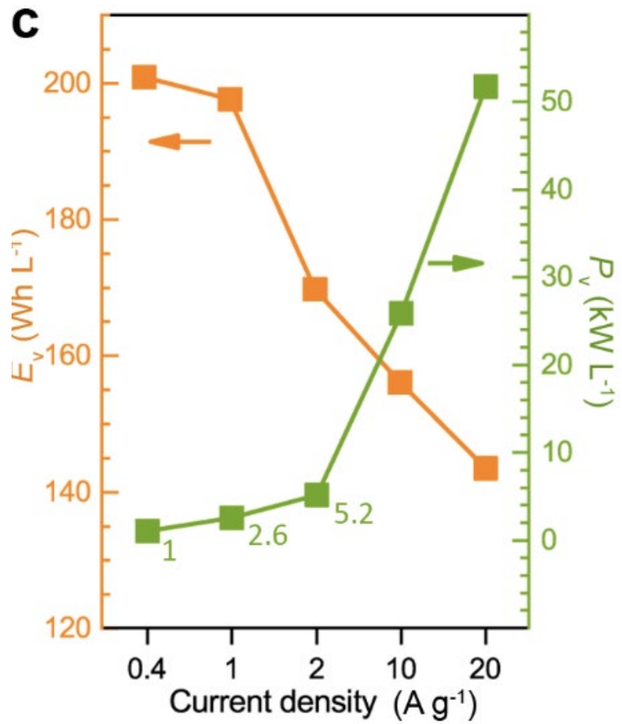
Scheme of El-Cell used for testing (figures taken from el-cell.com).

SC-GN3





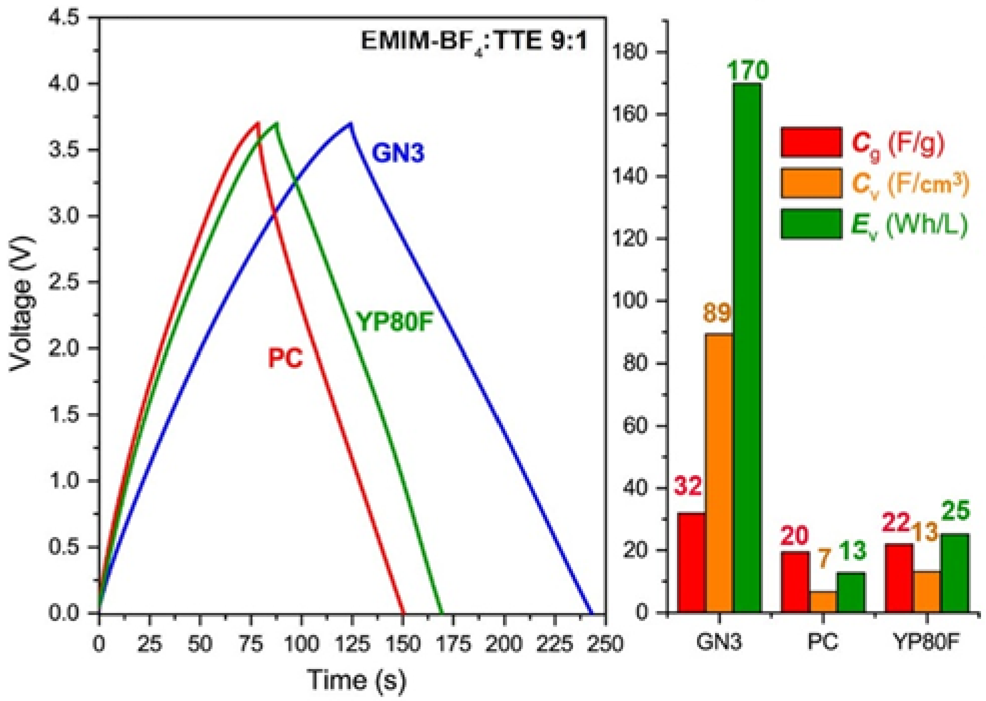
GCD profiles and supercapacitor performance comparison of commercial porous high surface area carbon materials and N-doped graphene (at 2 A g^{-1}).



