Summer School

Sustainable nanosensors for water pollution detection

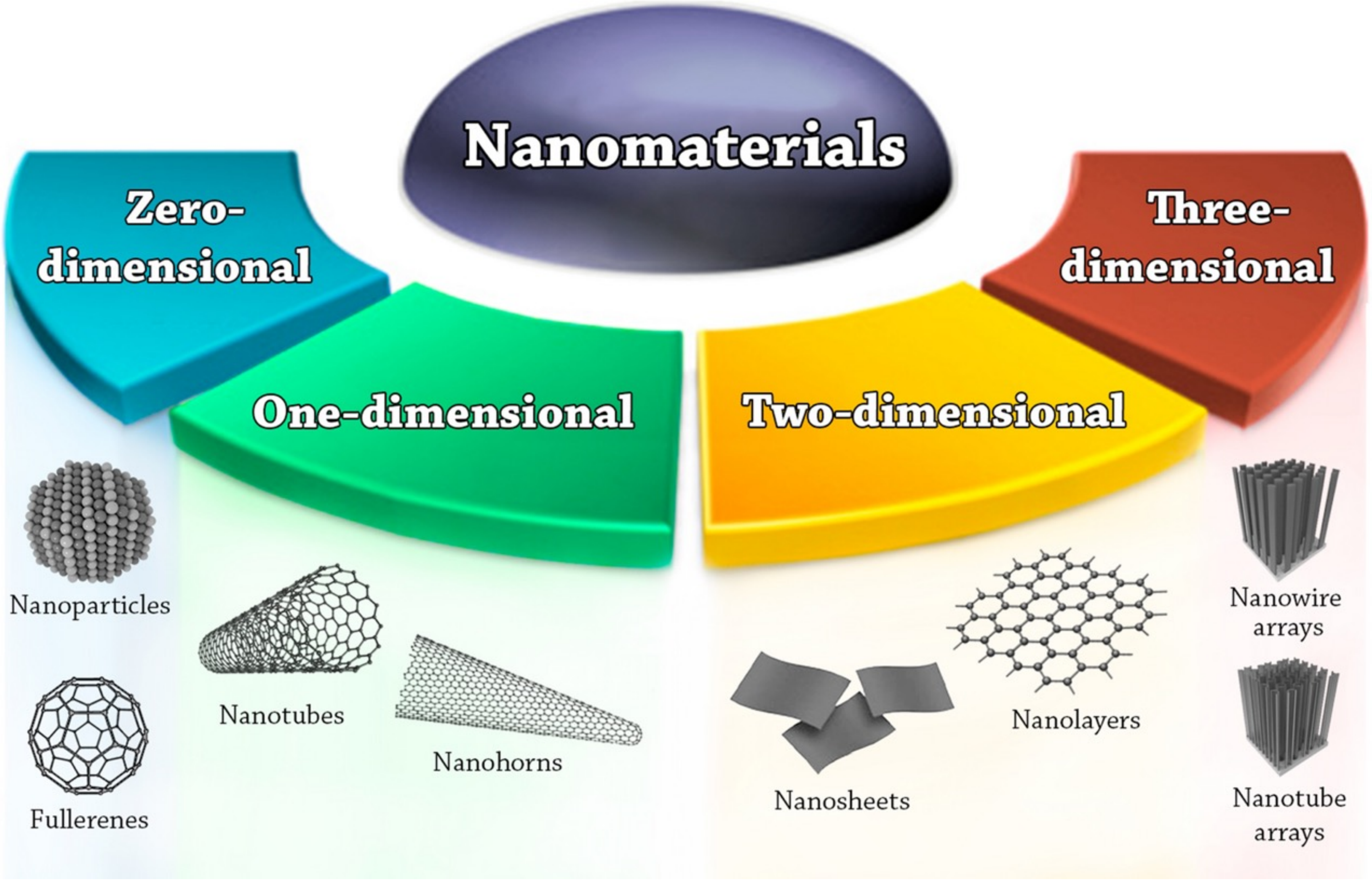
Barcelona, April 15-17, 2024

Graphene derivatives and their applications

by Michal Otyepka

Funded by the European Union

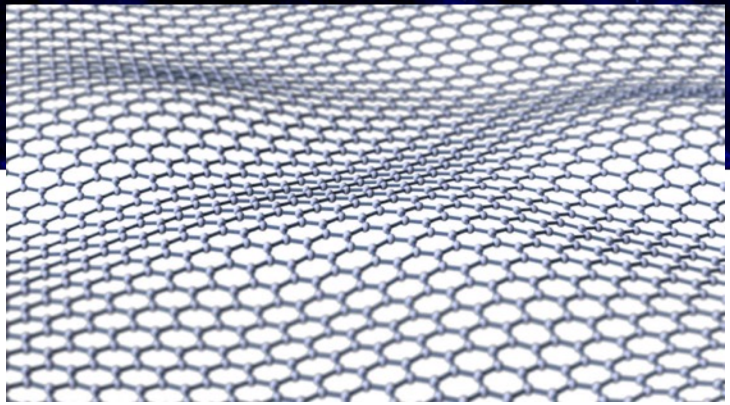
Classification of nanomaterials based on "dimensionality"

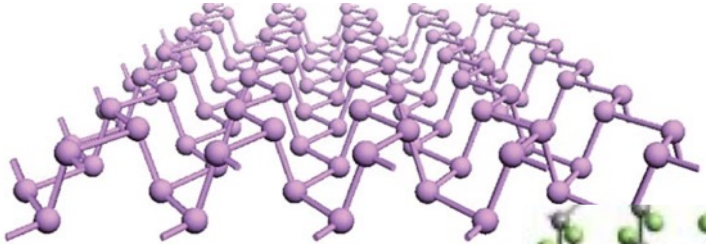


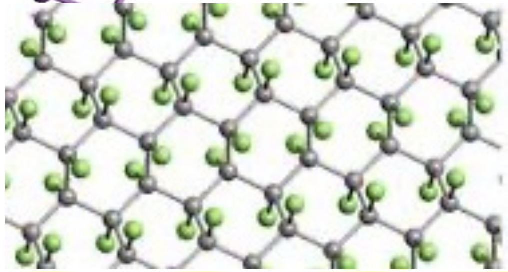
Taken from J. Nanobiotech. 20: 262 (2022)

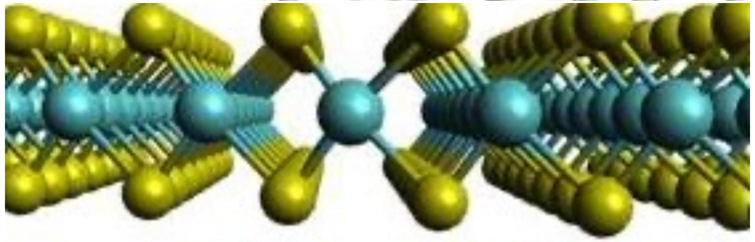
2D materials

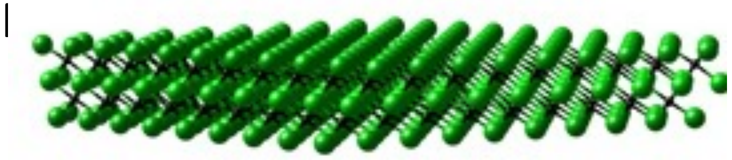
- Graphene - 2004 by Novoselov and Geim
- Wide family of 2D materials
  - One element
    - graphene (C), phosphorene (P) …
  - More elements
    - graphene derivatives – graphane (C_xH_x), fluorographene (C_xF_x), graphene oxide
    - graphene analogs – hBN
    - G-C_3N_4
    - MXenes (Ti_3C_2 …)
 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

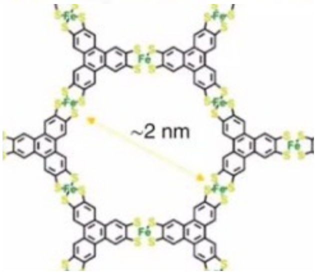






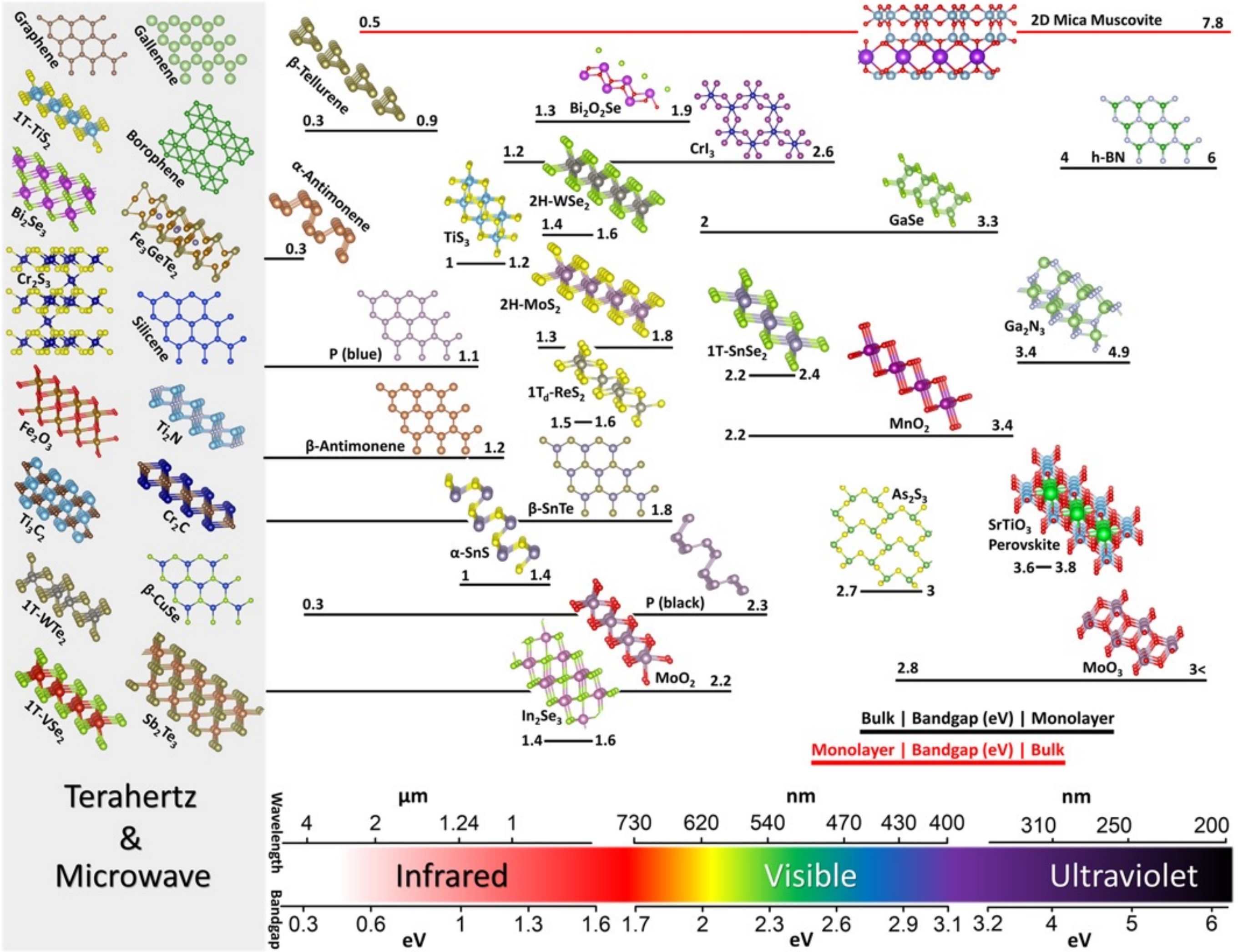






CATRIN Czech Advanced Technology Research Institute

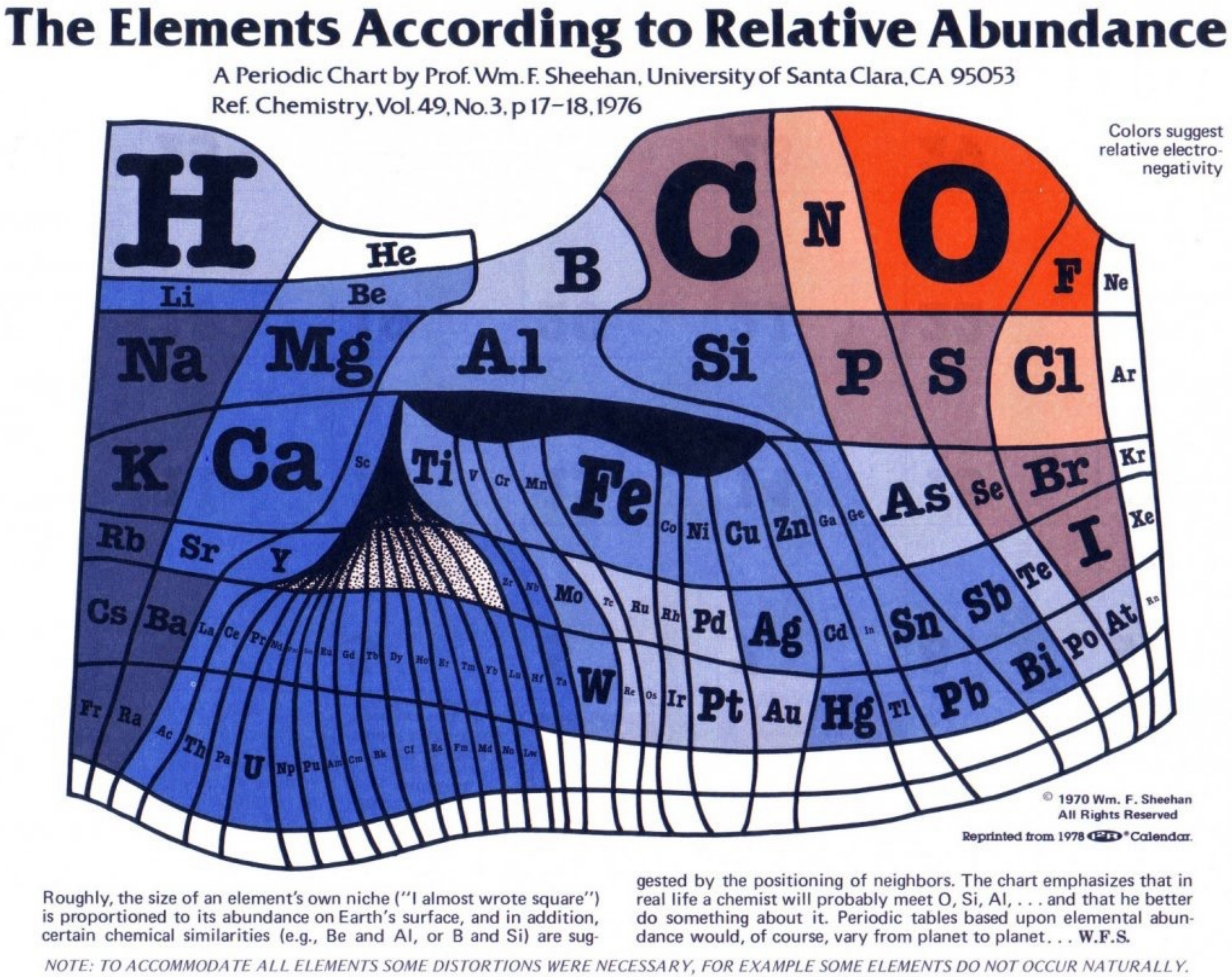
Band-gaps of 2D materials



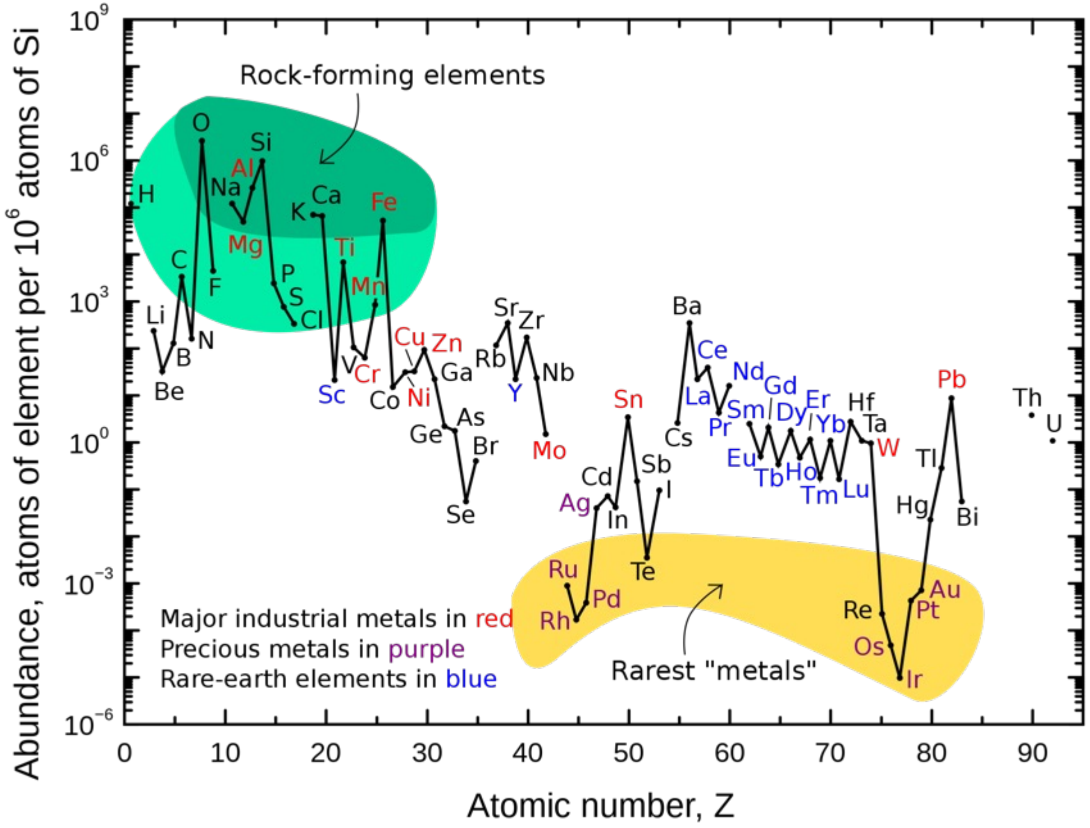
2D materials are chosen for their experimental significance and demonstration, with depictions of a perspective view of their crystal structures. Arrangement is in accordance with their bandgap, guided by the bottom wavelength/bandgap scale, whereas the bar beneath each structure indicates bandgap range from bulk to monolayer. Typically, the bulk bandgap is smaller than that of its monolayer (black bars), but there are exceptions (red bars). 2D materials on the far left, indicated by a gray box, are zero or near-zero bandgap, metallic, or semimetallic.

npj 2D Materials and Applications 4, 29 (2020)

For applications and upscaling …



Abundance (atom fraction) of the chemical elements in Earth‘s upper continental crust

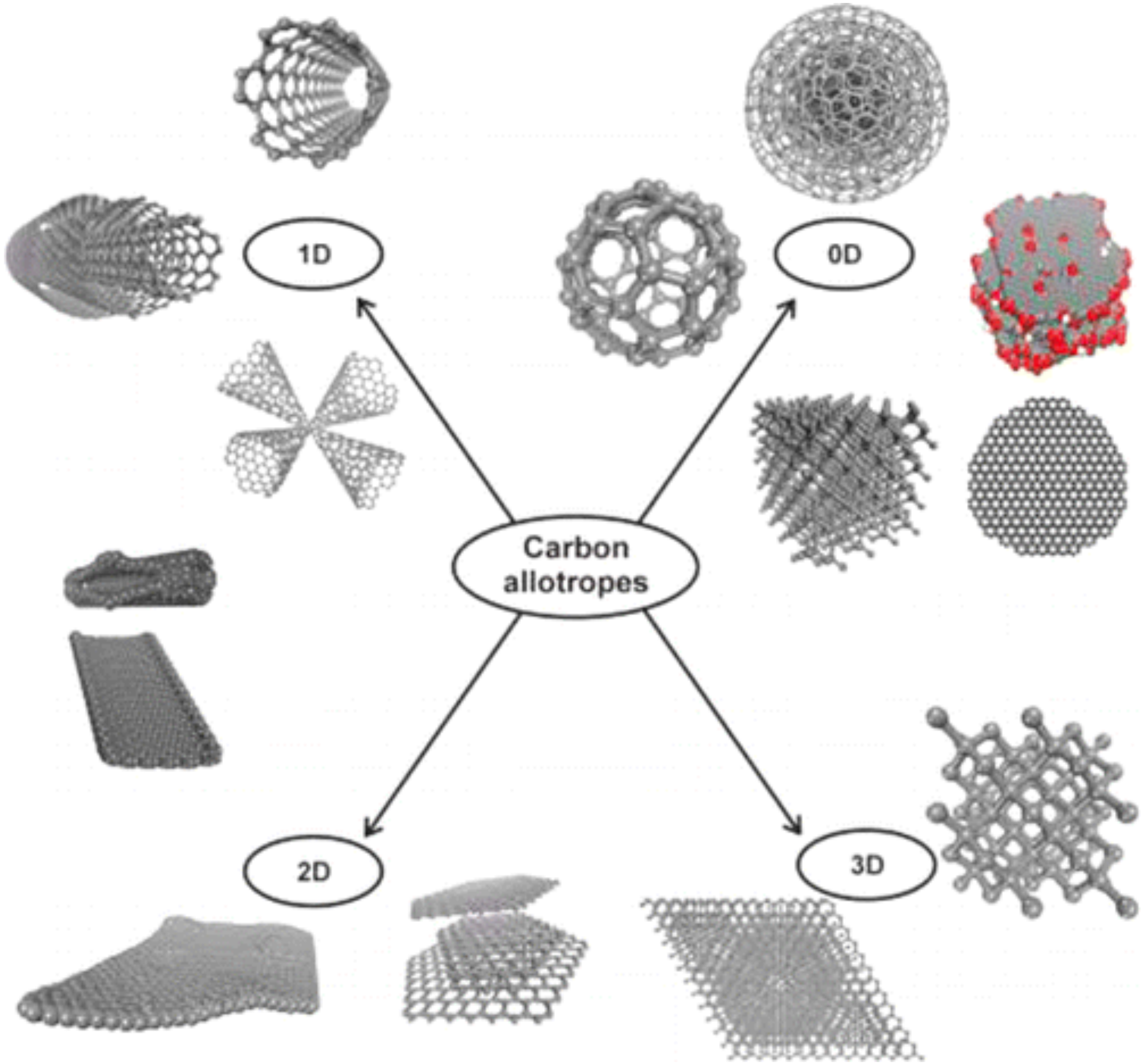


taken from Wikipedia

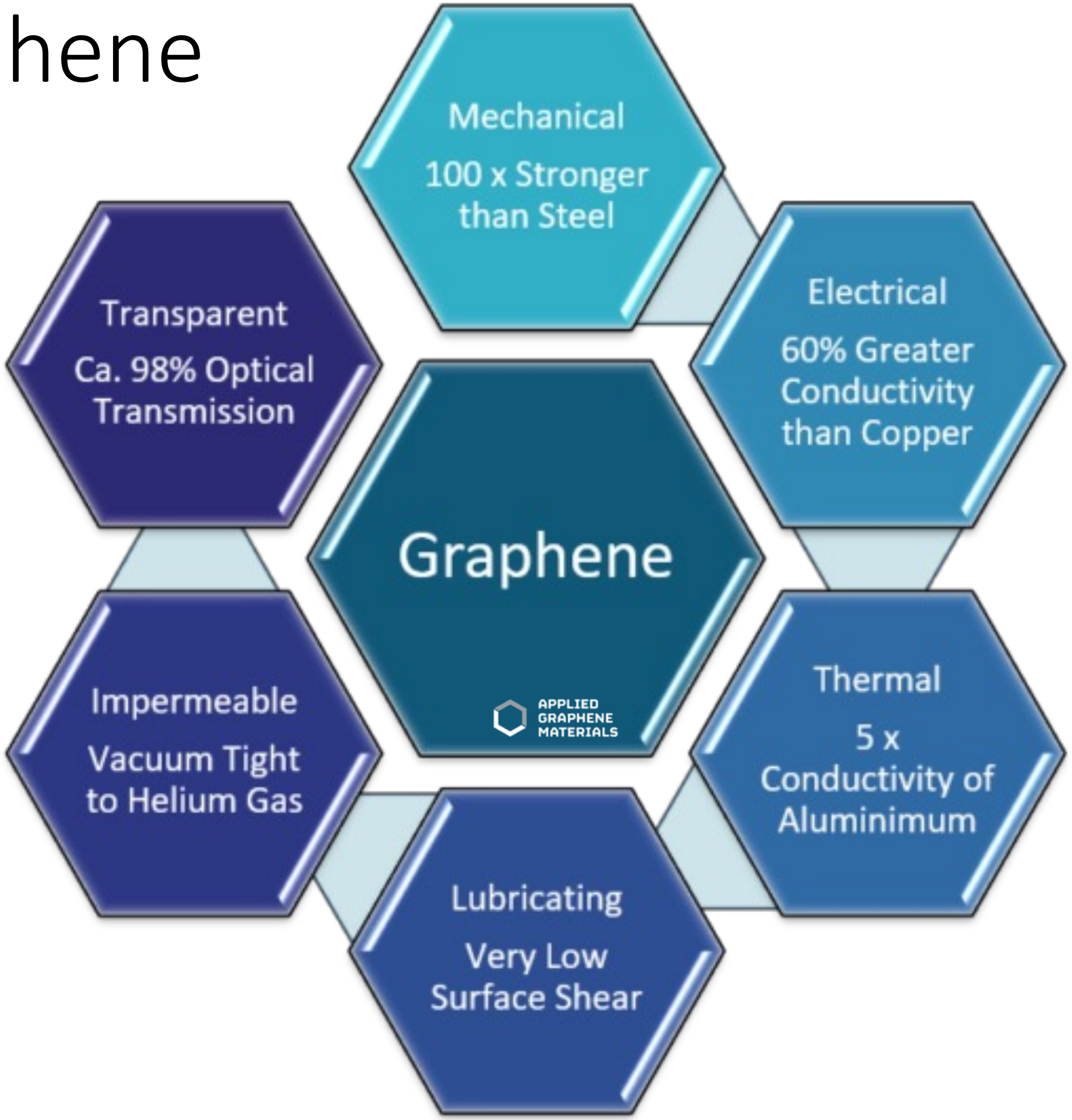
Carbon nanoallotropes

(i) 0D carbon nanostructures such as fullerenes, OLC structures, C-dots, and nanodiamonds, (ii) 1D nanoallotropes such as CNTs, carbon nanofibers, and SWNHs (although the latter are organized into 3D aggregates), and (iii) 2D nanoallotropes such as graphene, graphene nanoribbons, and few-layer graphenes

Chem. Rev. 2015, 115, 11, 4744–4822



Graphene



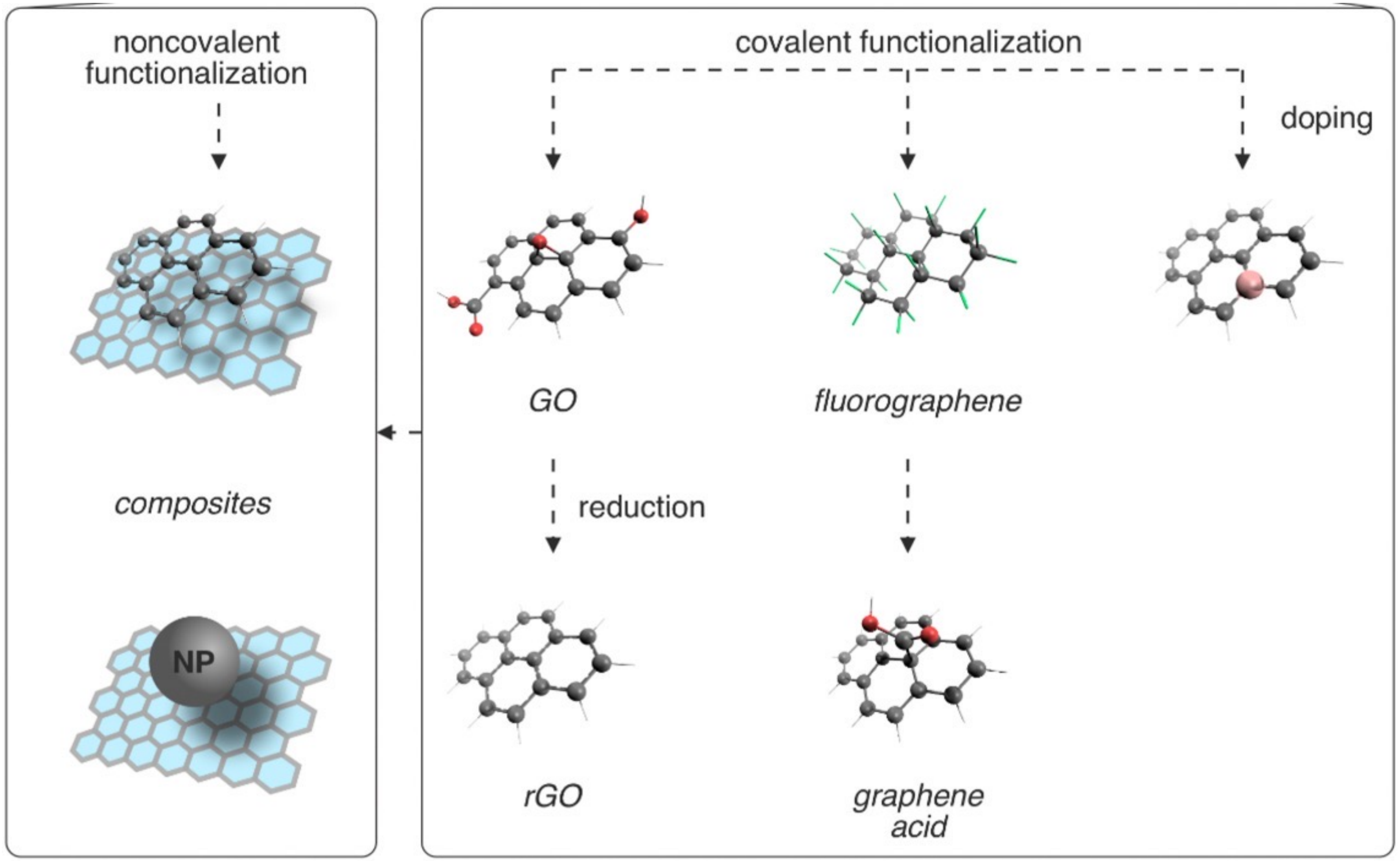
Enhance/Introduce/Control

Water dispersibility
Chemical functional groups
Lateral size
Keep conductivity

but

Graphene is quite chemically inert

Graphene functionalization



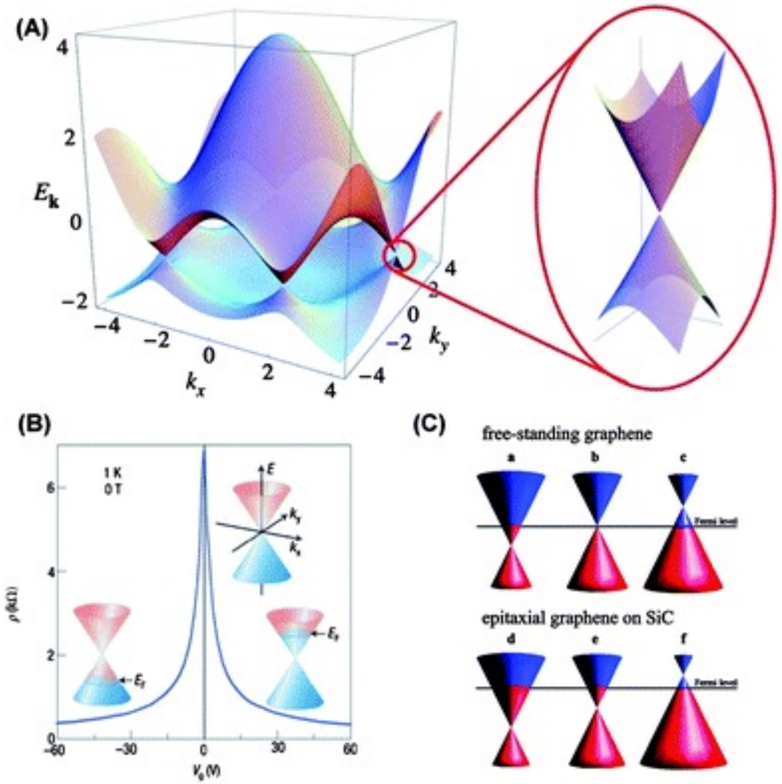
Biosens. Bioelectron., 166, 112436, 2020

CDs: carbon dots
GO graphene oxide
rGO reduced GO
NP nanoparticle.

Georgakilas V, Otyepka M, Bourlinos AB, Chandra V, Kim N, Kemp KC, Hobza P, Zbořil R, Kim KS: Functionalization of Graphene: Covalent and Non-Covalent Approaches, Derivatives and Applications. *Chem. Rev., 112(11), 6156-6214, 2012*.

Noncovalent functionalization

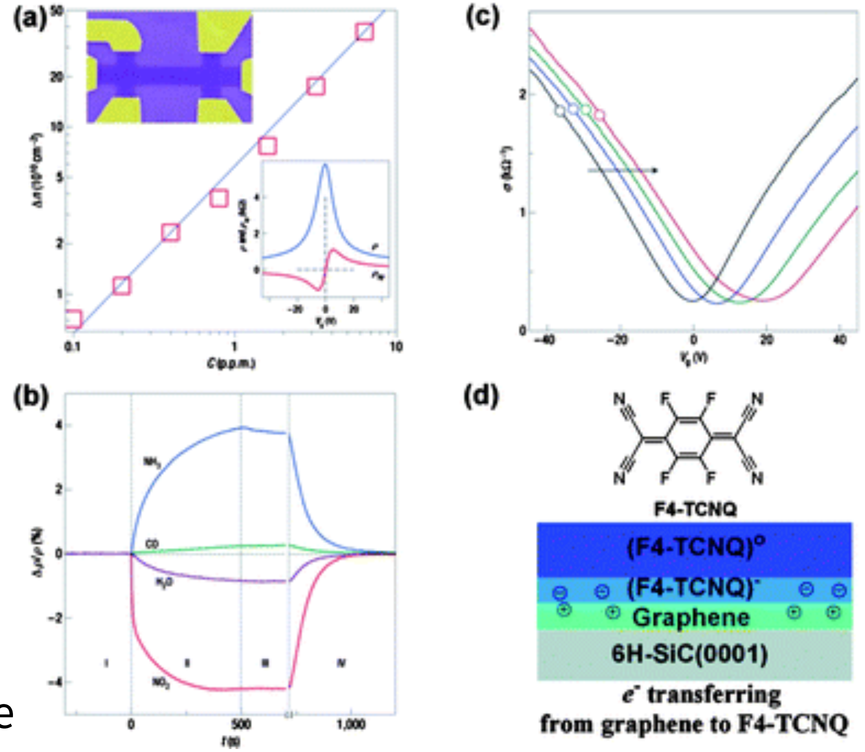
Nature Materials 6, 652, 2007



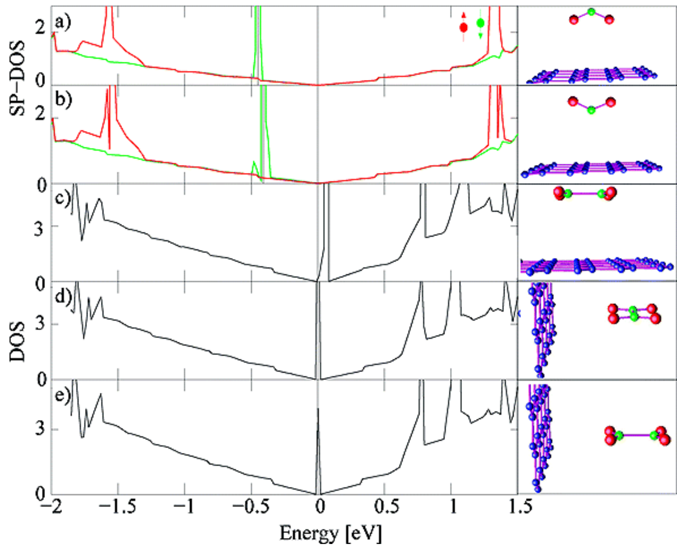
(A) Band structure of graphene and zoom-in of the energy bands close to the Dirac points. (B) Ambipolar electric field effect in single-layer graphene. (C) Position of the Dirac point and FL as a function of doping. The upper panel is n-type doped, pristine and p-type doped free standing graphene (a-c). The lower panel is n-type doped, pristine and p-type doped epitaxial graphene grown on silicon carbide (SiC) (d to f).

p-type

n-type



Concentration, $\triangle n$, of induced charge carriers in single-layer graphene exposed to different concentrations, C, of NO_2. (b) Changes in resistivity, ⍰, at zero B caused by graphene's exposure to various gases diluted in concentration to 1 ppm. The positive (negative) sign of changes is chosen here to indicate electron (hole) doping. (c) Constant mobility of charge carriers in graphene with increasing chemical doping. The parallel shift implies a negligible scattering effect of the charged impurities induced by chemical doping.



Nano Lett. 2008, 8, 1, 173

J. Mater. Chem., 2011, 21, 3335 (+ refs therein)

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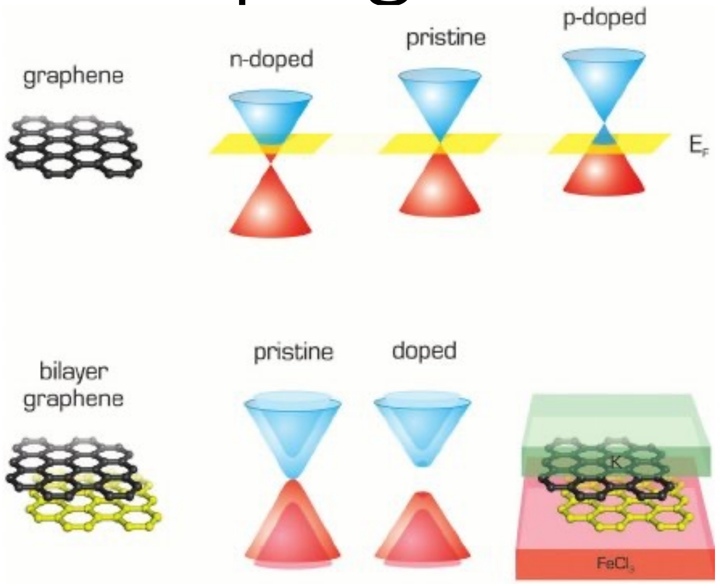
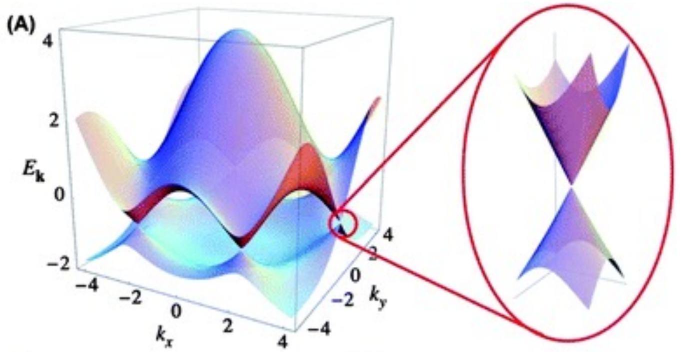
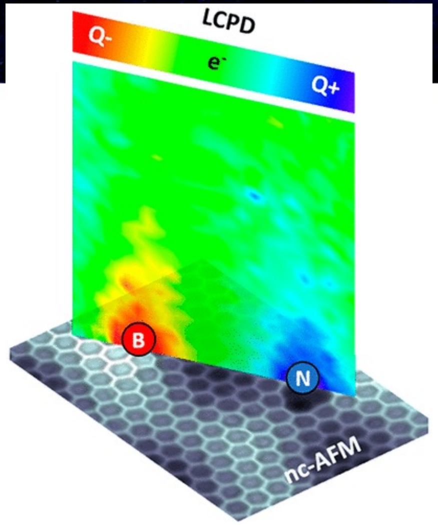
Doping





J. Mater. Chem., 2011, 21, 3335

$G + XH_x$

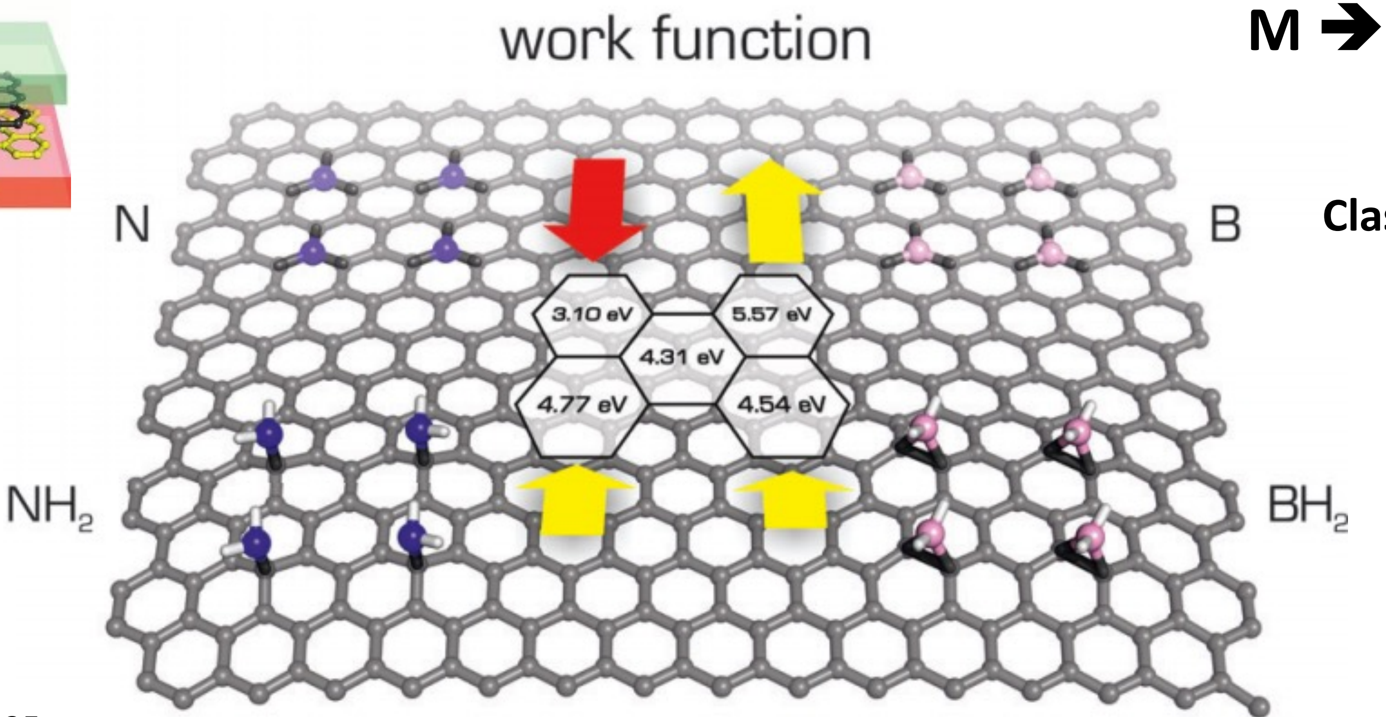


local potential difference (LCPD)
measured above the dopant atoms

ACS Sustainable Chem. Eng. 2020, 8, 8, 3437

W_f

$M \rightarrow M^+ + e^-$



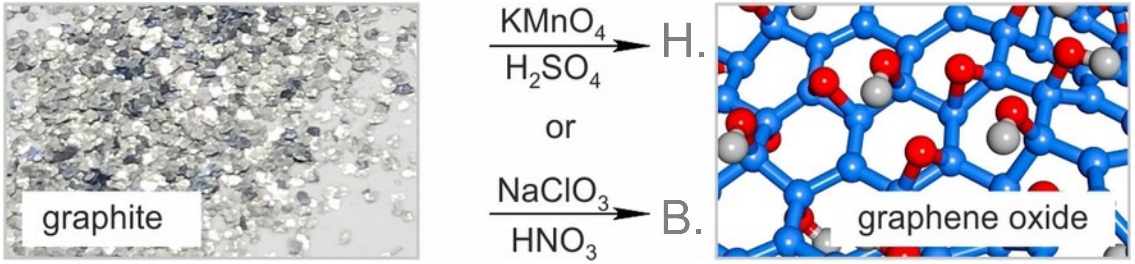
Classical n/p doping

Smaller effect but the
same trend for N/B

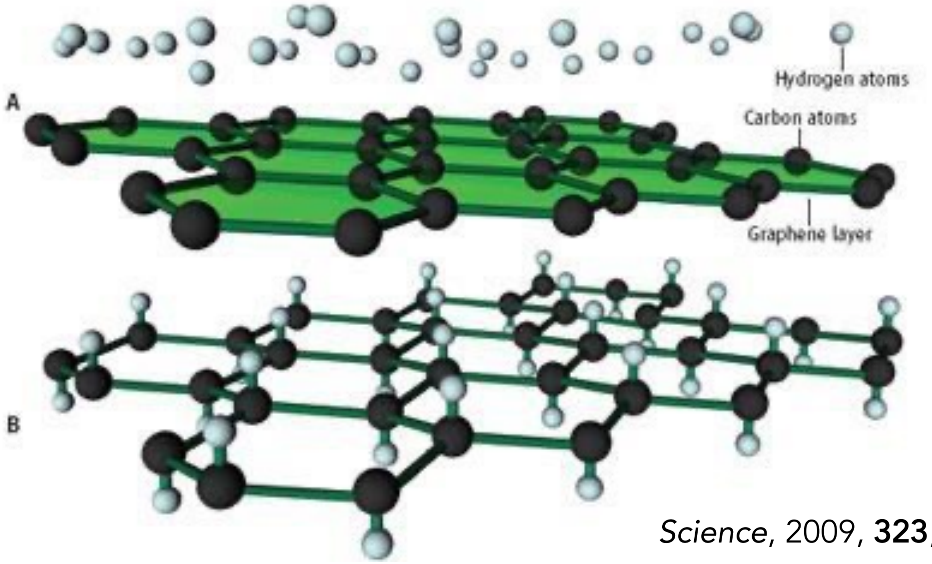
PCCP, 16, 14231, 2014

Early history of graphene functionalization

- 1859 – Graphite oxide by Brodie
- 1957 – Hummer`s graphite oxide
- 2007 – Graphene oxide
  - Stankovich S et al. Carbon 45, 1558 (2007)
- 2007 – Graphane and Graphene fluoride predicted
  - Sofo JO et al. PRB 75, 153401 (2007)
- 2009 – Graphane synthesized
  - Elias DC et al. Science, 323, 610 (2009)
- 2010 – Fluorographene/G. fluoride prepared
  - Fluorination of graphene
    - Robinson JT et al. Nano Letters 10, 3001 (2010)
    - Cheng SH et al. PRB 81, 205435 (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)