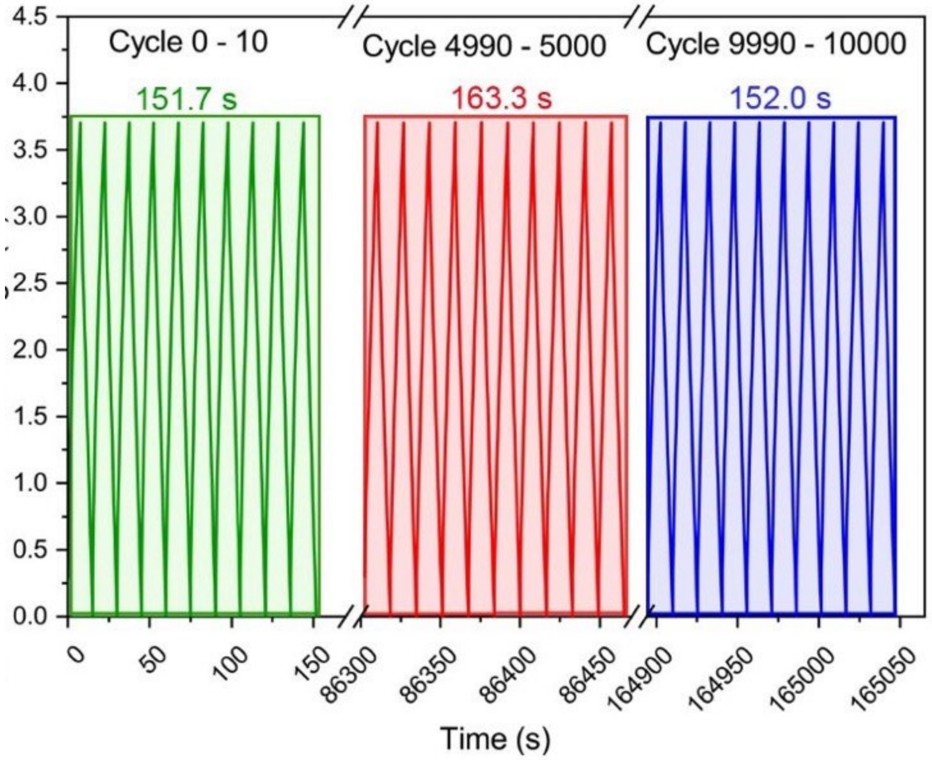
Energy and power density of SC-GN3 at increasing specific currents. SC-GN3 delivers energy densities of 200 Wh L^{-1} at a power of 2.6 kW L^{-1} and 143 Wh L^{-1} at 52 kW L^{-1}.

porous carbon (PC) from ACS Material (0.3 g cm^{-3}, 2000 m^2 g^{-1} according to N_2 BET) and YP-80F Kuraray carbon (KC) (0.6 g cm^{-3}, 2363 m^2 g^{-1} according to N_2 BET