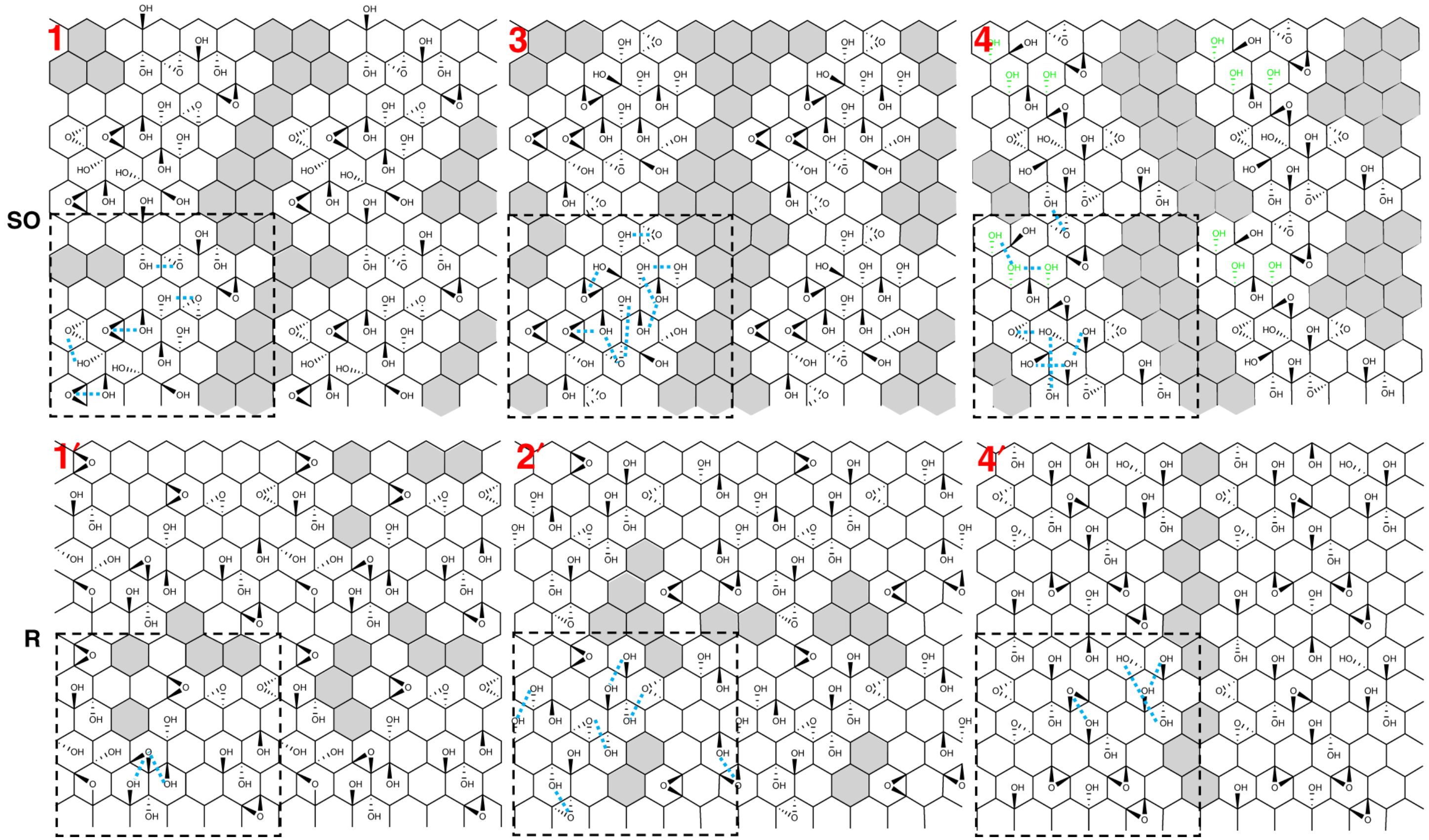
Chem. Eur. J. 25, 2019, 8955



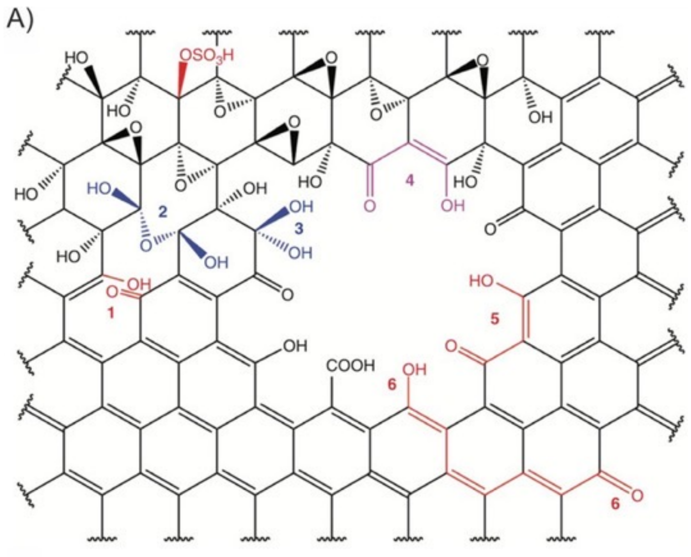
Science, 2009, **323**, 610

Graphene oxide

- Prepared by oxidation of graphene/graphite + exfoliation, hydrophilic material, non-conductive
- Chemically very complex material



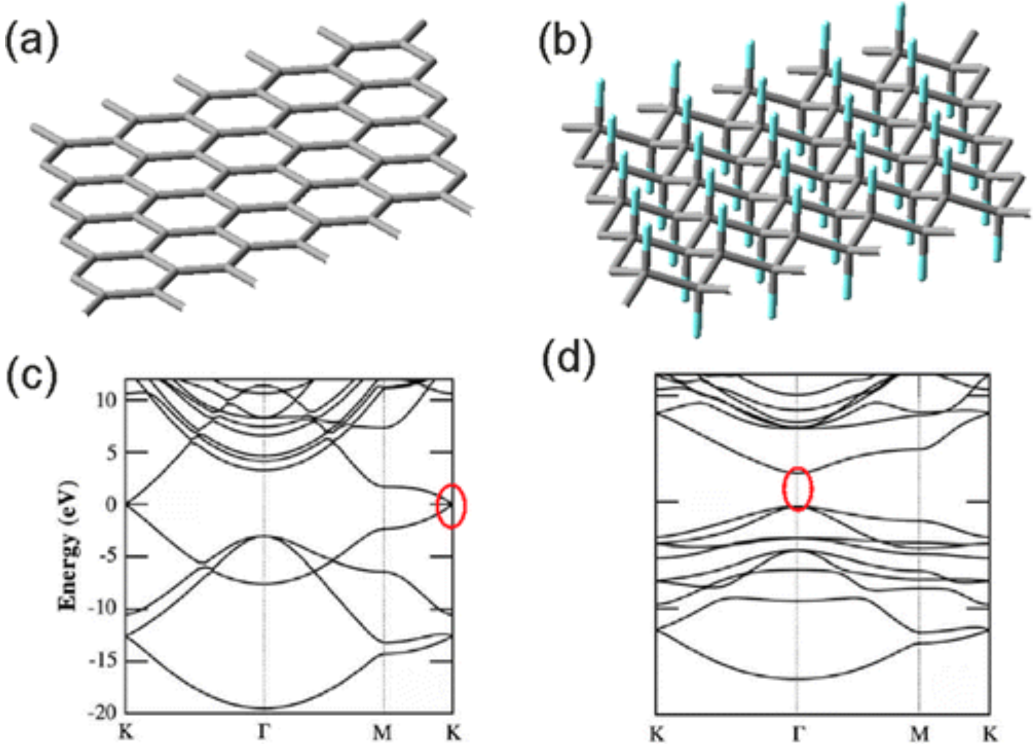
Nature Communications 11, 1566 (2020)



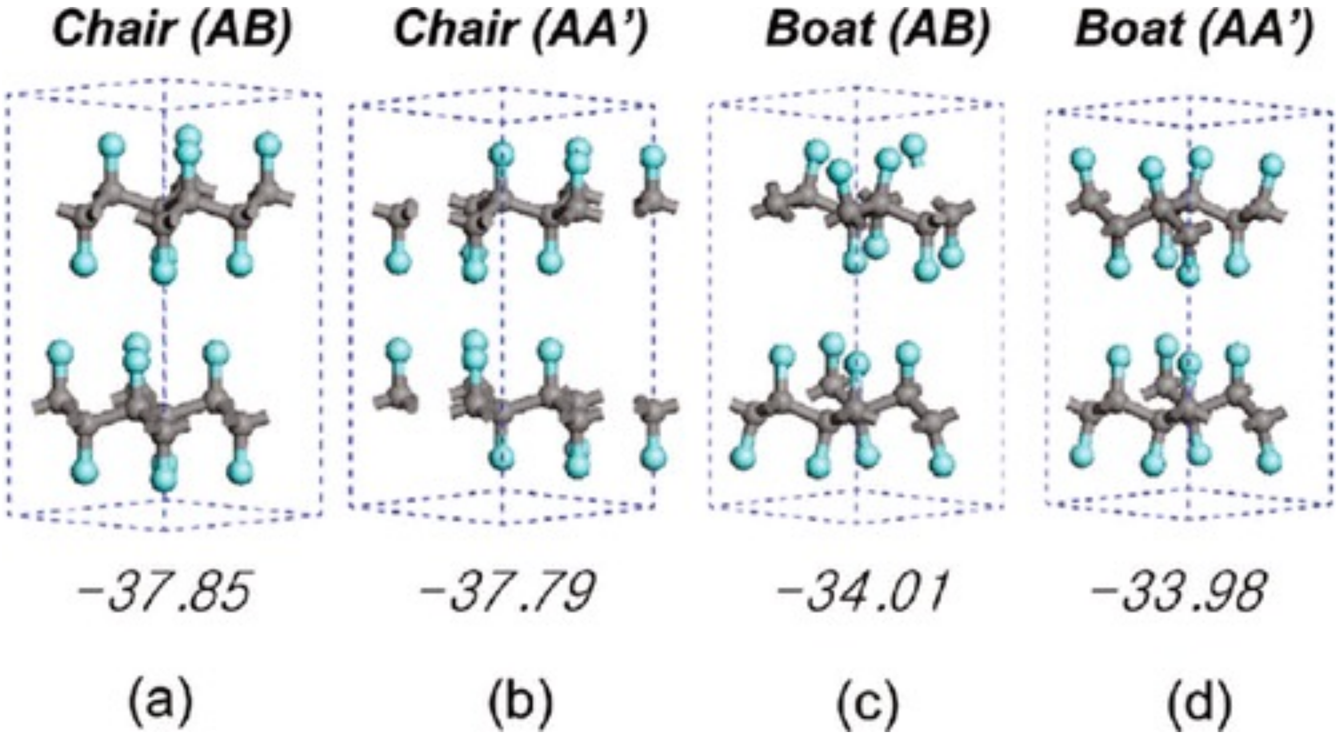
ChemNanoMat 4, 3, 224, 2018

Graphene functionalization

sp^2 carbons to sp^3, decrease in conductivity
depends on the element, DF, topography/arrangement, …



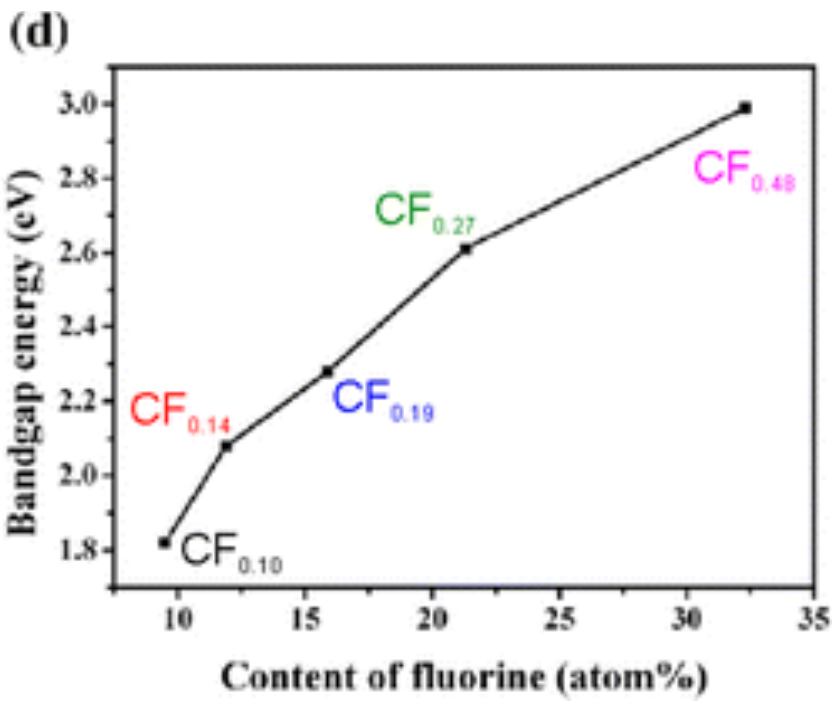
ACS Nano 2013, 7, 8, 6434



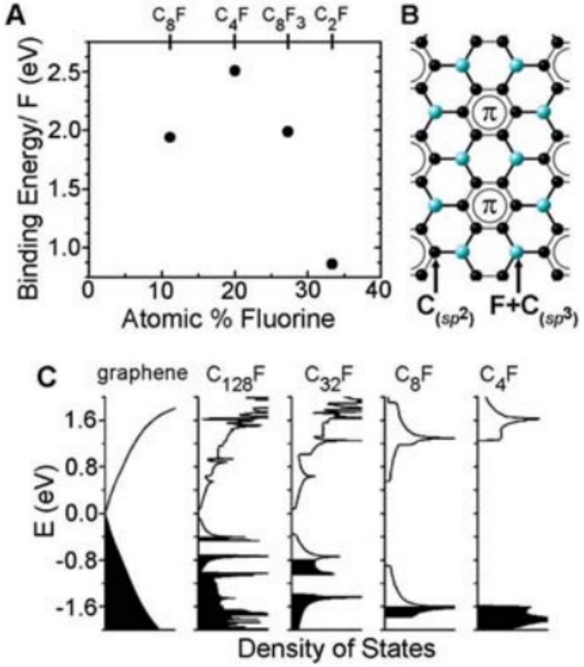
Chem. Mater. 2010, 22, 2142

Graphene functionalization

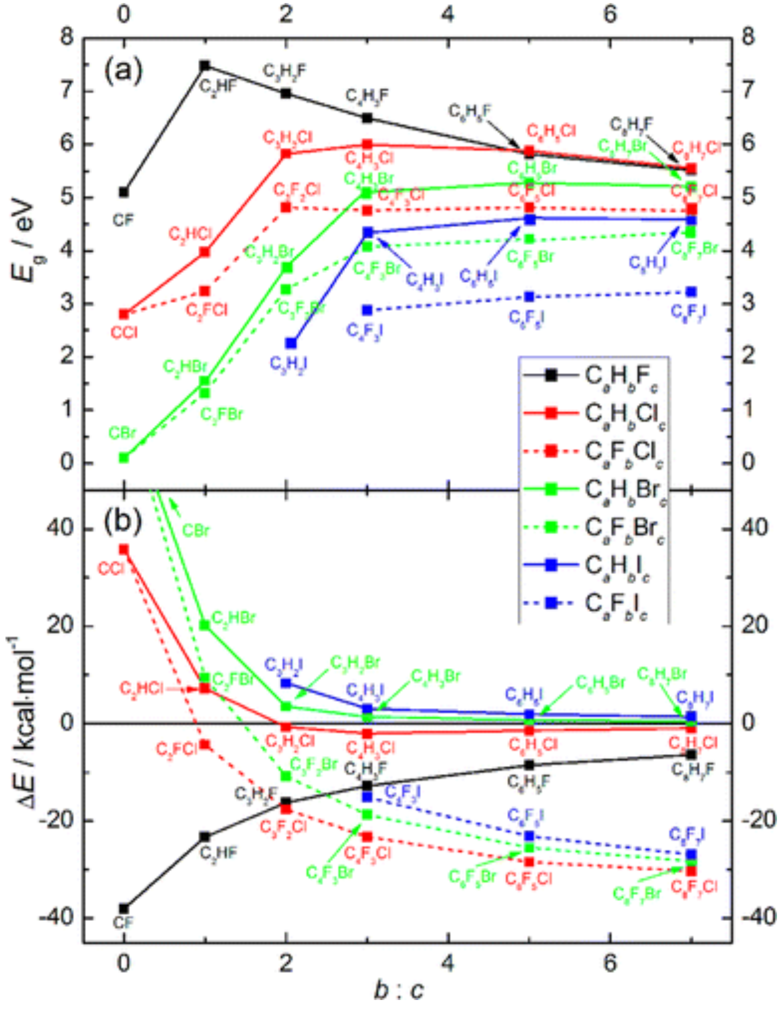
sp^2 carbons to sp^3, decrease in conductivity
depends on the element, DF, topography/arrangement, …



Carbon 2012, 50, 5403



Nano Lett. 2010, 10, 3001



J. Chem. Phys. 2012, 137, 034709

Graphene derivatives

- Noncovalent
  - Affecting properties of both graphene/adsorbate
  - Can be used for detection …

- Covalent
  - Significant effect on properties – band gap opening
    - Depend on element, degree of functionalization and topography

Fluorographene

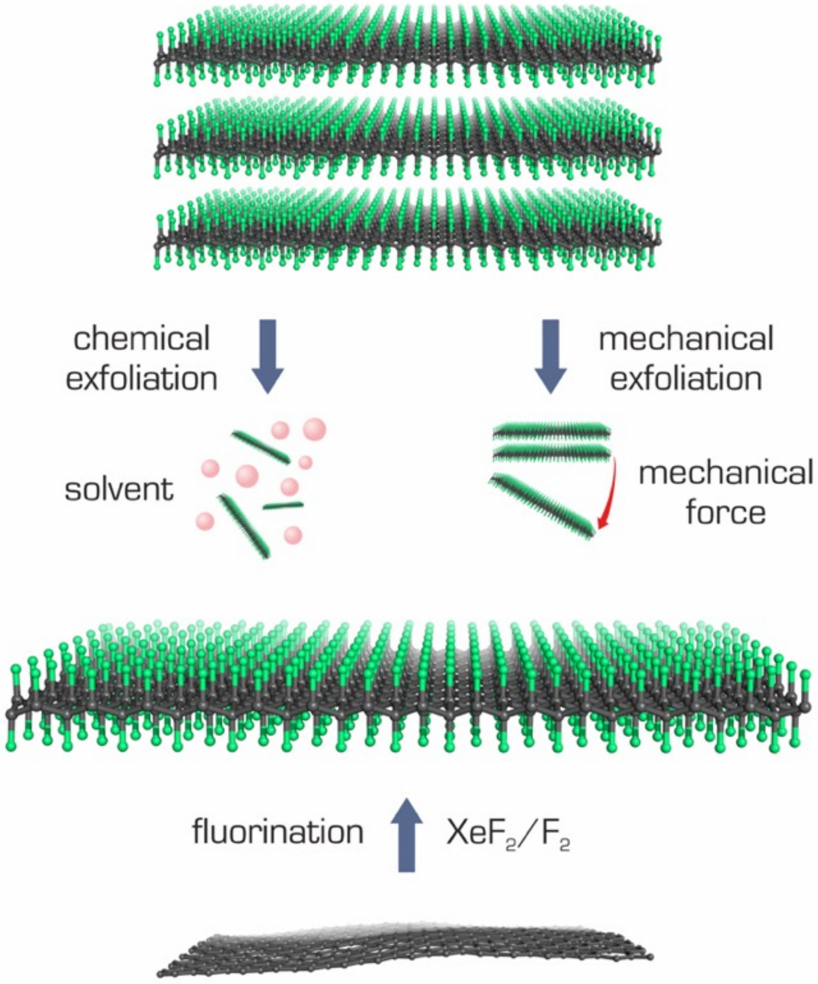
Discovered in 2010

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)

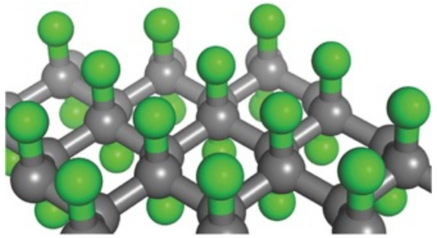
Graphite fluoride is produced ~300 mt/y (Procedia Engineering 138, 240 (2016)) – industrial lubricant, electrode for primary Li

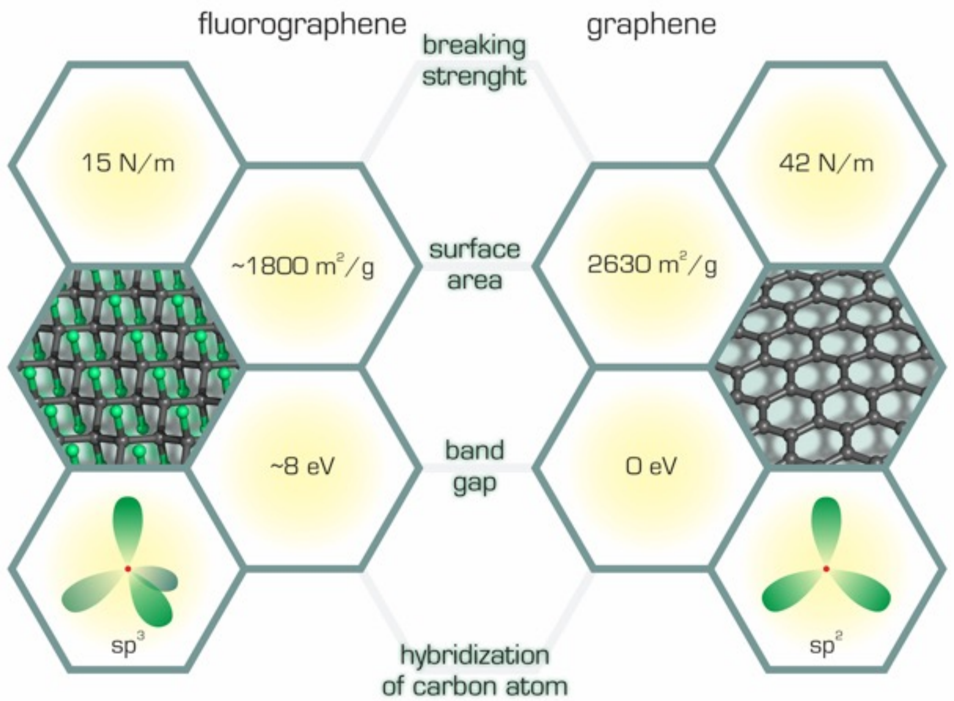


ACS Nano 7, 6434, 2013
Appl. Mater. Today, 9, 60, 2017

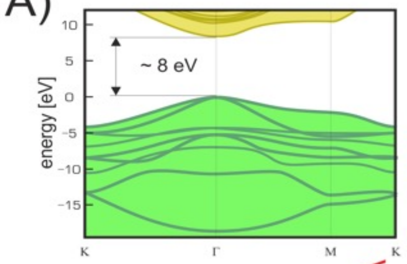
Properties of Fluorographene

$C_1F_{1(1.1)}$



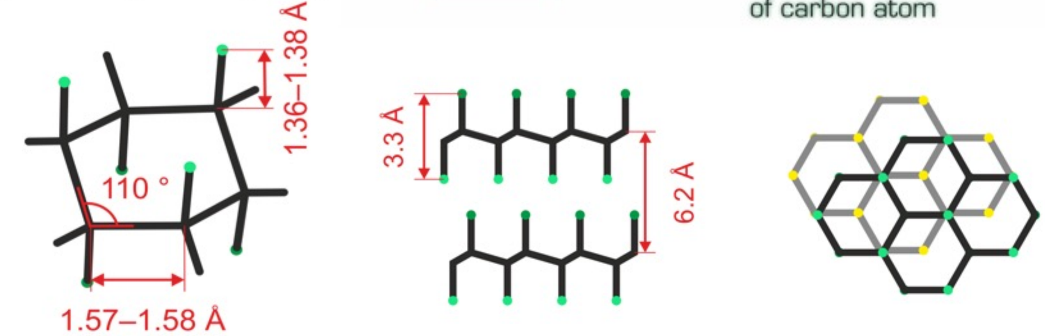


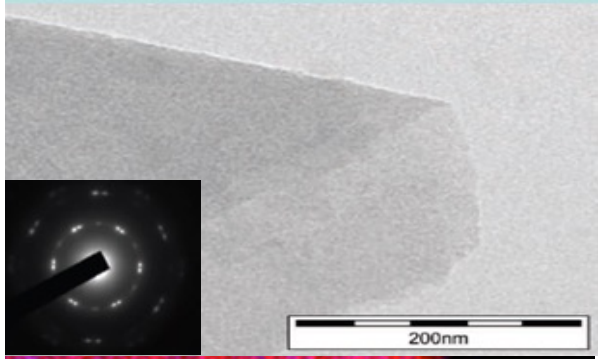
A)

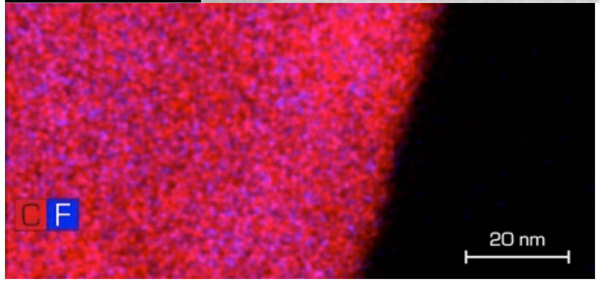


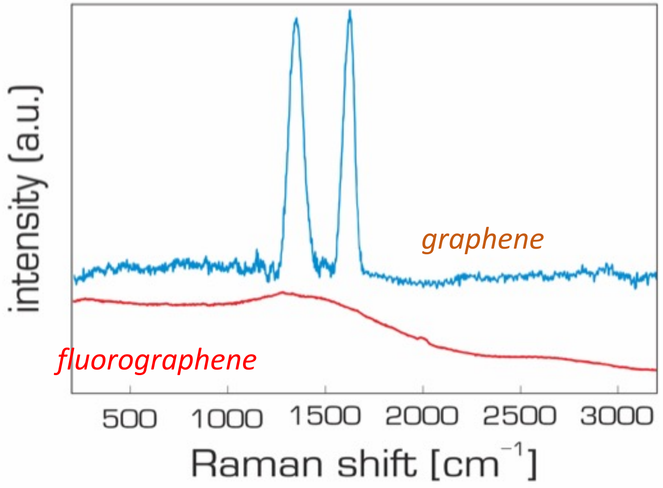
C)

D)









ACS Nano 7, 6434, 2013

Appl. Mater. Today, 9, 60, 2017

Fluorographene is Reactive

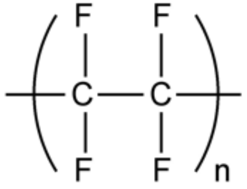
Fluorinated graphene

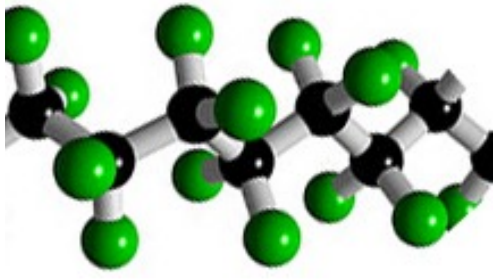
Fluorographene: A Two-Dimensional Counterpart of Teflon

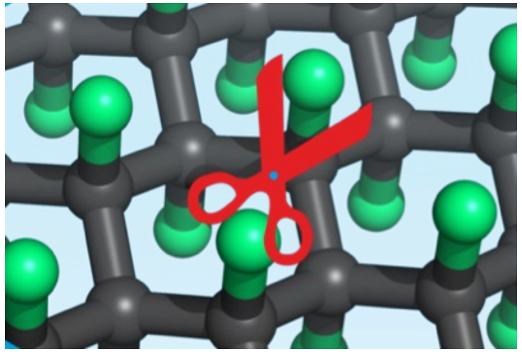
Rahul R. Nair, Wencai Ren, Rashid Jalil, Ibtsam Riaz, Vasyl G. Kravets, Liam Britnell, Peter Blake, Fredrik Schedin, Alexander S. Mayorov, Shengjun Yuan, Mikhail I. Katsnelson, Hui-Ming Cheng, Wlodek Strupinski, Lyubov G. Bulusheva, Alexander V. Okotrub, Irina V. Grigorieva, Alexander N. Grigorenko, Kostya S. Novoselov,* and Andre K. Geim**

A stoichiometric derivative of graphene with a fluorine atom attached to each carbon is reported. Raman, optical, structural, micromechanical, and transport studies show that the material is qualitatively different from the known graphene-based nonstoichiometric derivatives. Fluorographene is a high-quality insulator (resistivity > 10^{12} Ω) with an optical gap of 3 eV. It inherits the mechanical strength of graphene, exhibiting a Young's modulus of 100 N m^{-1} and sustaining strains of 15%. Fluorographene is inert and stable up to 400 °C even in air, similar to Teflon.

Nair et al., Small 6, 2878, 2010







Graphene

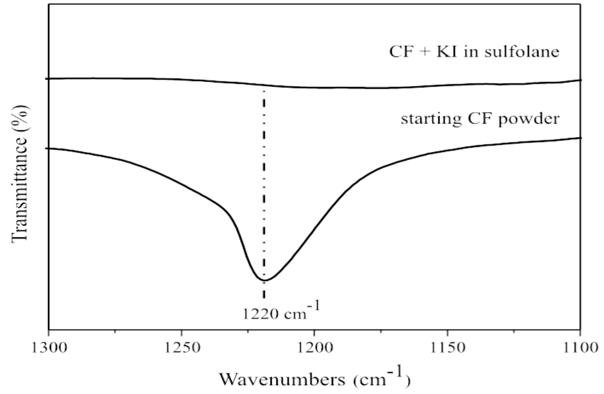
Graphene Fluoride: A Stable Stoichiometric Graphene Derivative and its Chemical Conversion to Graphene

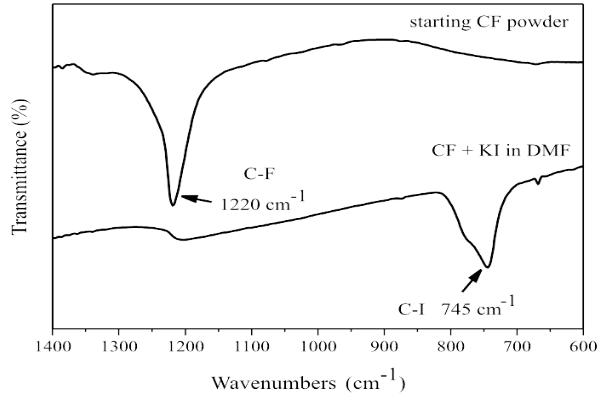
Radek Zbořil, František Karlický, Athanasios B. Bourlinos, Theodore A. Steriotis, Athanasios K. Stubos, Vasilios Georgakilas, Klára Šafářová, Dalibor Jančík, Christos Trapalis, and Michal Otyepka**

Stoichiometric graphene fluoride monolayers are obtained in a single step by the liquid-phase exfoliation of graphite fluoride with sulfolane. Comparative quantum-mechanical calculations reveal that graphene fluoride is the most thermodynamically stable of five studied hypothetical graphene derivatives; graphane, graphene fluoride, bromide, chloride, and iodide. The graphene fluoride is transformed into graphene via graphene iodide, a spontaneously decomposing intermediate. The calculated bandgaps of graphene halides vary from zero for graphene bromide to 3.1 eV for graphene fluoride. It is possible to design the electronic properties of such two-dimensional crystals.

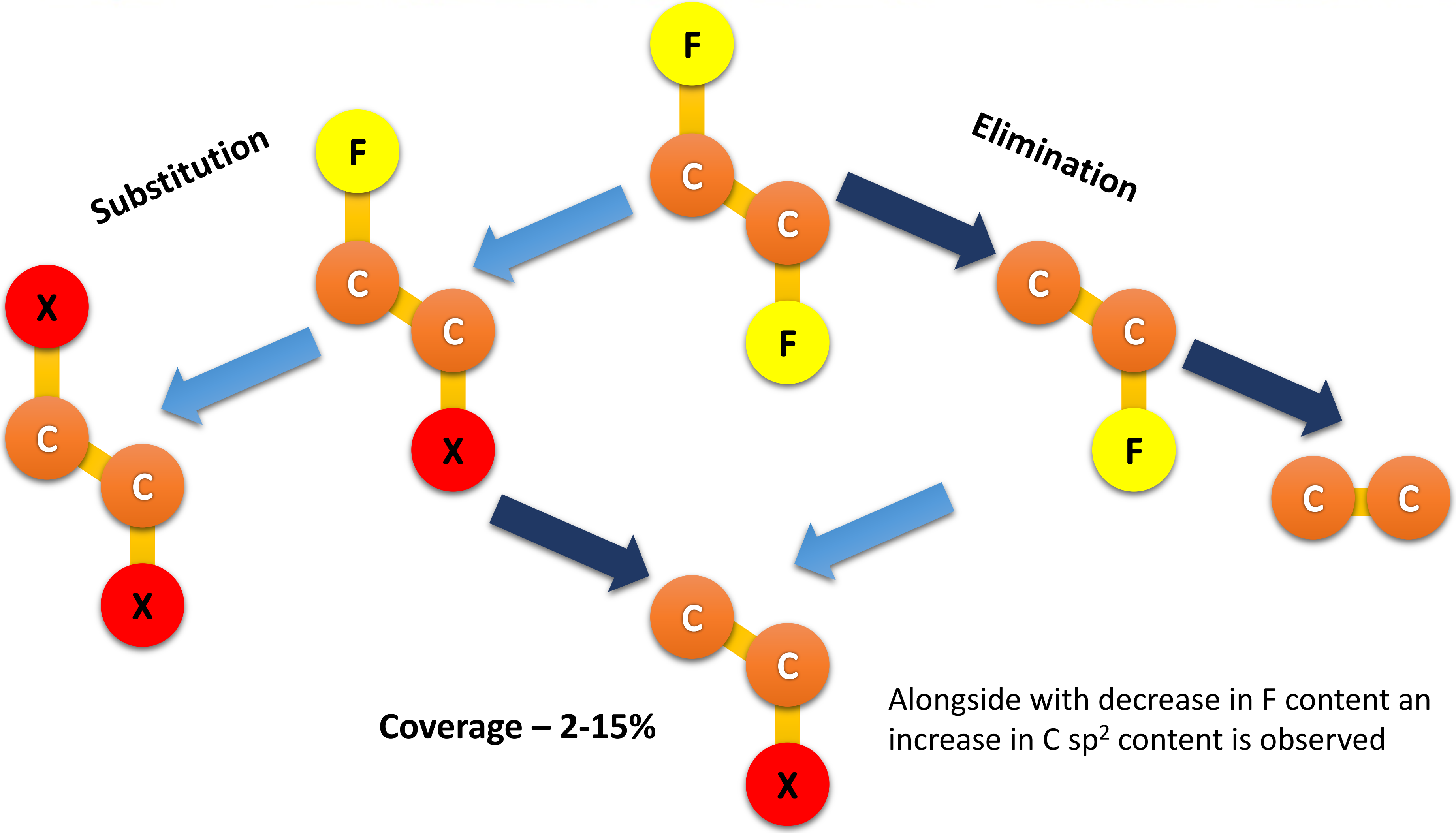
Zbořil et al., Small 6, 2885, 2010

$$CF + KI \rightarrow KF + [CI]\ ;\ \ [CI] \rightarrow C + \tfrac{1}{2} I_2 \qquad (180\ ^\circ C)$$





Fluorographene Reactivity



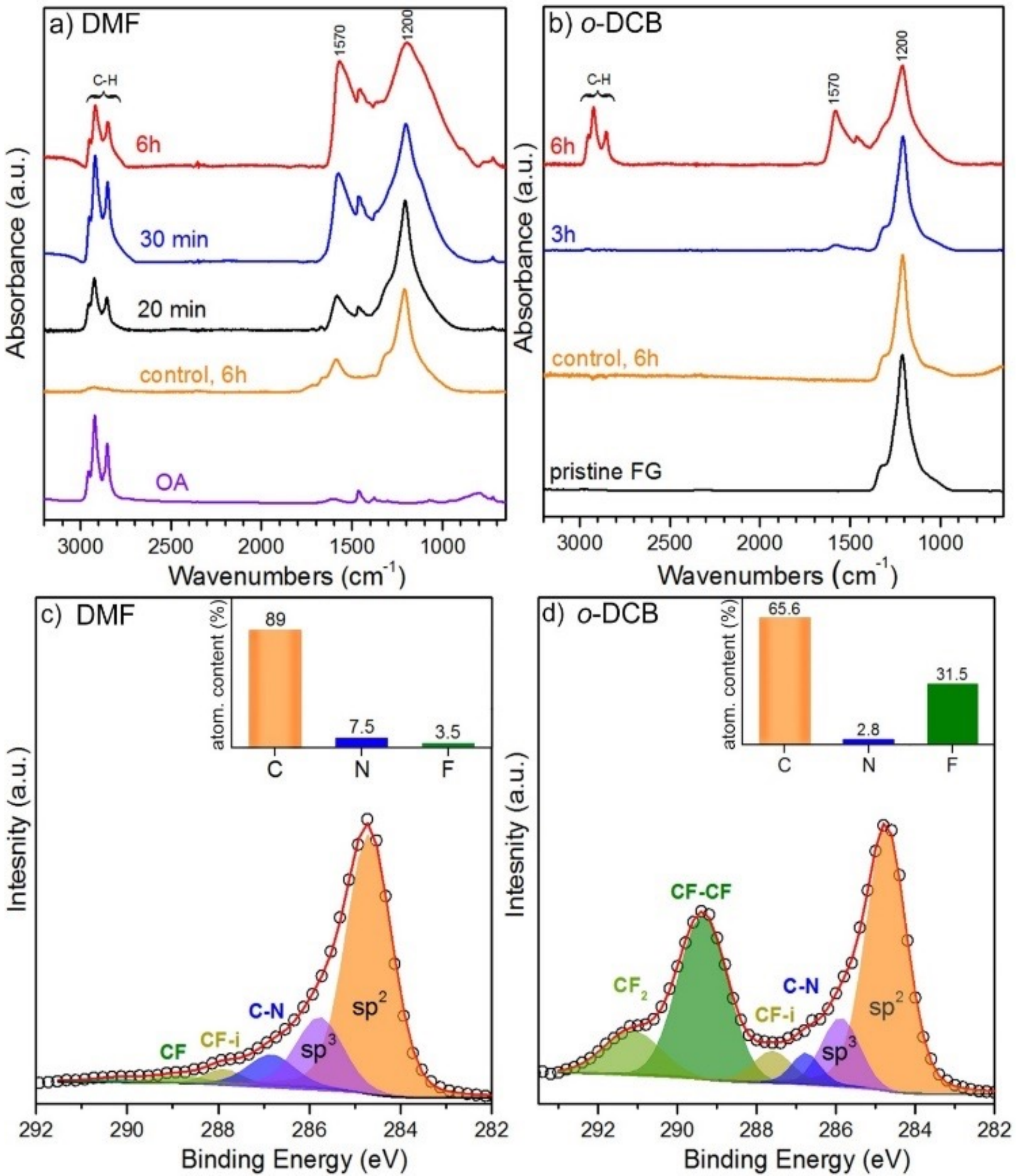
Coverage – 2-15%

Alongside with decrease in F content an increase in C sp^2 content is observed

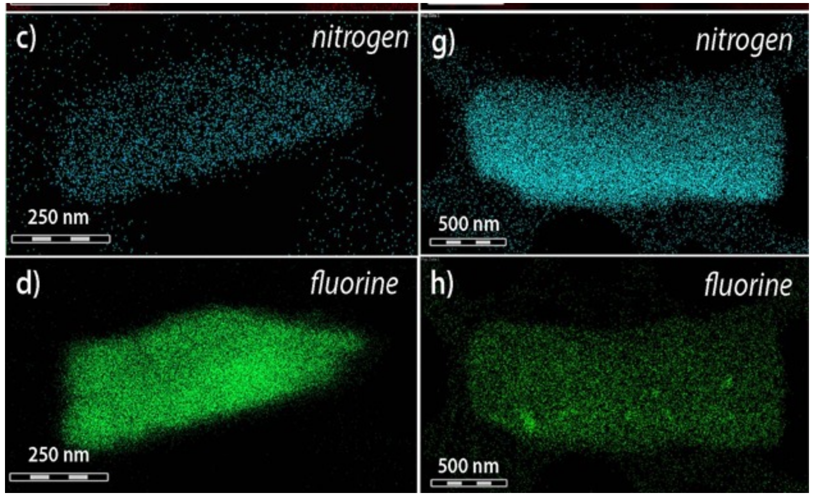
Reductive defluorination occurs simultaneously with substitution

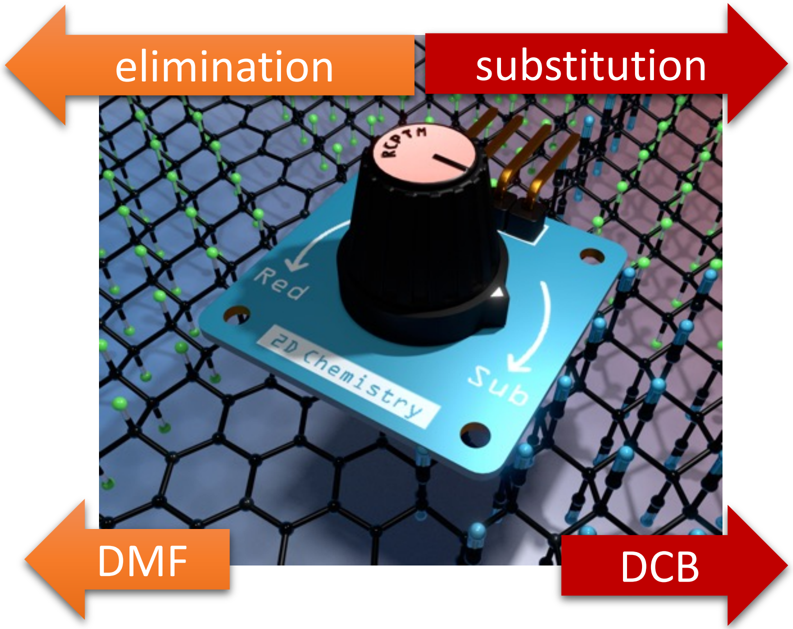
Appl. Mater. Today, 9, 60, 2017
Nanoscale, 10, 4696, 2018