SC-GN3

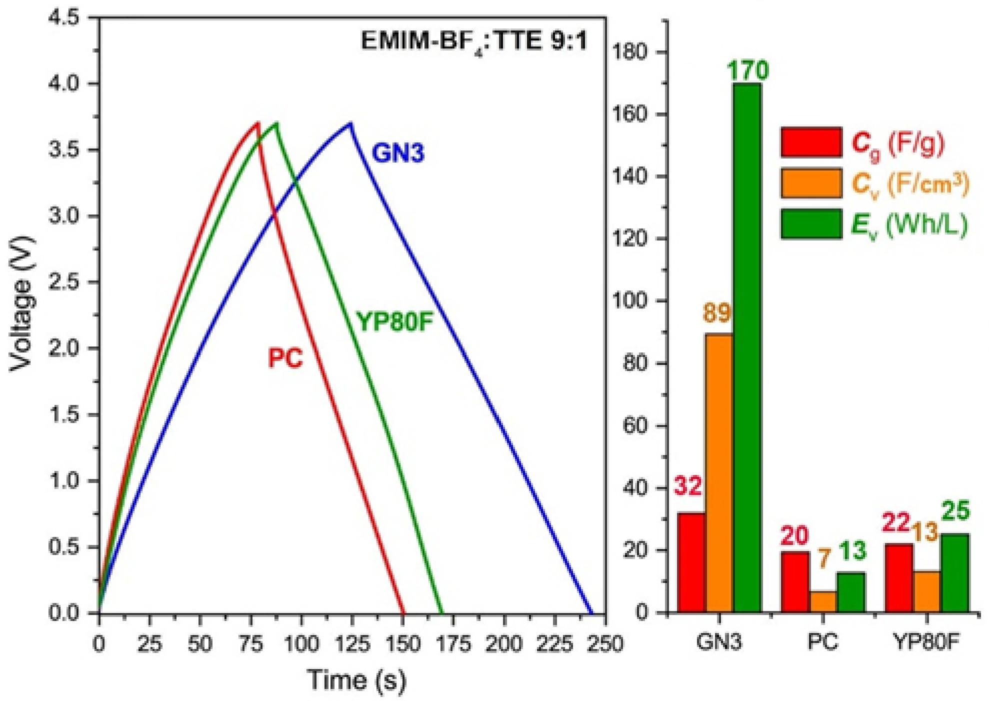


GCD profiles and supercapacitor performance comparison of commercial porous carbon materials and N-doped graphene.

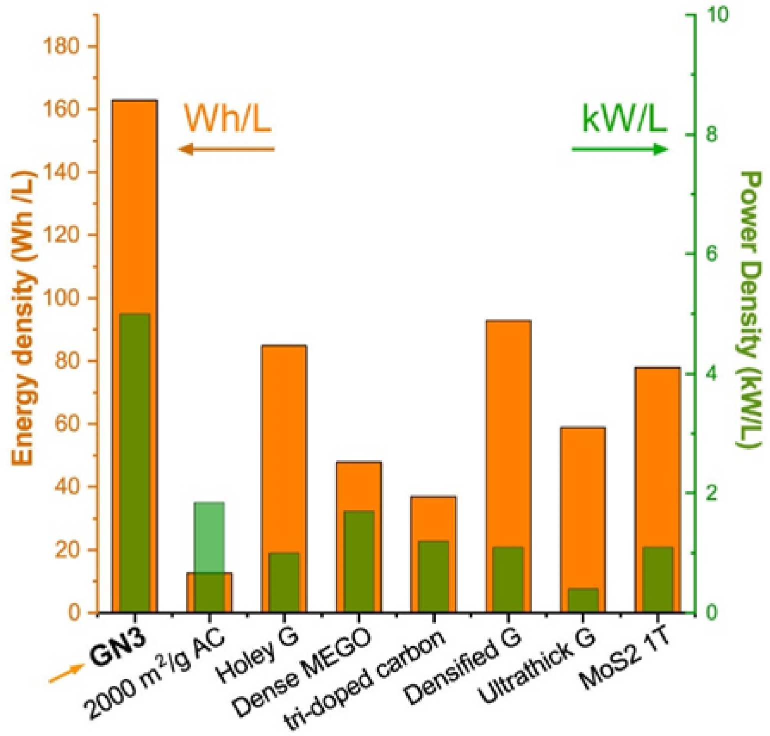


Stability of GN3 showing the GCD profiles at the beginning, mid-point, and end of a 10,000 cycle test.