Reaction control by solvent



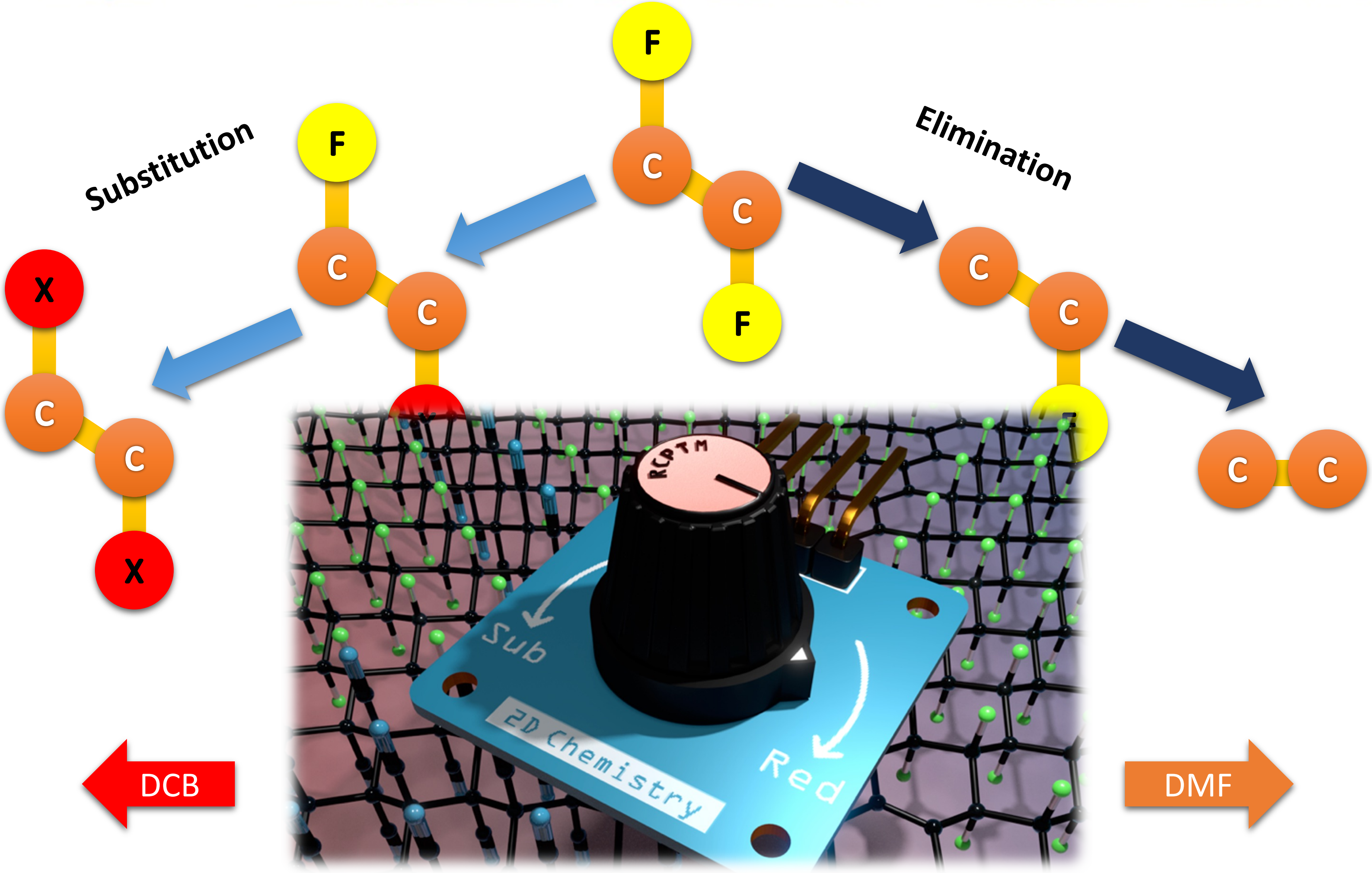
FG + Octylamine





J. Phys. Chem. Lett. 9, 3580, 2018

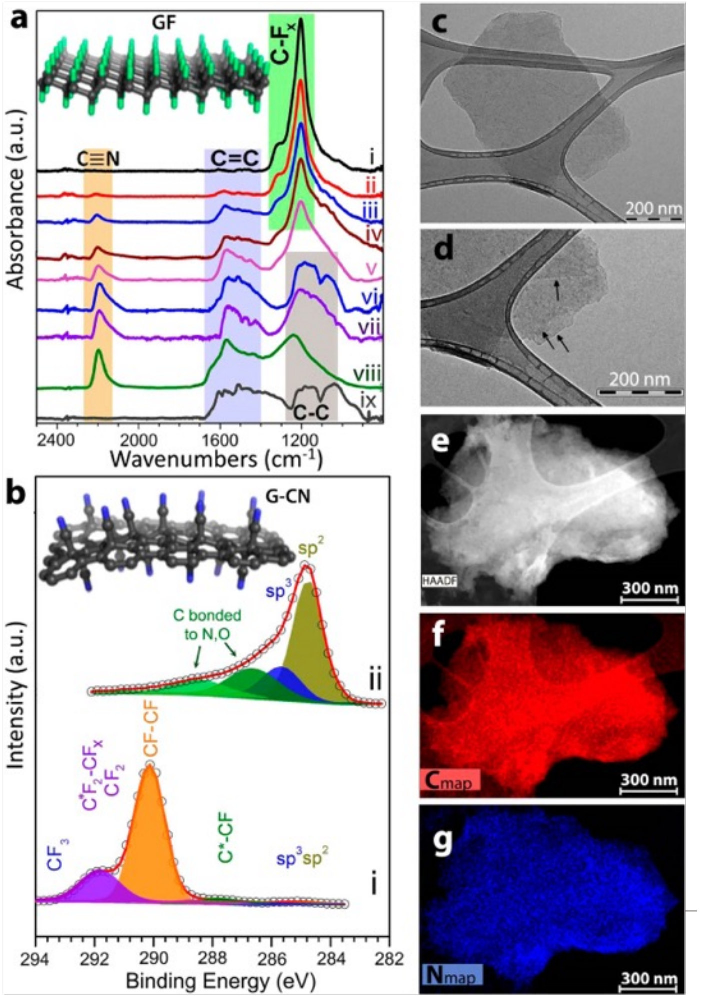
Reaction control



J. Phys. Chem. Lett. 9, 3580, 2018

Cyanographene a 2D-ligand

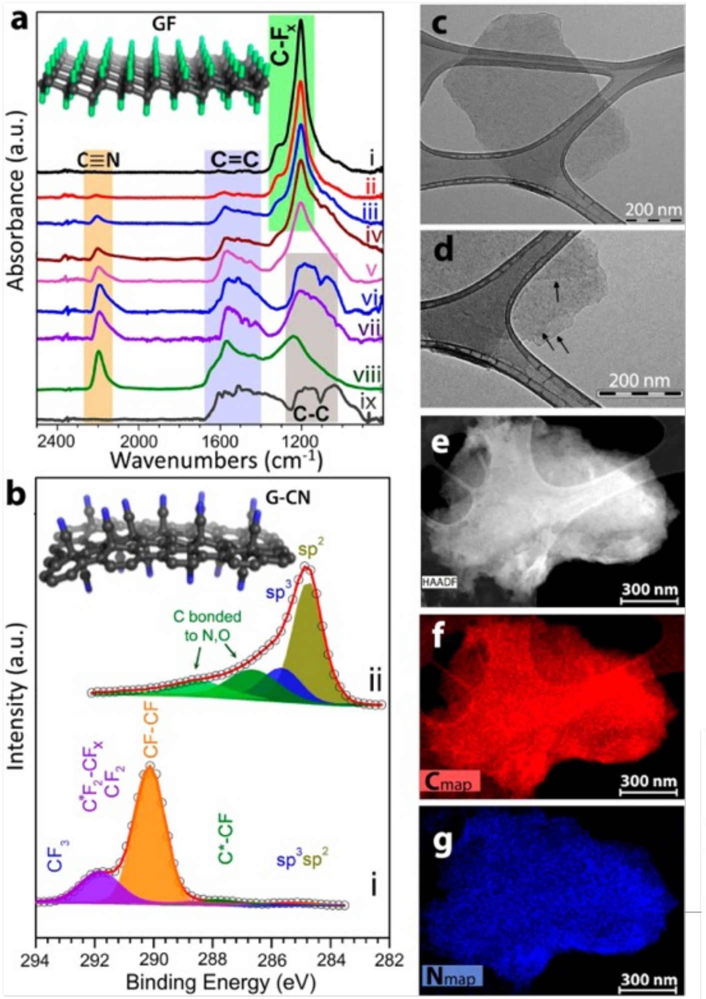
FG + NaCN → G-CN



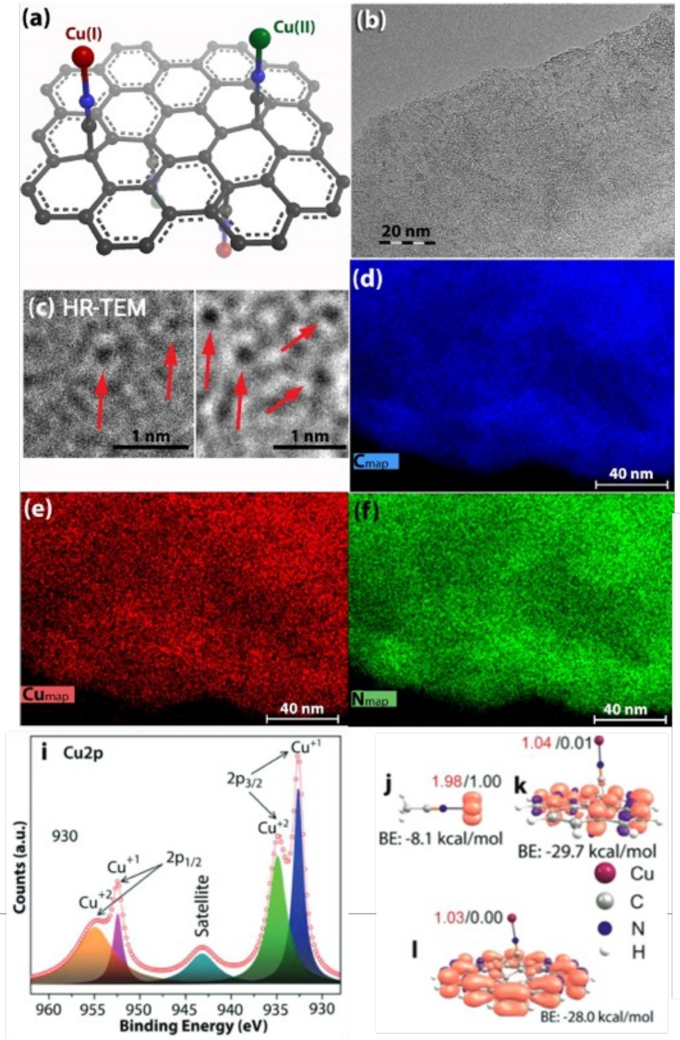
ACS Nano 11, 2982, 2017

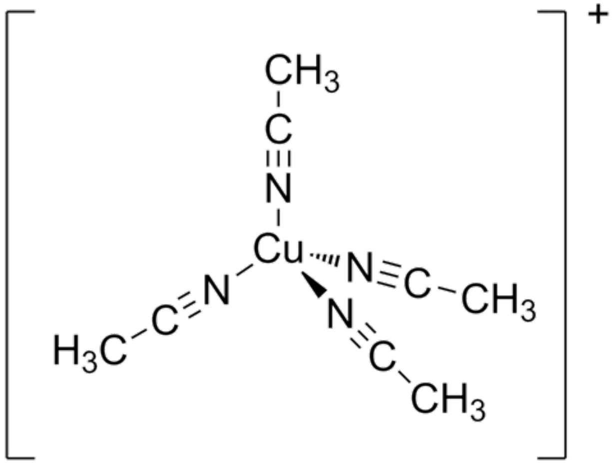
Cyanographene a 2D-ligand

FG + NaCN → G-CN



ACS Nano 11, 2982, 2017





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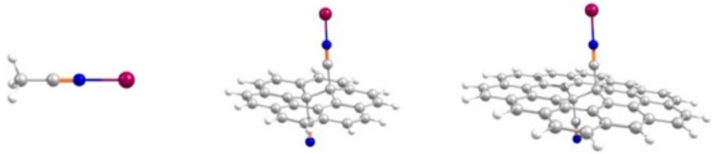
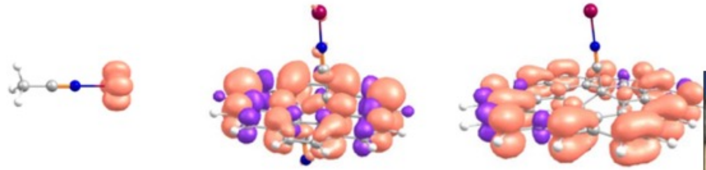
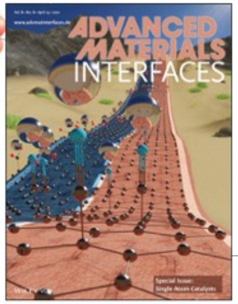
Cyanographene a 2D-ligand

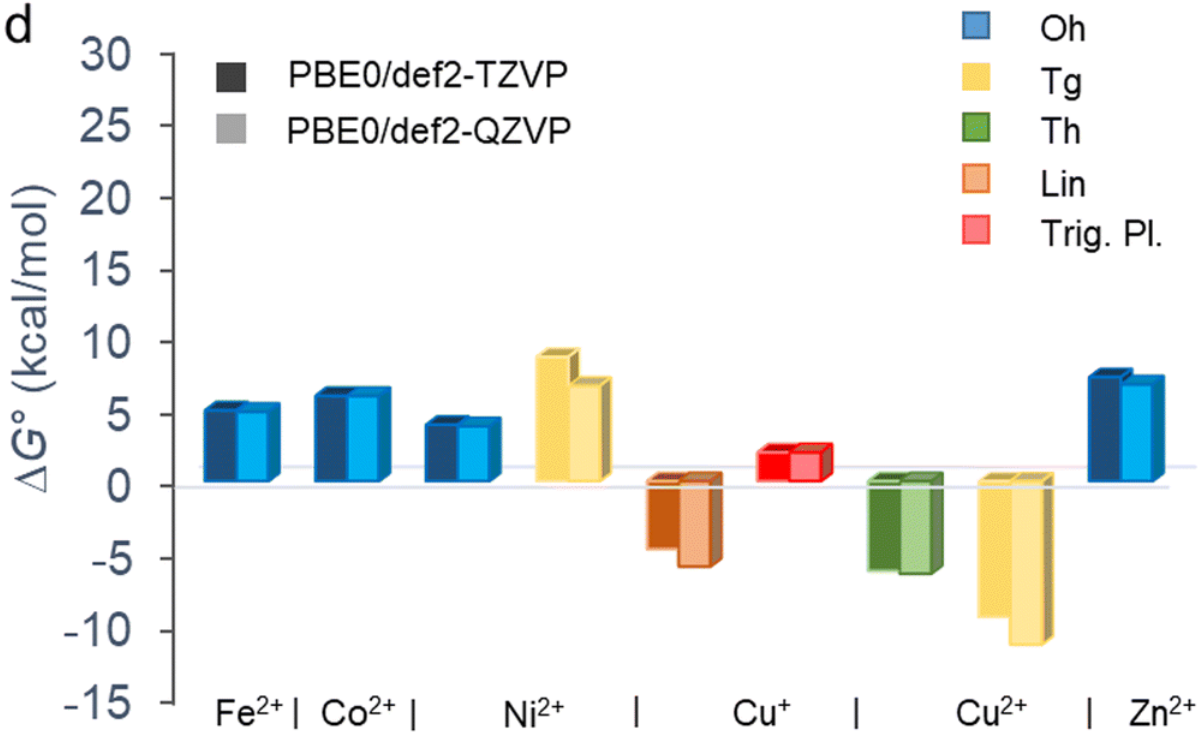
Table S2. The binding of Cu(II) cations to G-CN in various solvents. The structures, selected bond lengths (Å), binding energies (kcal mol^{-1}), spin density plots (contour value: 0.001), atomic spin, and natural charge densities (a.u.) on the copper atom of model R-CN-Cu(II) systems were computed at the U-B3LYP/6-31+G(d)/SMD level of theory. The structures were obtained via constrained geometry optimizations at the same level of theory (see text for details on the constraints).

Model	ACN-Cu(II)	Corronene-2CN-Cu(II)	Cyc14-2CN-Cu(II)
Structure			
$R_{C\text{-}N}/R_{N\text{-}Cu}$			
Water	1.157/2.108	1.159/1.867	1.159/1.863
PAM	1.156/2.090	1.157/1.871	1.158/1.872
BAM	1.157/2.071	1.157/1.873	1.158/1.875
Binding energy			
Water	–8.1	–29.7 (–28.7)[a]	–28.0
PAM	–17.7	–56.5 (–55.7)	–59.5
BAM	–28.7	–87.6 (–86.8)	–92.8
Spin density			
Spin density on Cu			
Water	1.00	0.01	0.00
PAM	0.72	0.00	0.00
BAM	0.68	0.00	0.00
Charge density on Cu			
Water	1.96 (1.68)[b]	1.04 (0.74)	1.03 (0.77)
PAM	1.67 (1.31)	1.02 (0.72)	1.01 (0.78)
BAM	1.63 (1.28)	1.01 (0.71)	1.00 (0.74)

[a]The values in parentheses were obtained from the RO-B3LYP calculations.
[b]The values in parentheses were determined via Mulliken population analysis.



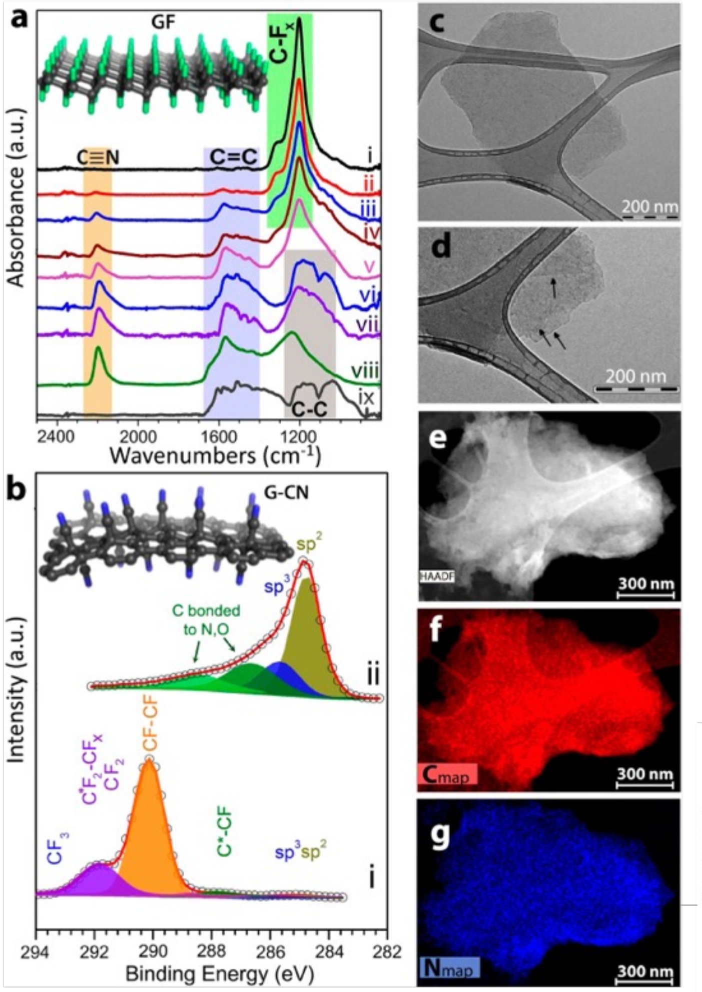
Adv. Mater. 31(17), 1900323, 2019



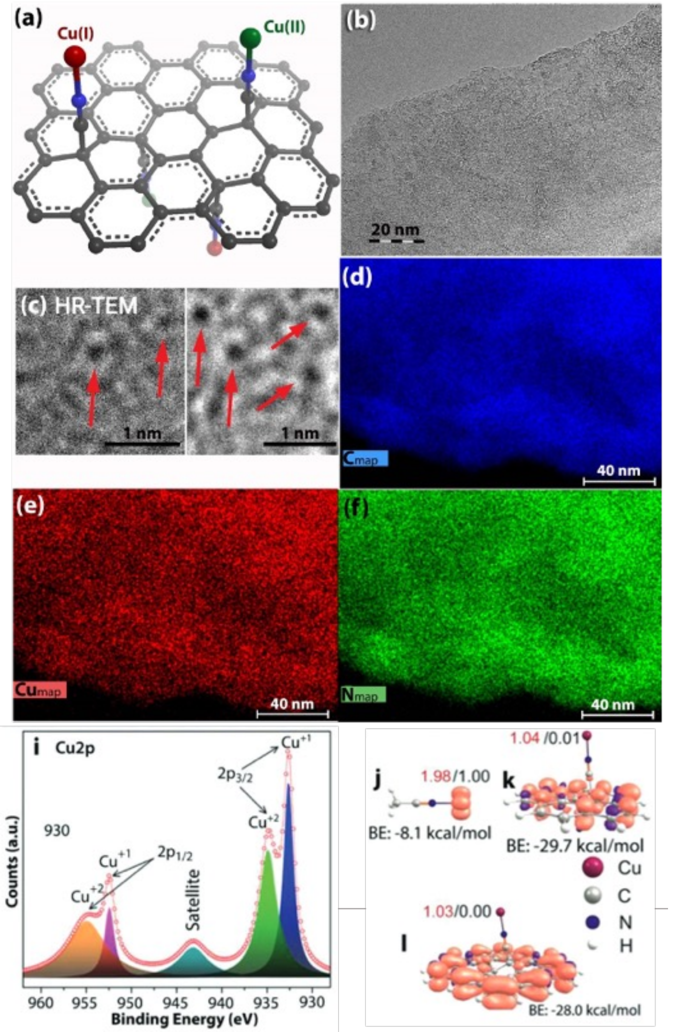
Phys. Chem. Chem. Phys., 2023, **25**, 286-296

Cyanographene a 2D-ligand

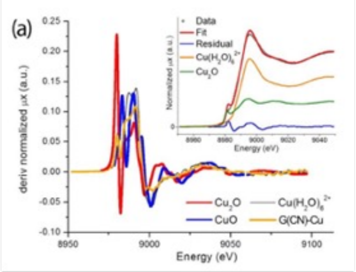
FG + NaCN → G-CN



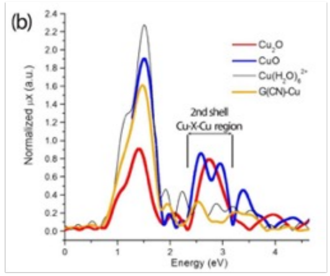
ACS Nano 11, 2982, 2017



XANES

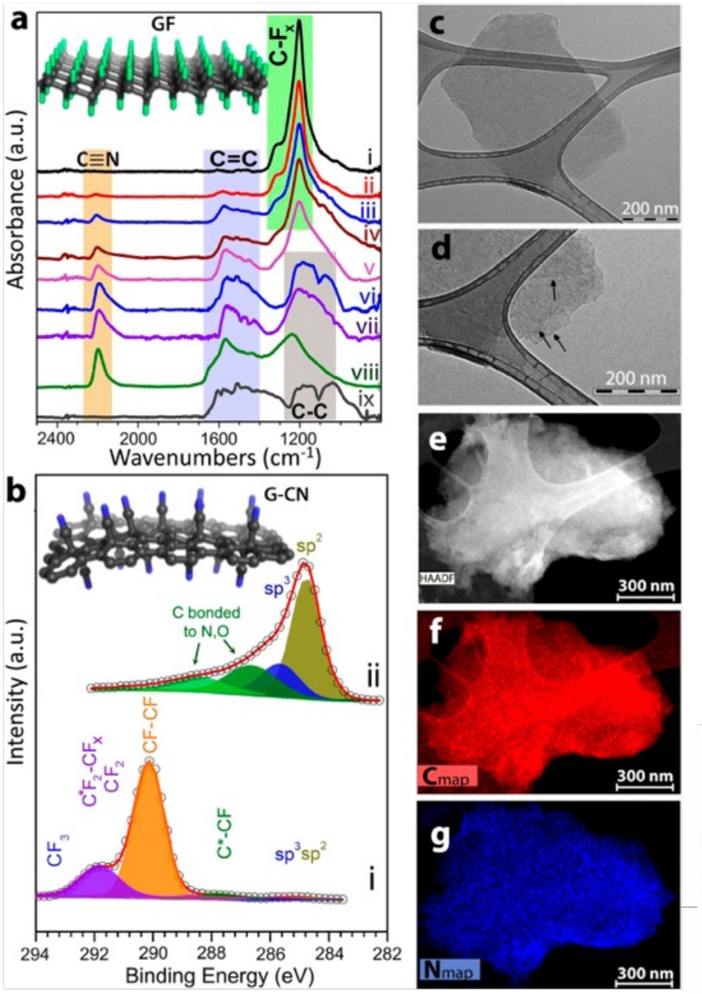


EXAFS

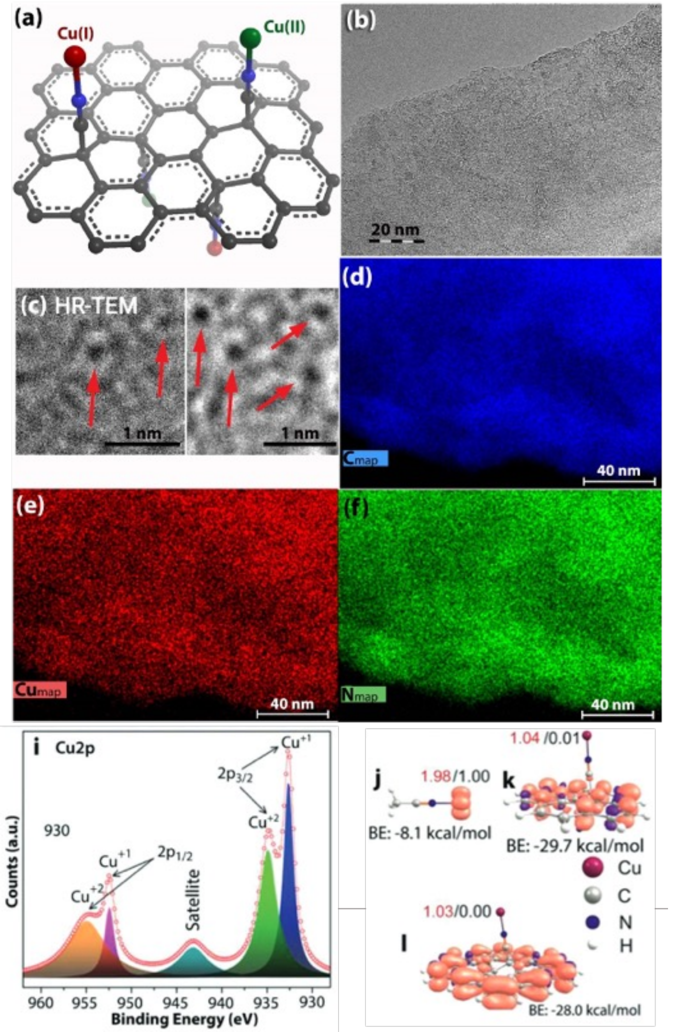


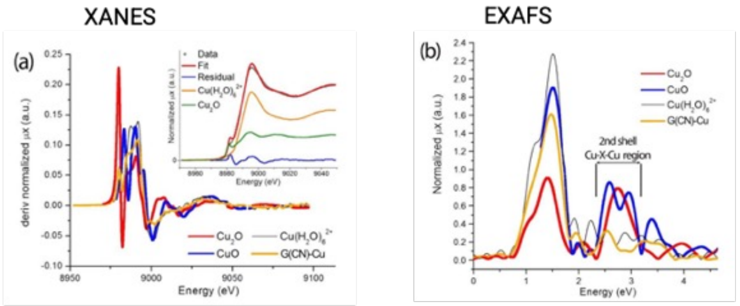
Cyanographene a 2D-ligand

FG + NaCN → G-CN

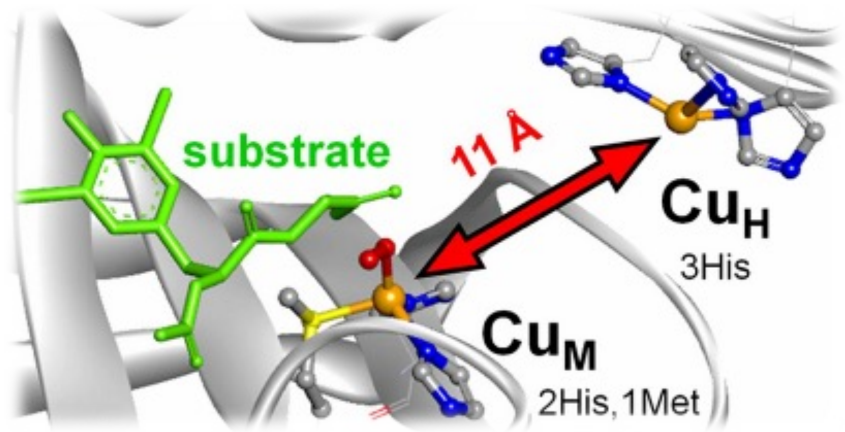


ACS Nano 11, 2982, 2017



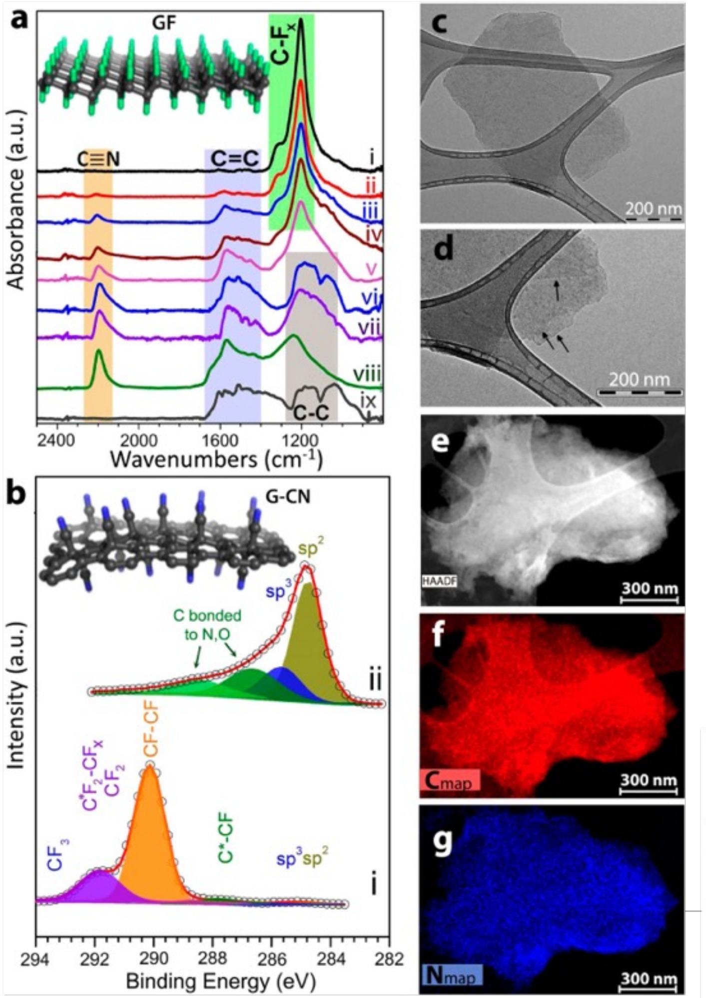


Enzymes use binuclear Cu(I)/Cu(II) sites for O_2 activation

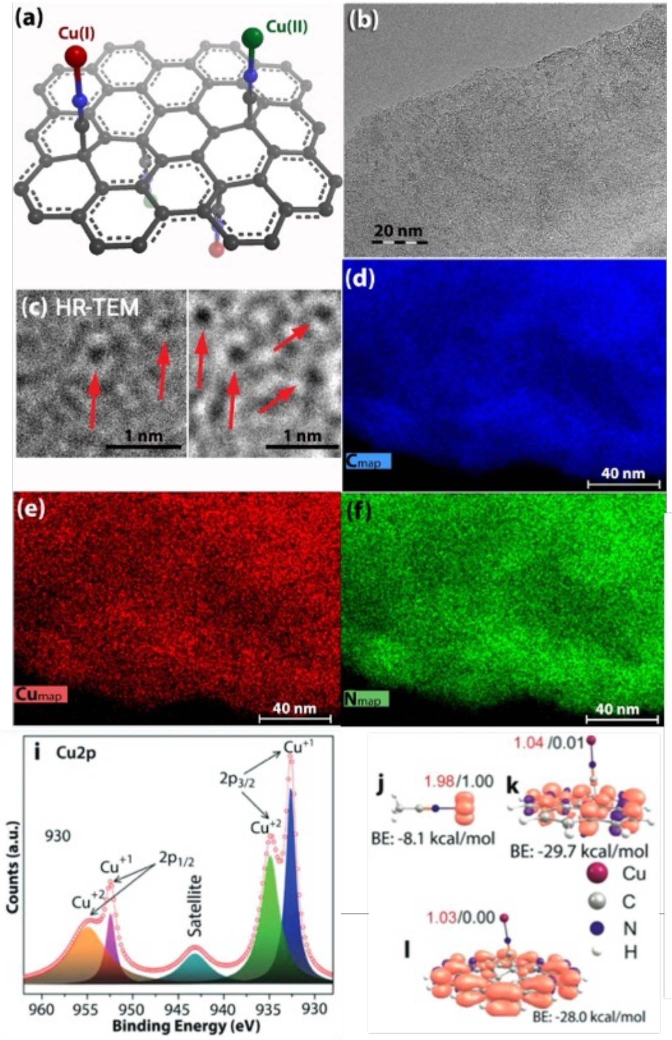


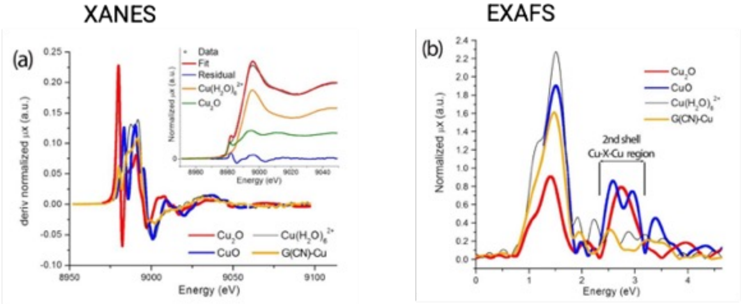
Cyanographene a 2D-ligand

FG + NaCN → G-CN

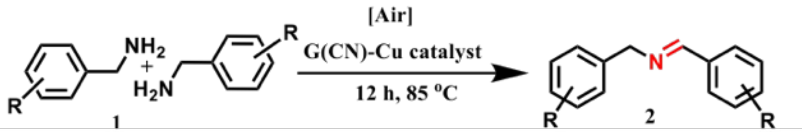


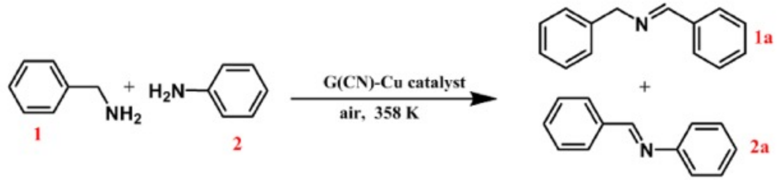
ACS Nano 11, 2982, 2017





GCN – Cu(I/II) – excellent Single Atom Catalyst for oxidative amine coupling





Entry	Copper–based Catalysts	Conv. (%)[b]	Product 1a Select. (%) (homo)	Product 2a Select. (%) (hetero)
1	CuCl	47	93	7
2	$CuCl_2$	60	100	0
3	CuCl + $CuCl_2$	56	92	8
4				
5	GCN-Cu (3.4wt%)	>99	8	92

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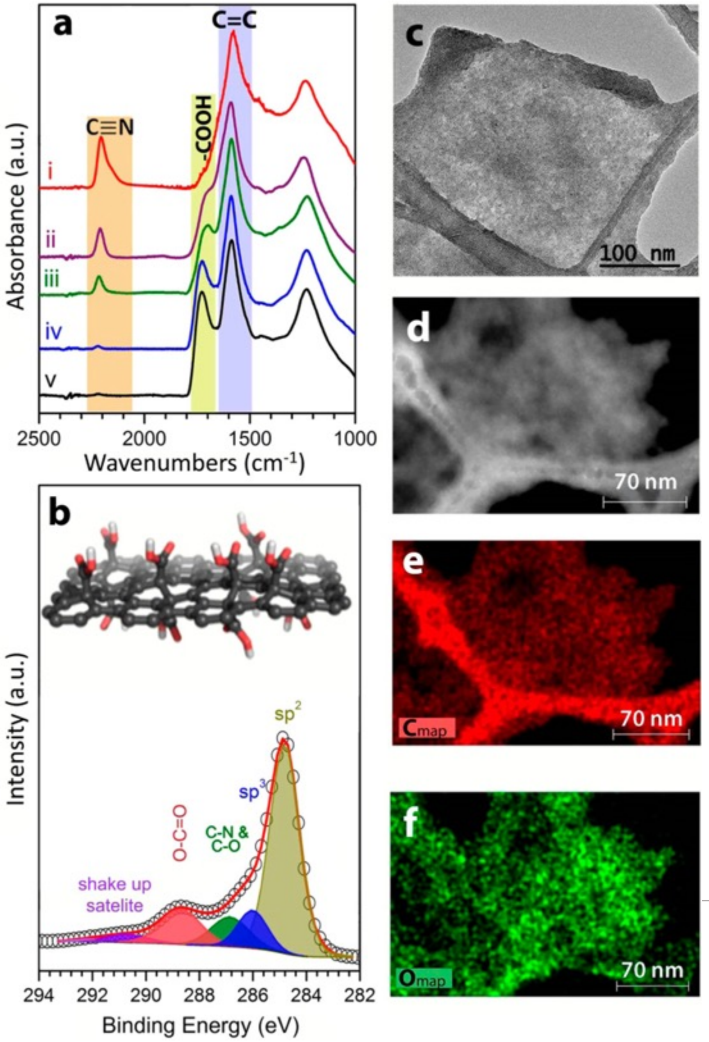
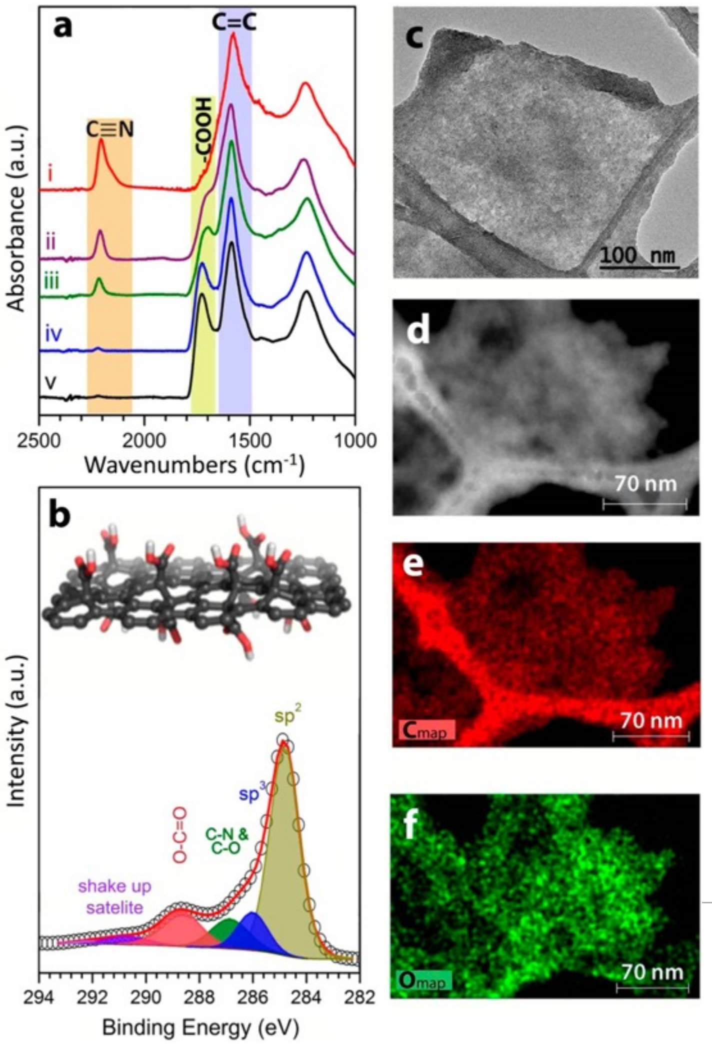
$G\text{-}CN + HNO_3 \rightarrow G\text{-}COOH$