SC-GN3



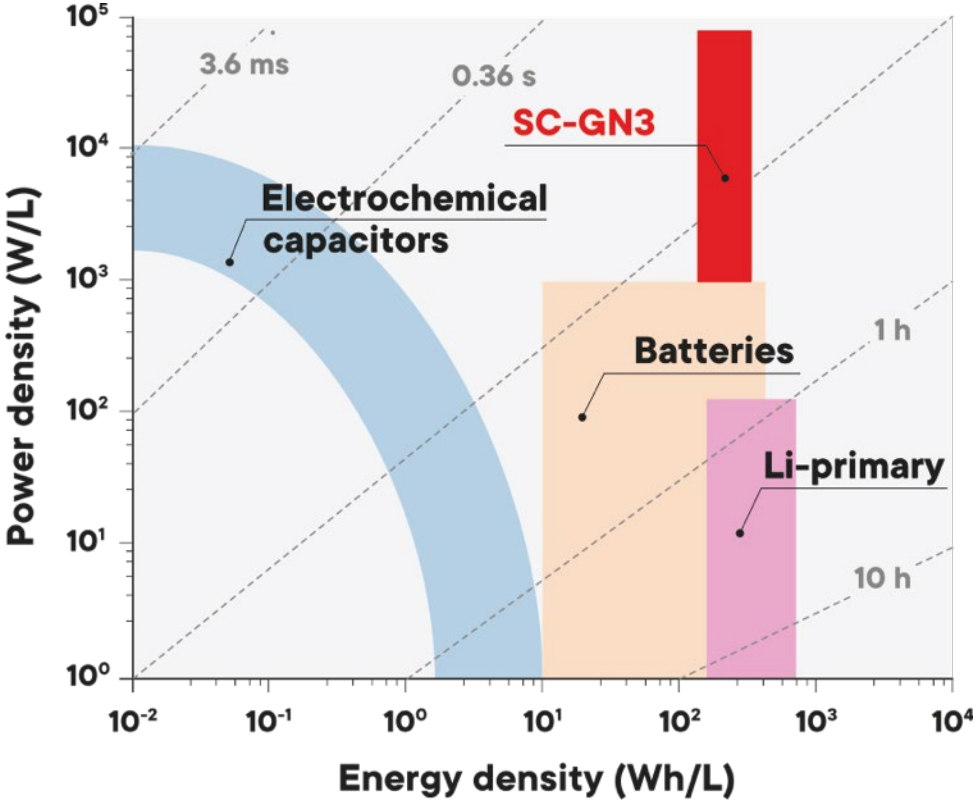
GCD profiles and supercapacitor performance comparison of commercial porous carbon materials and N-doped graphene.



Current state-of-art comparison.

1. *Angewandte Chemie International Edition 58, 2397–2401 (**2019**).*
2. *Nature Communications 5, 5554 (**2014**).*
3. *Nano Energy 2, 764–768 (**2013**).*
4. *Science 341, 534–537 (**2013**).*
5. *Energy Environ. Sci. 9, 3135–3142 (**2016**).*
6. *Nature Nanotechnology 10, 313–318 (**2015**)*

SC-GN3



new material with record

energy density: 200 Wh/L
power density: 50 kW/L

Market Opportunity
Mini/Micro e-mobility

	BATTERIE	ENERGY-C
CONSTRUCTION	2 x 12V 75 Ah in series	6 x 5000F in series
RATED VOLTAGE	24V	24V
EFFECTIVE STORAGE ENERGY	1.800Wh	40Wh
RANGE	6 ~ 8h	700 meters (ca. 12 min)
CHARGE TIME	ca. 4h	<2min
VOLUME	16l	5l
WEIGHT	53kg	4,4kg (in future 2kg)
NUMBER OF CYCLES	~1000 cycles	>500.000 cycles