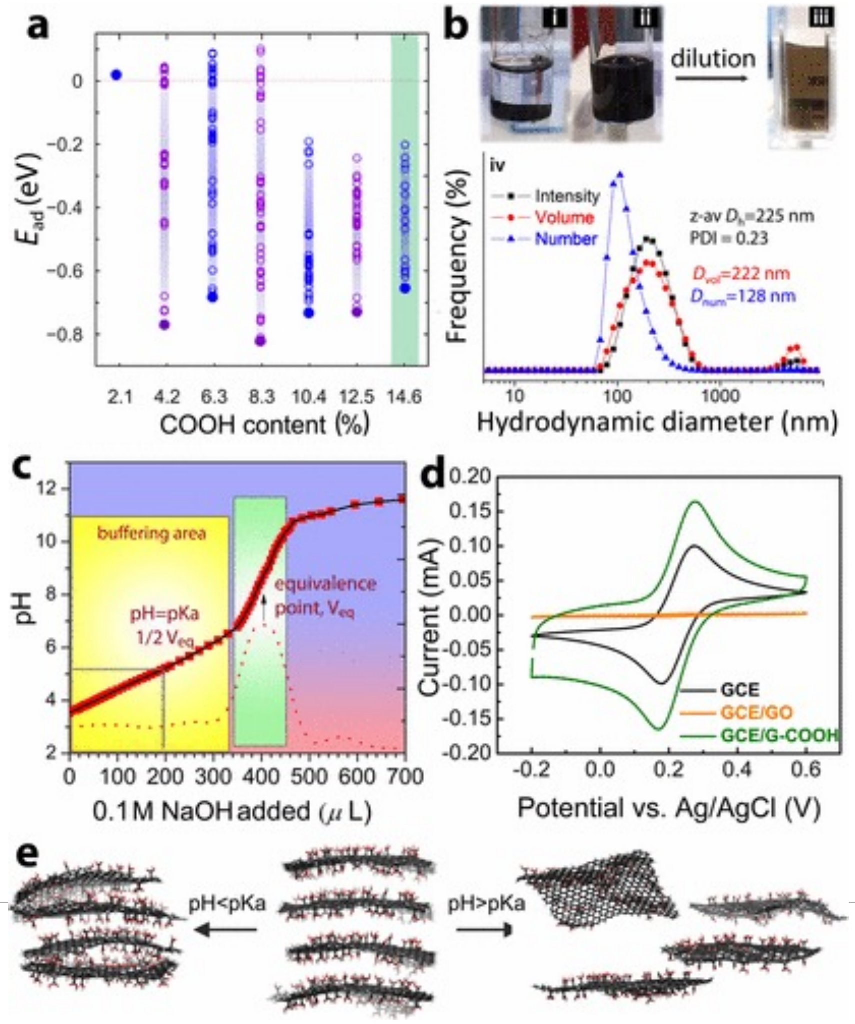
Cyanographene to Graphene Acid



G-CN + HNO_3 → G-COOH

Cyanographene to Graphene Acid

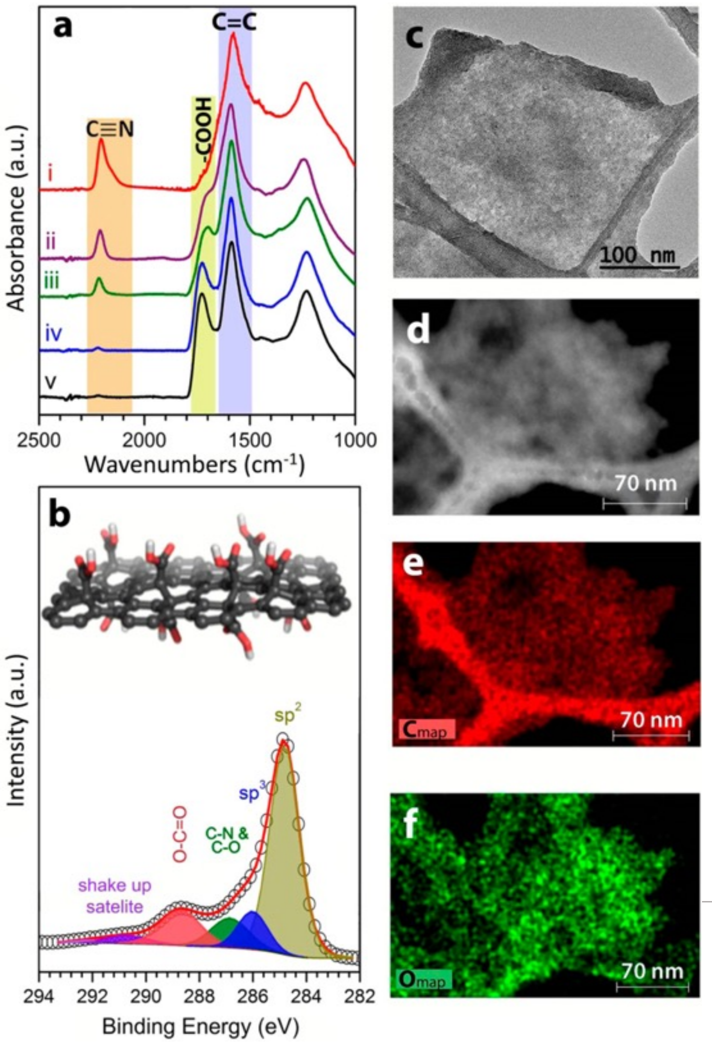


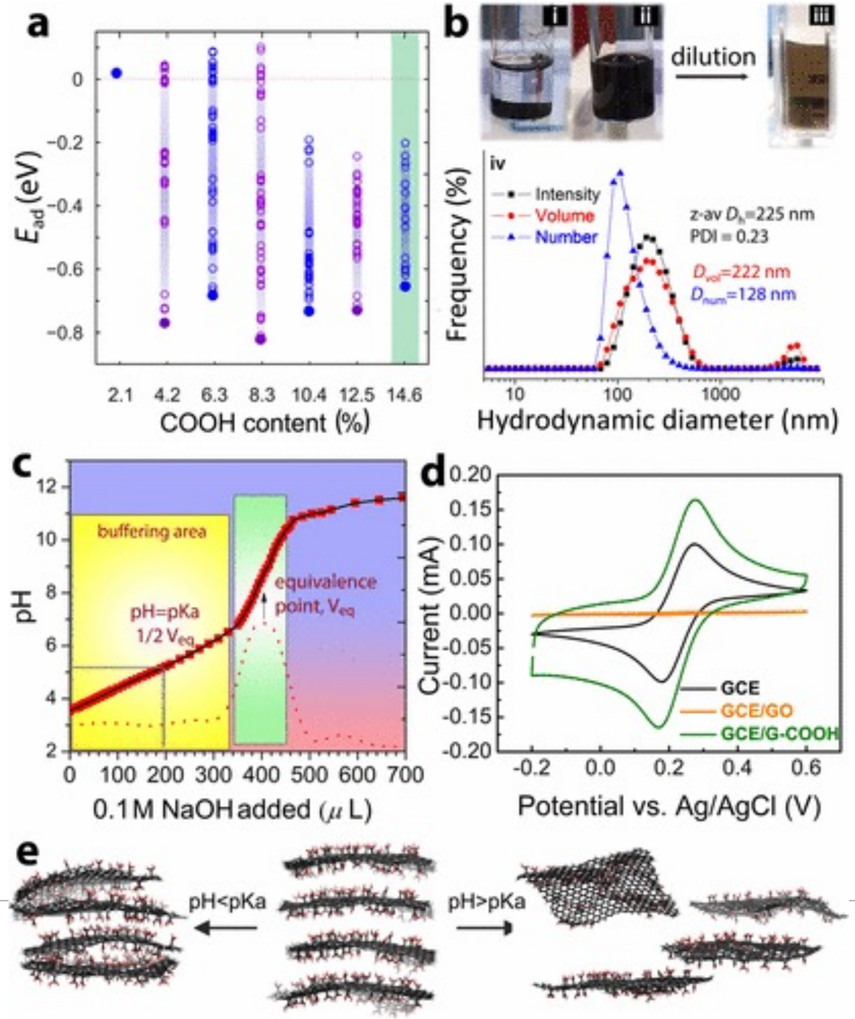


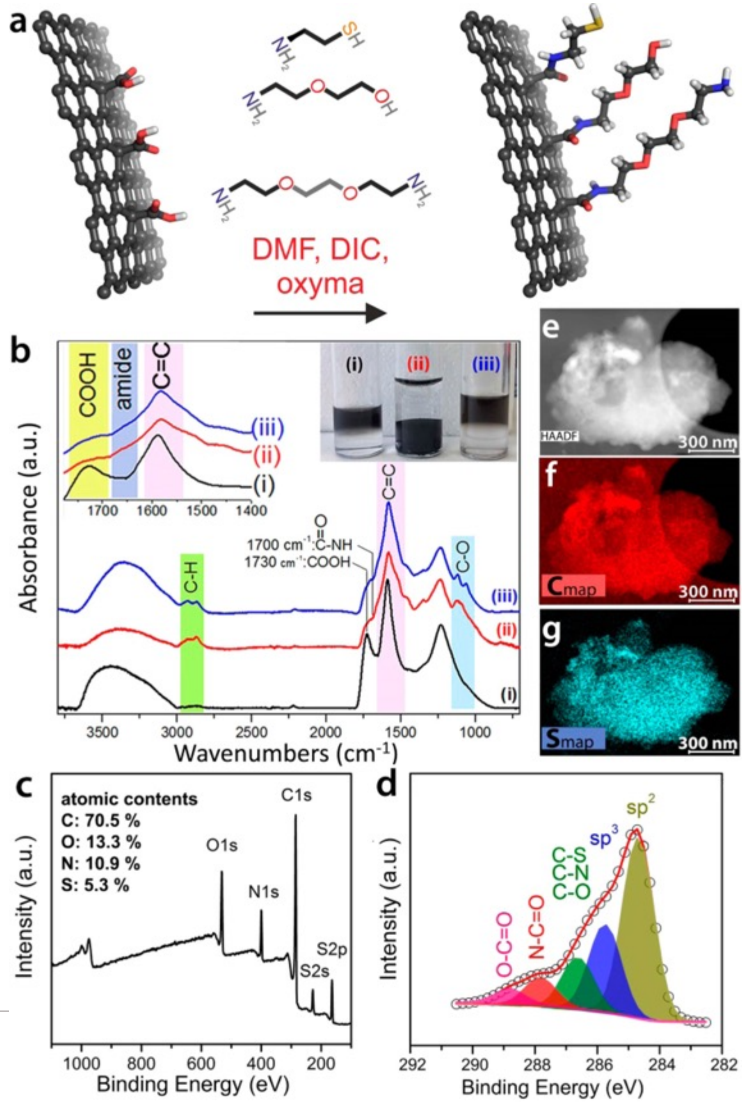
G-CN + HNO_3 → G-COOH

G-COOH + NH_2-R

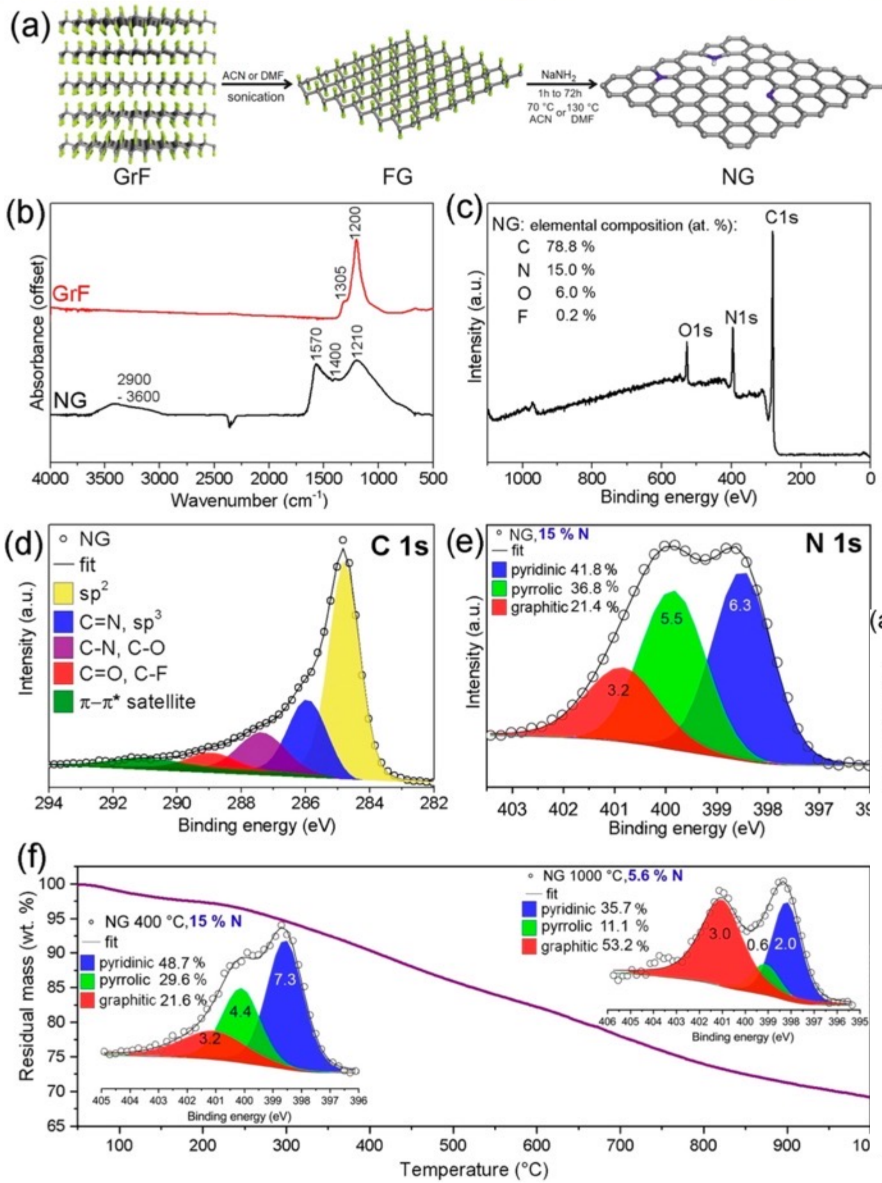
Functionalization of Graphene Acid

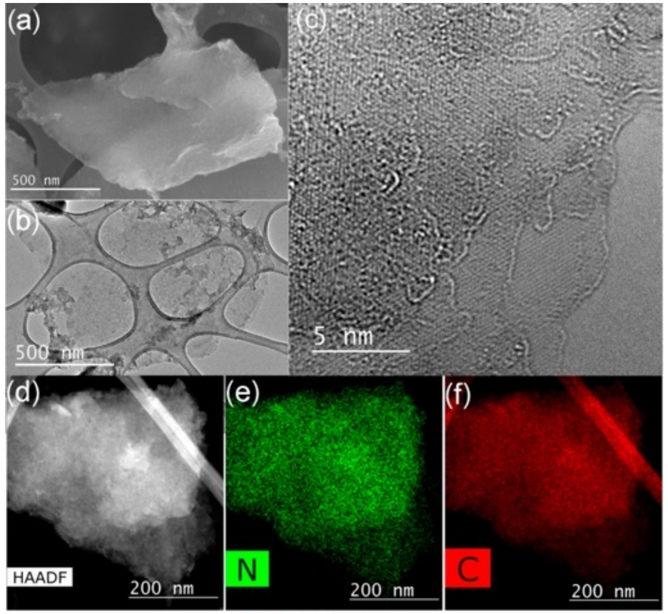


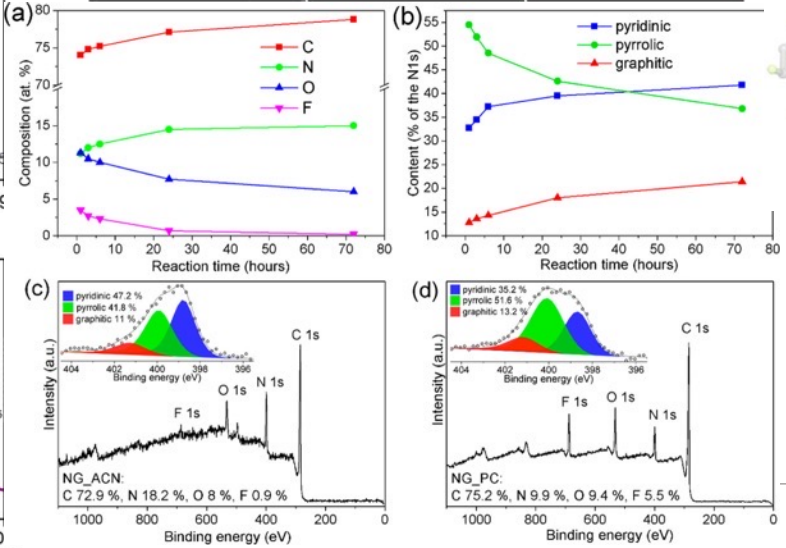


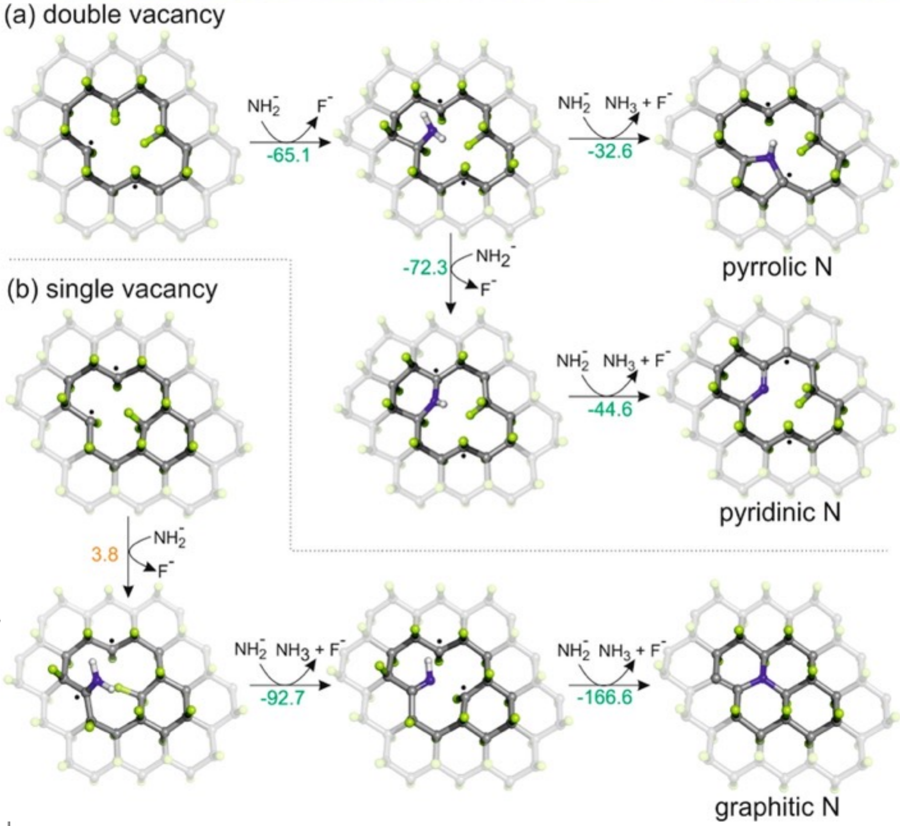


ACS Nano 11, 2982, 2017



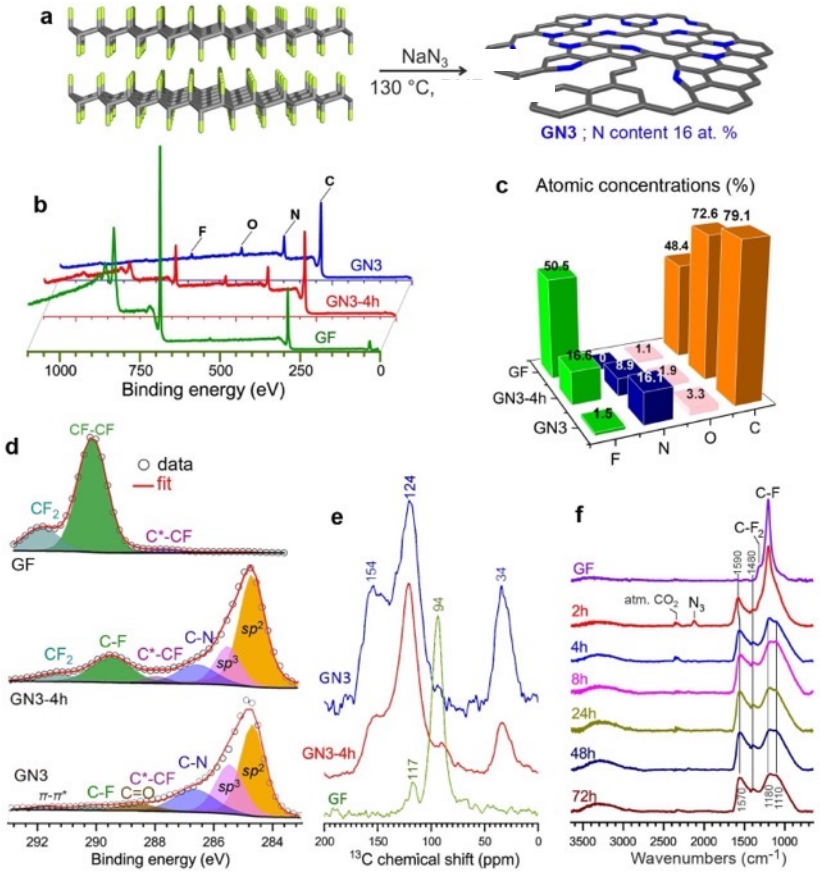




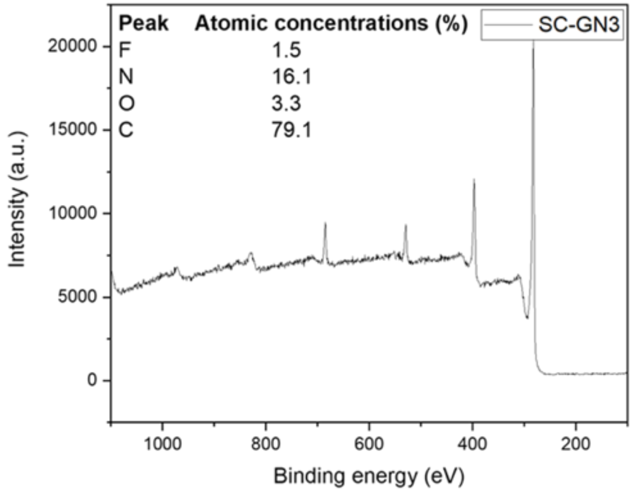


ACS Sustainable Chem. Eng., 8, 4764, 2020

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.

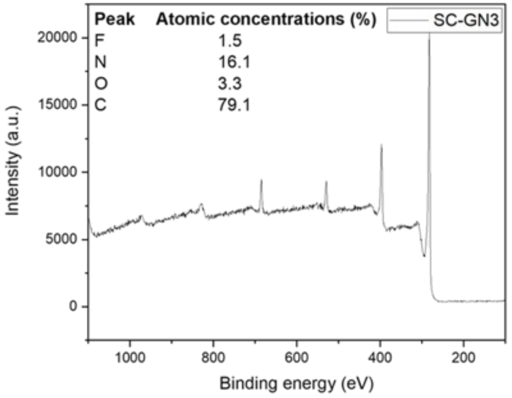
SC-GN3 material is highly N-doped (16 at. %) graphene-related material synthesized from graphite fluoride via wet chemistry in one step.

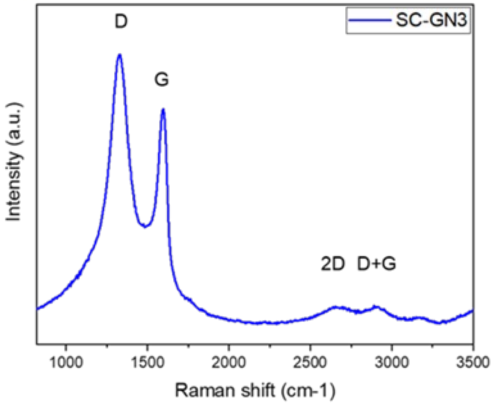
After synthesis purification steps are needed.

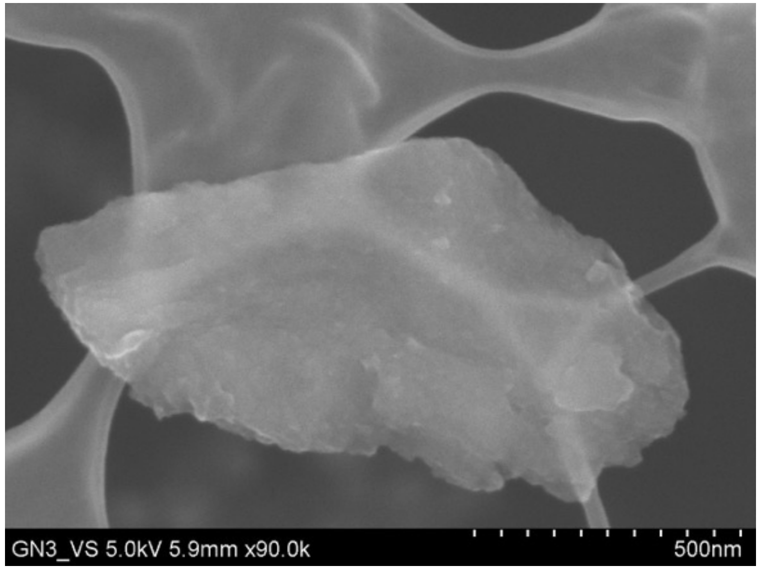
SC-GN3 is N-doped graphene

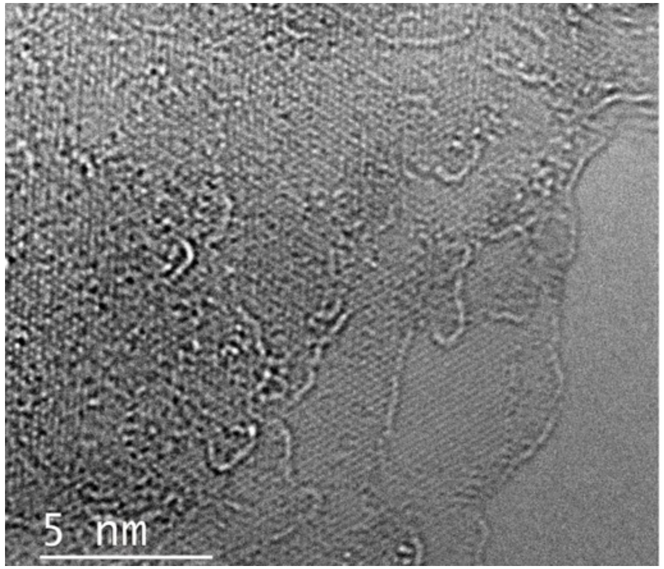
combines graphene-type layers with tetrahedral C-C bonds and high nitrogen doping (16 at. %), thermally stable to 400 ºC+, scalable synthesis

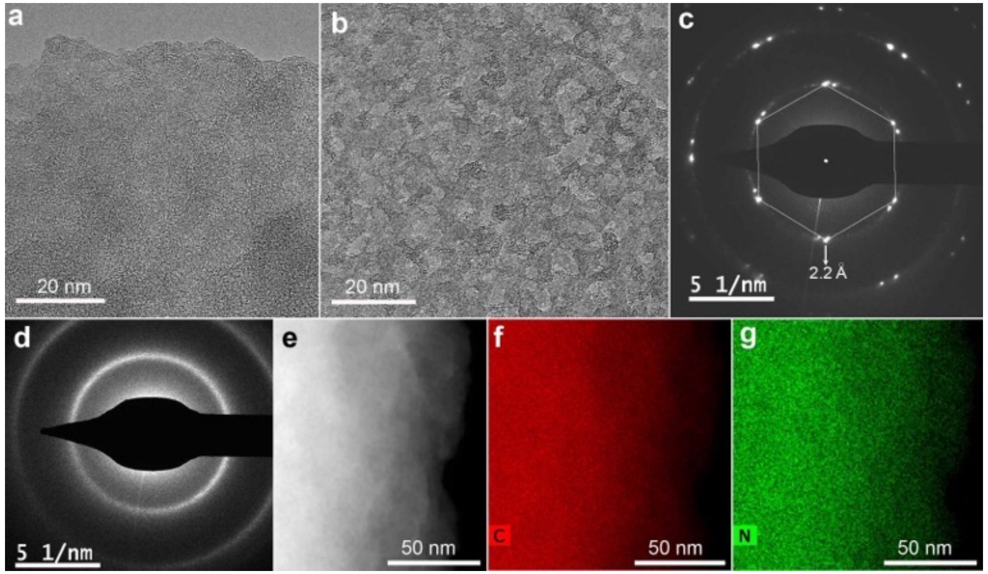
powder of SC-GN3









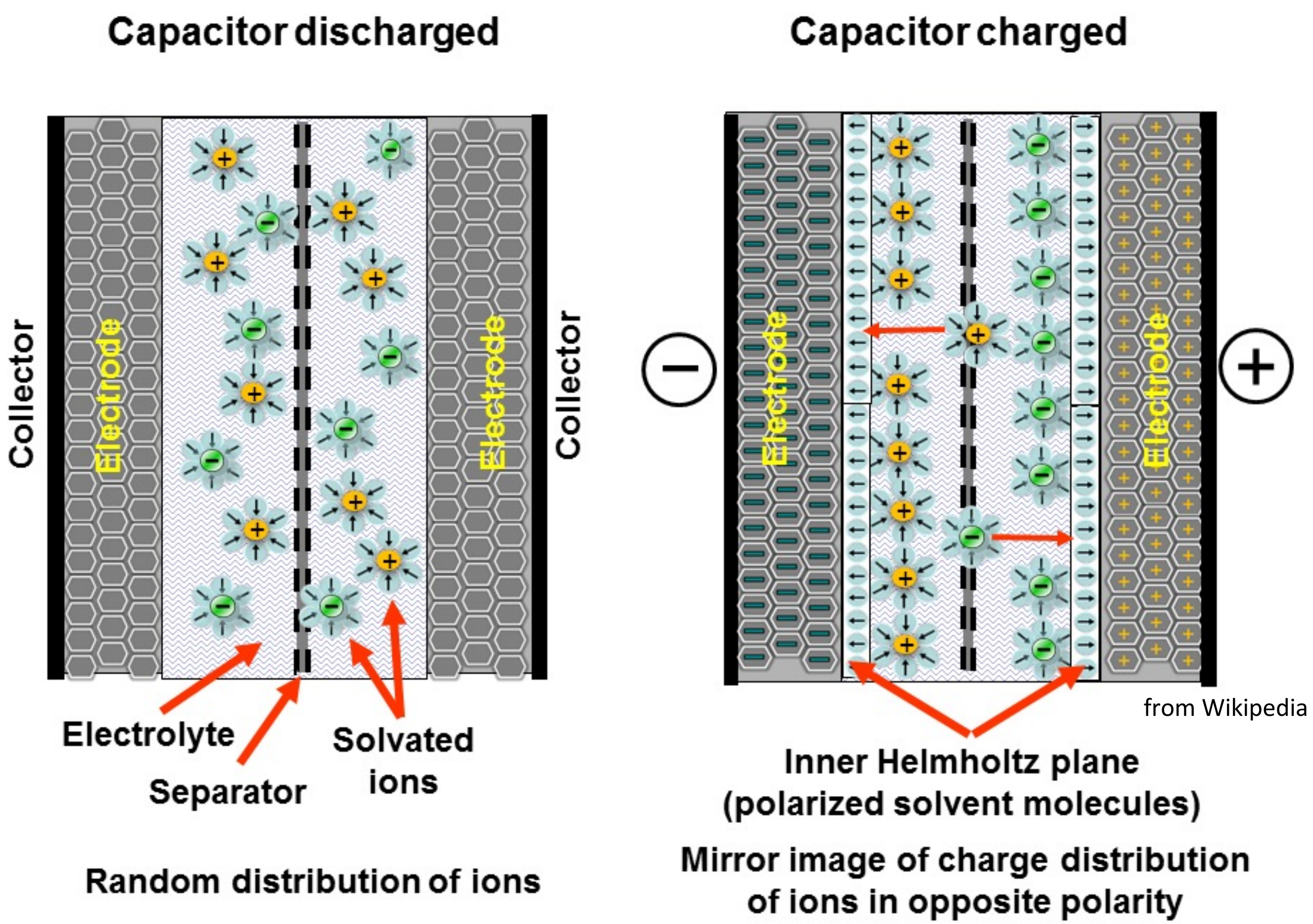


Supercapacitor

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

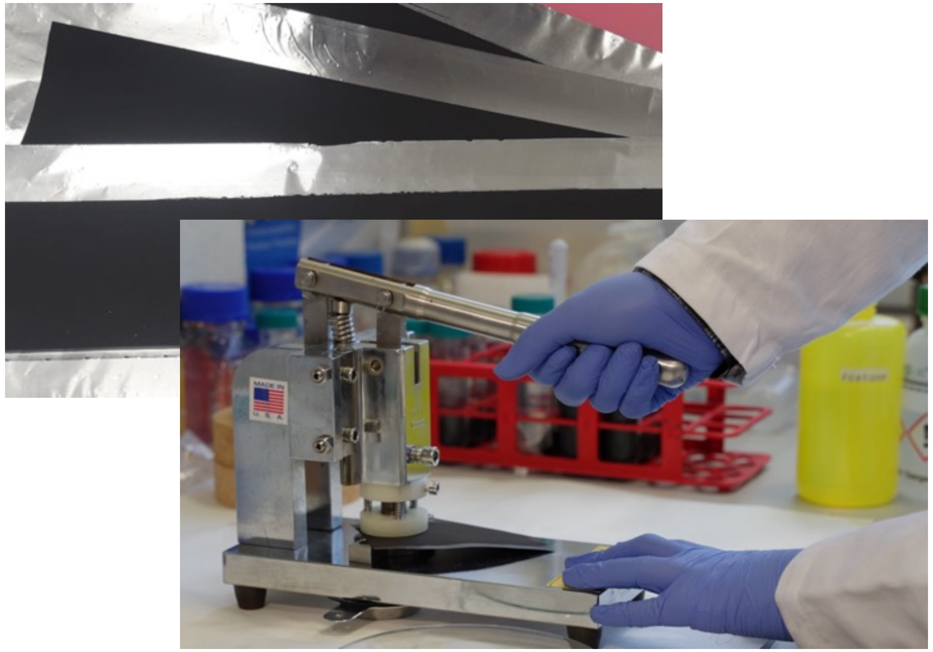
Quick and reversible charging/discharging

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

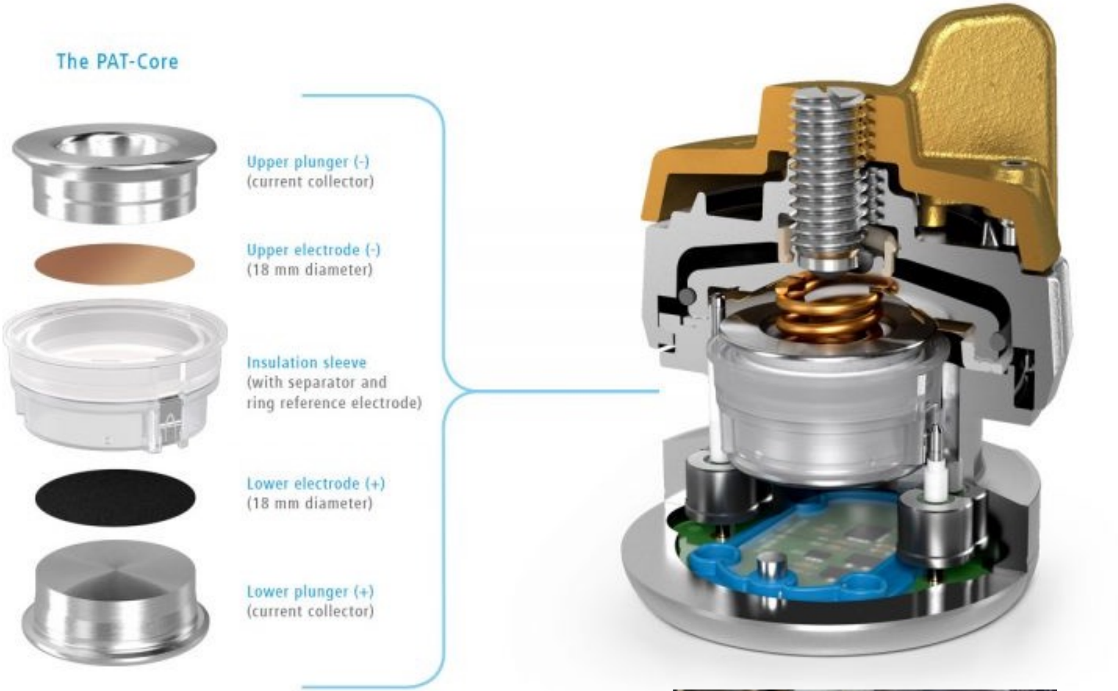


Operational principle of electrostatic double-layer capacitors (EDLCs)