Prototypes in 2024 **2025**

EIC Transition

Example of available devices

AVX PrizmaCap (4 Wh/L), rel. 7/21

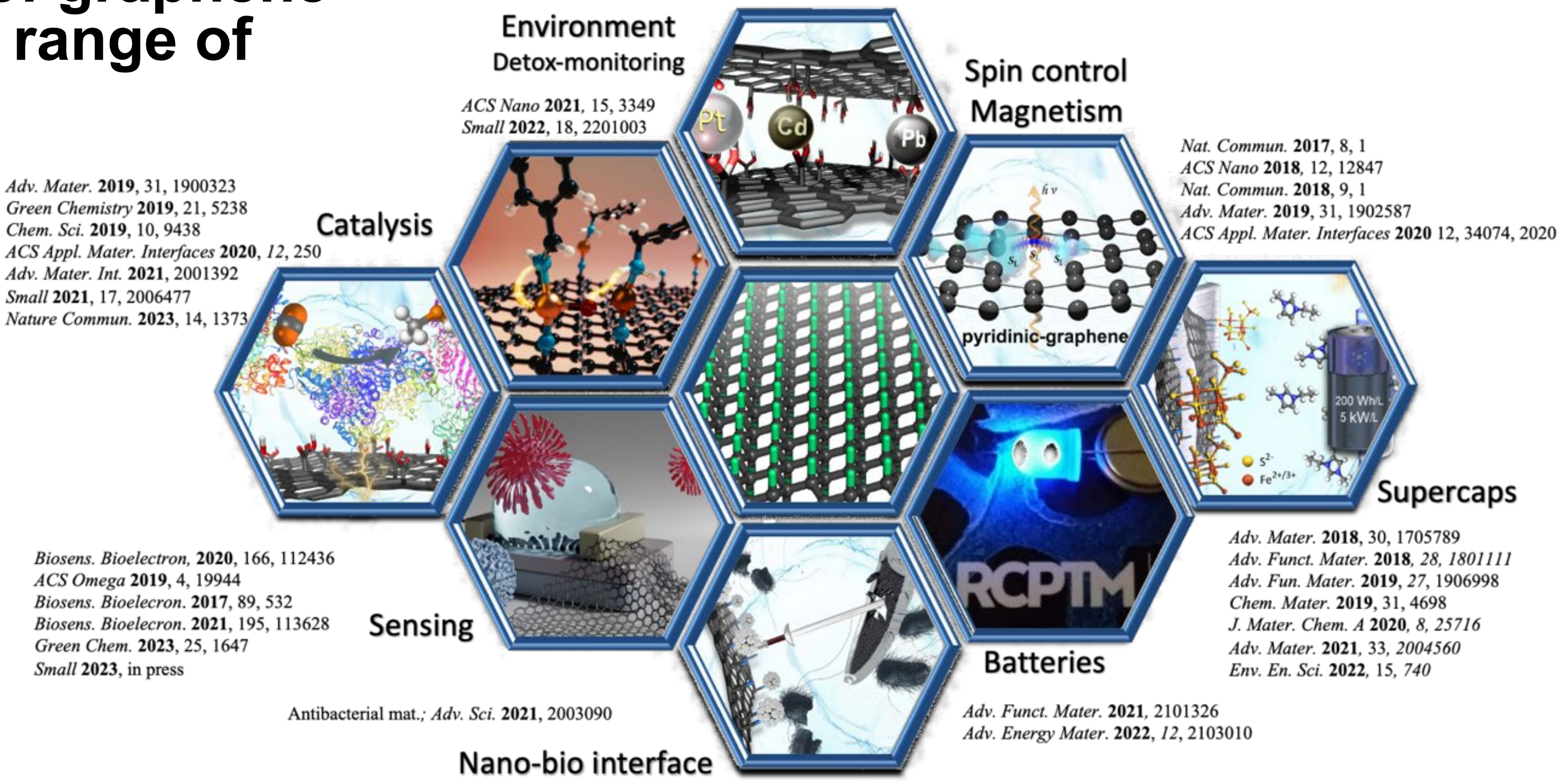
Skeleton SkelCap (16 Wh/L), rel. 9/21

Driverless transport AGV
Automated Guided Vehicles

Source: Jianghai-Europe

Fluorograhene

perspective material for scalable synthesis of graphene derivatives for wide range of applications.



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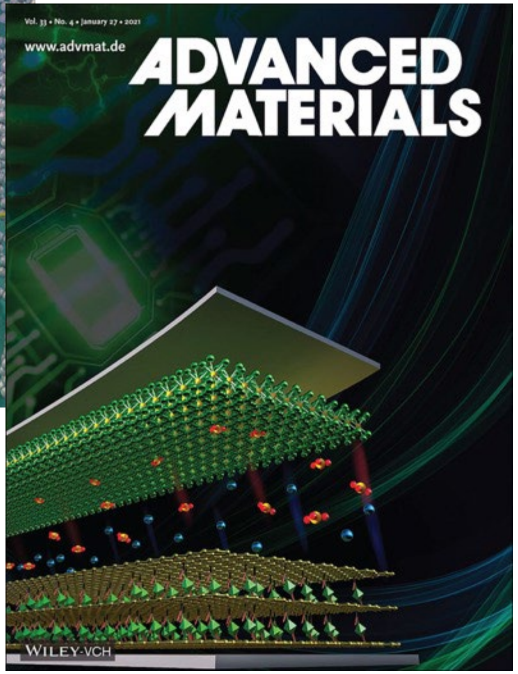
Luca Primavesi

erc European Research Council

eic European INNOVATION Council



Graphene acid available at https://graphene-derivatives.com/

General info: TRANS2DCHEM.ORG

Funded by the European Union

Contact: michal.otyepka@upol.cz