SC-GN3 testing

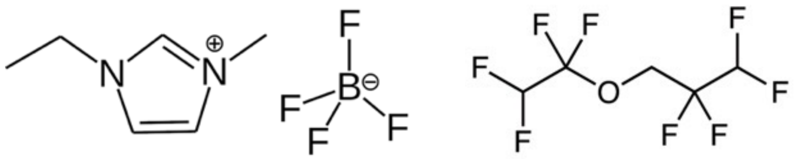


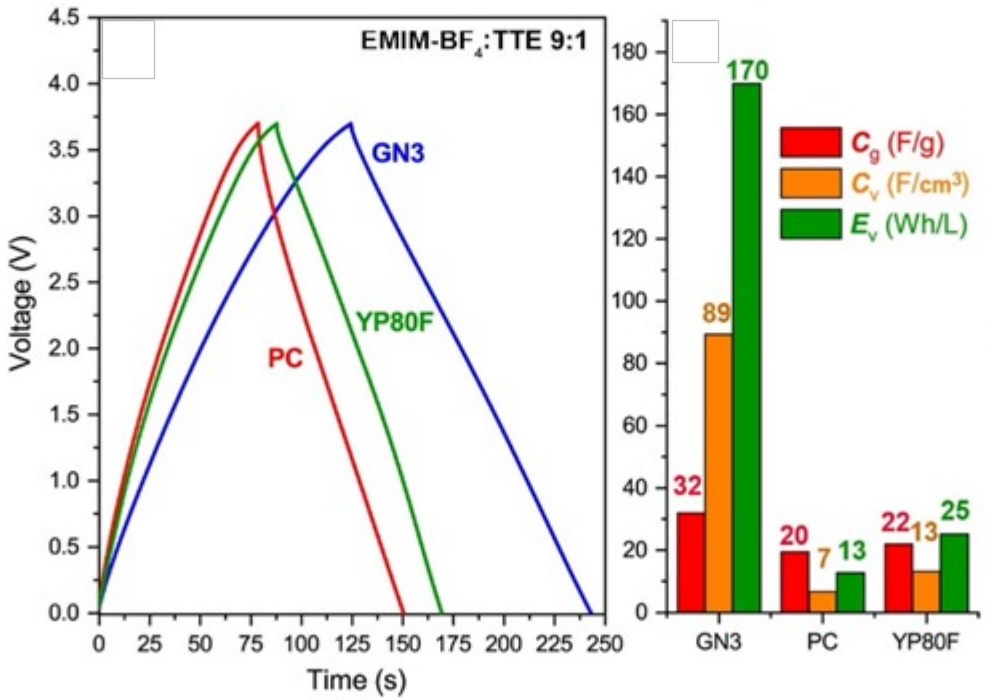
SC-GN3 is mixed with binder, electrodes are prepared.



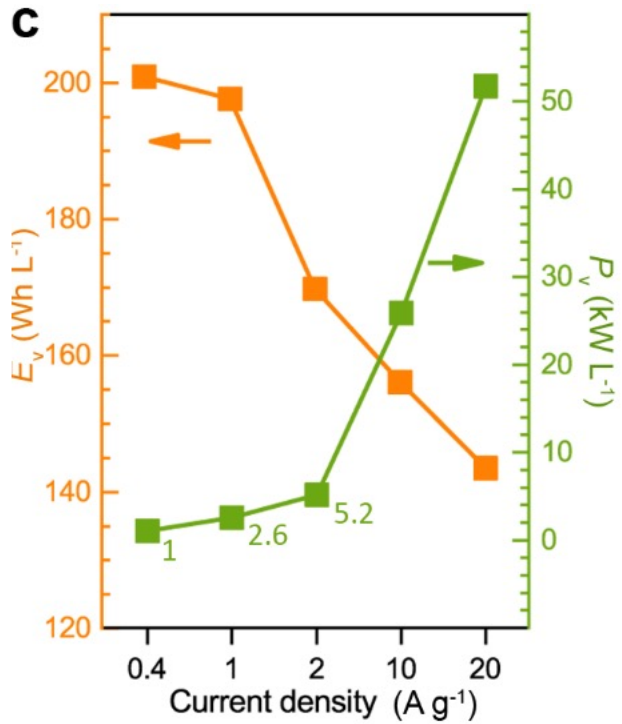
Scheme of El-Cell used for testing (figures taken from el-cell.com).

SC-GN3





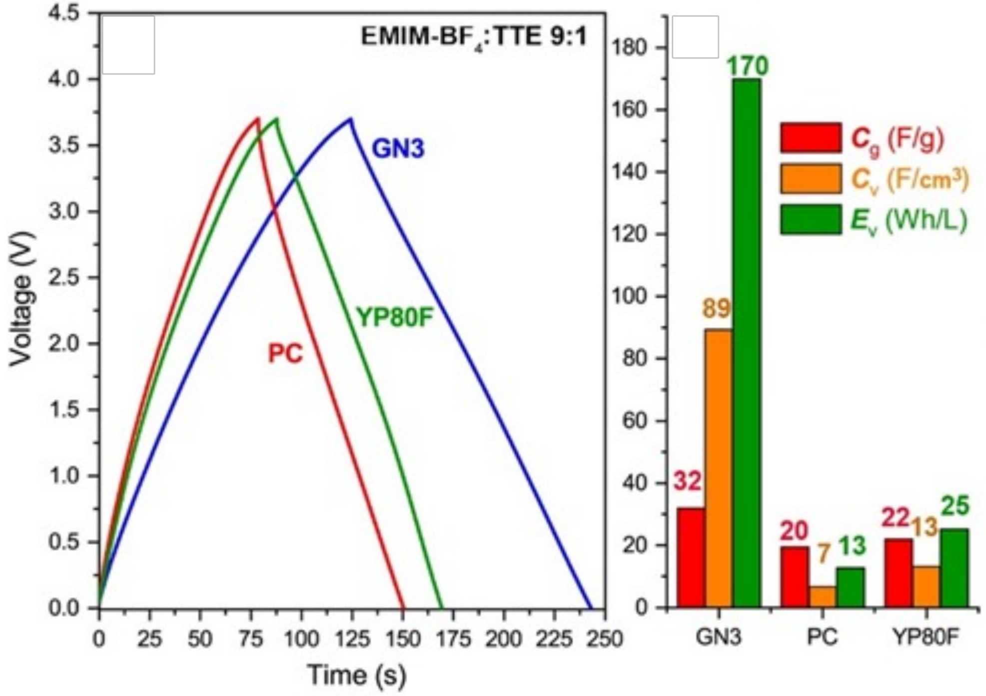
GCD profiles and supercapacitor performance comparison of commercial porous high surface area carbon materials and N-doped graphene (at 2 A g^{-1}).



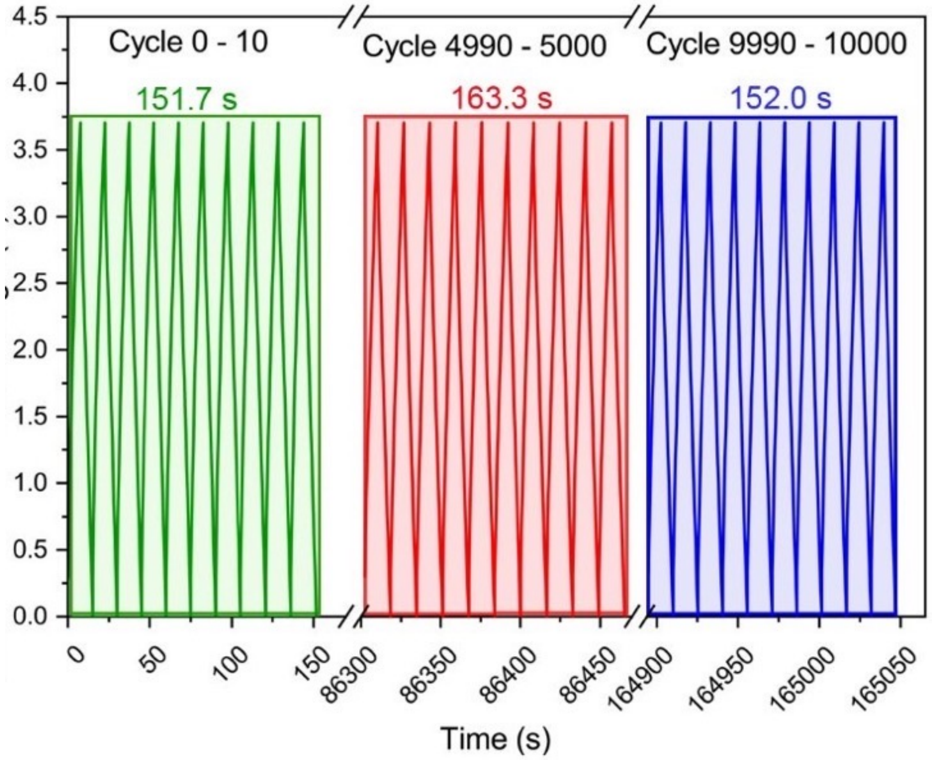
Energy and power density of SC-GN3 at increasing specific currents. SC-GN3 delivers energy densities of 200 Wh L^{-1} at a power of 2.6 kW L^{-1} and 143 Wh L^{-1} at 52 kW L^{-1}.

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

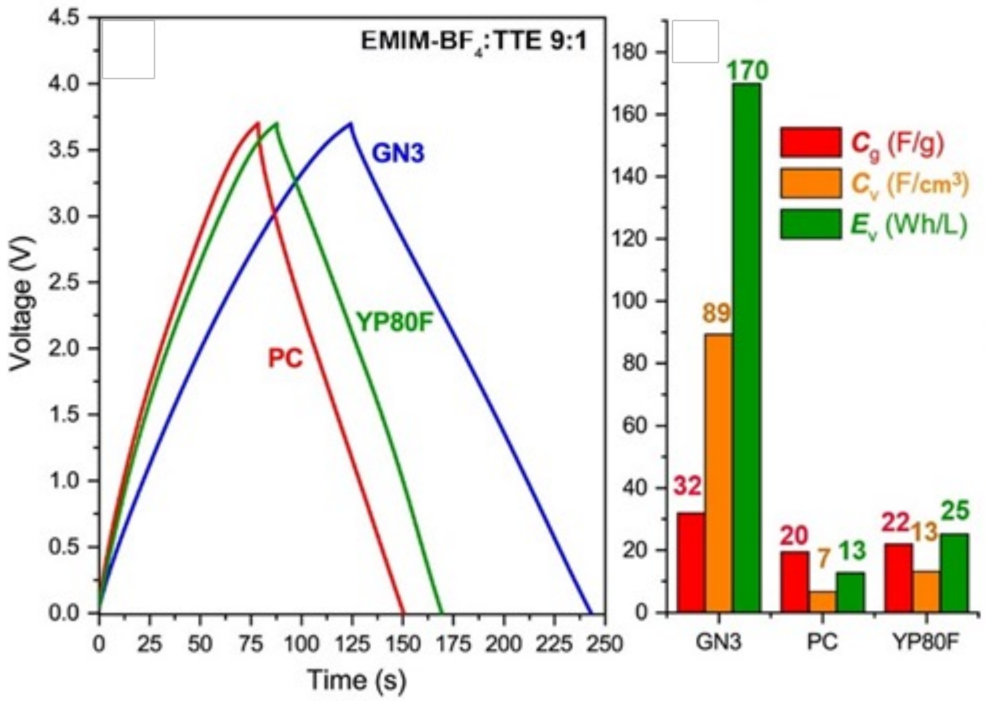


GCD profiles and supercapacitor performance comparison of commercial porous carbon materials and N-doped graphene.

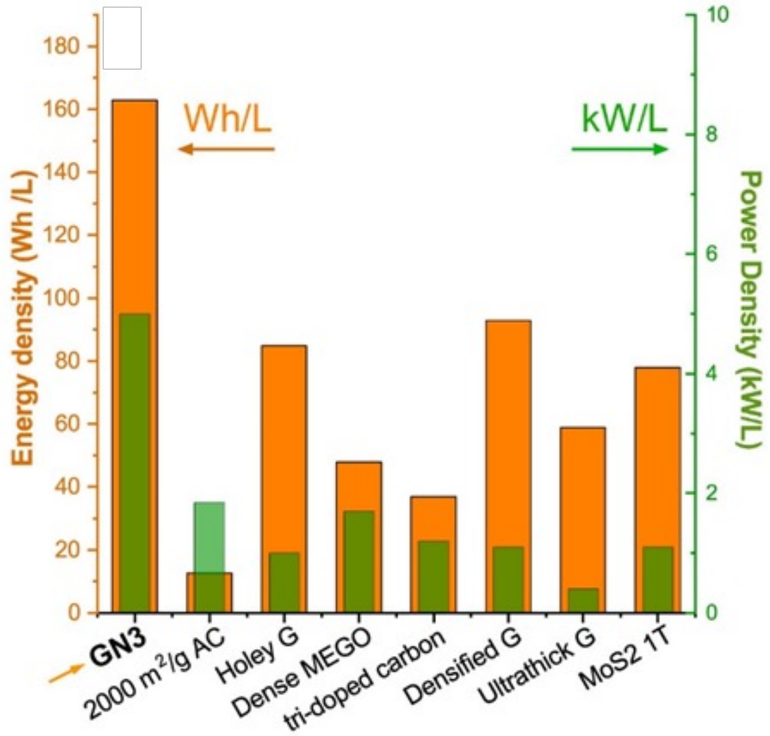


Stability of GN3 showing the GCD profiles at the beginning, mid-point, and end of a 10,000 cycle test.

SC-GN3



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



Current state-of-art comparison.

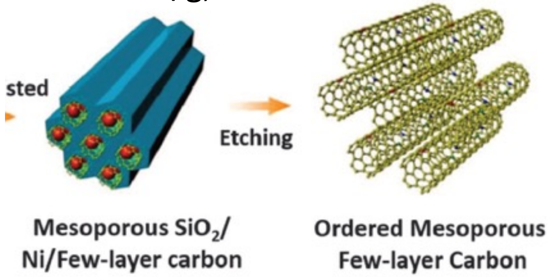
1. *Angewandte Chemie International Edition 58, 2397–2401 (**2019**).*
2. *Nature Communications 5, 5554 (**2014**).*
3. *Nano Energy 2, 764–768 (**2013**).*
4. *Science 341, 534–537 (**2013**).*
5. *Energy Environ. Sci. 9, 3135–3142 (**2016**).*
6. *Nature Nanotechnology 10, 313–318 (**2015**)*

Comparison - State of the art

Science [350, 1508–1513 (2015)](#)

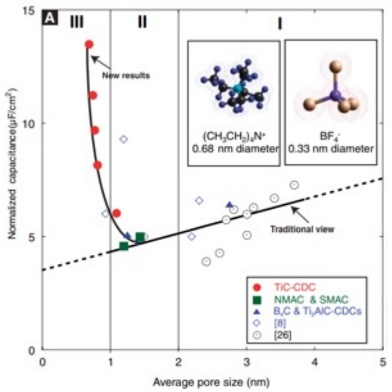
Nitrogen-doped mesoporous carbon of extraordinary capacitance for electrochemical energy storage

2000 m^2/g, 22 Wh L^{-1}



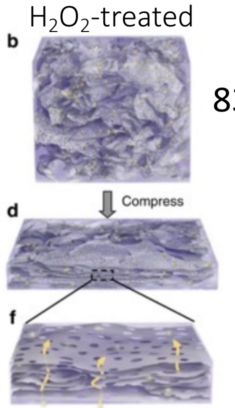
Science [350, 1508–1513 (2015)](#)

Anomalous Increase in Carbon Capacitance at Pore Sizes Less Than 1 Nanometer



nature COMMUNICATIONS [Nat. Commun., 2014, 5 , 5554](#)

Holey graphene frameworks for highly efficient capacitive energy storage



830 m^2/g, 0.7 g/cm^3

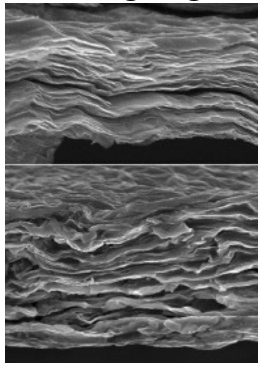
0.7 g/cm^3

85 Wh L^{-1}

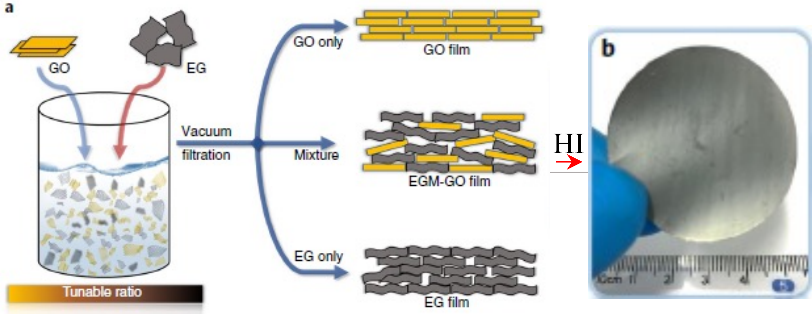
nature energy [Nat Energy 5, 160–168 (2020)](#)

Tuning the interlayer spacing of graphene laminate films for efficient pore utilization towards compact capacitive energy storage

300 m^2/g, 1 g/cm^3



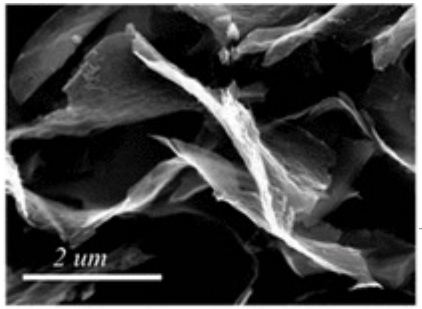
113 Wh L^{-1}



ACS NANO [9, 3, 2556–2564 (2015)](#)

Hierarchical Porous Nitrogen-Doped Carbon Nanosheets Derived from Silk for Ultrahigh-Capacity Battery Anodes and Supercapacitors

2494 m^2/g, N: 4.7%, 0.5 g/cm^3

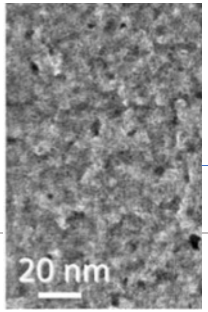


45 Wh L^{-1}

Science [332, 1537–1541 (2011)](#)

Carbon-Based Supercapacitors Produced by Activation of Graphene

3100 m^2/g, 0.34 g/cm^3



compression

0.34 g/cm^3

0.74 g/cm^3

48 Wh L^{-1}

[Nano Energy, 2, 764 (2013)](#)

26 Wh L^{-1}

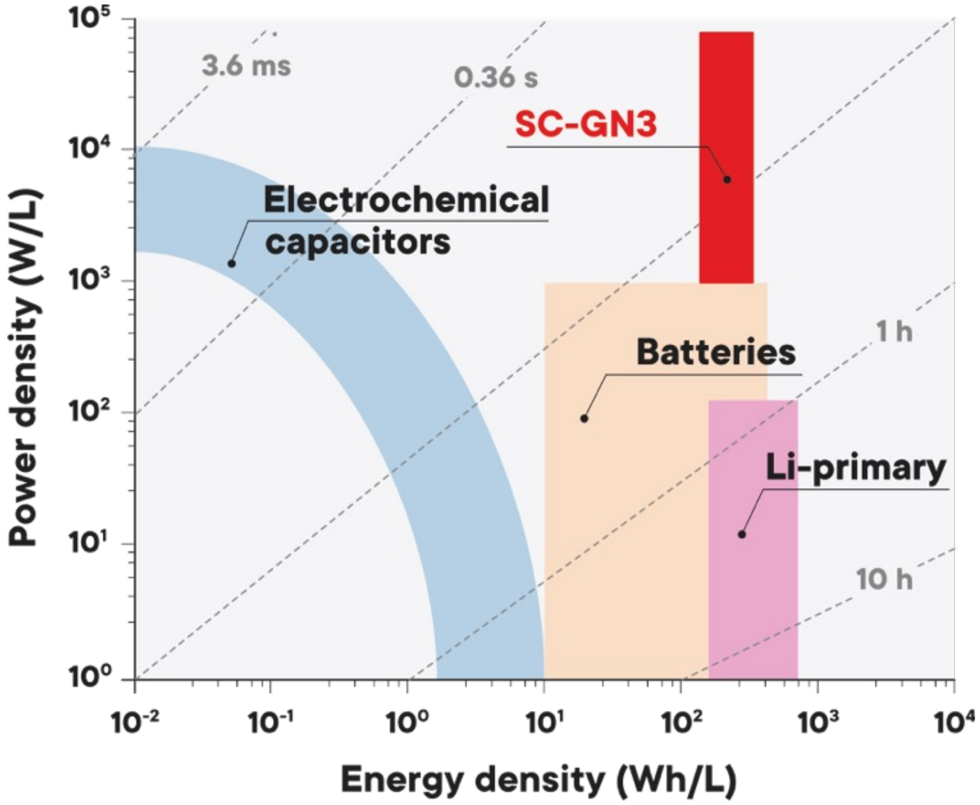
Science [341, 534–537 (2013)](#)

Liquid-Mediated Dense Integration of Graphene Materials for Compact Capacitive Energy Storage

3100 m^2/g, 1.3 g/cm^3

80 Wh L^{-1}

SC-GN3



new material with high

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

Market Opportunities
Space

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

Driverless transport AGV
Automated Guided Vehicles

Source: Jianghai-Europe

Prototypes in 2024

Q: 2025

EIC Transition

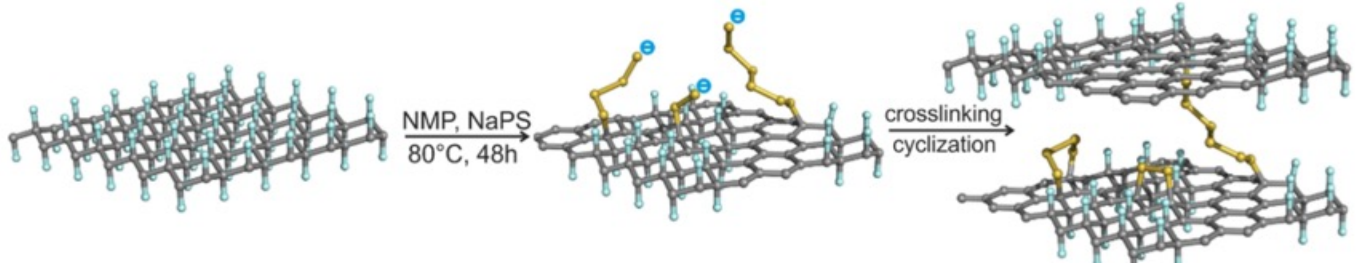
Example of available devices

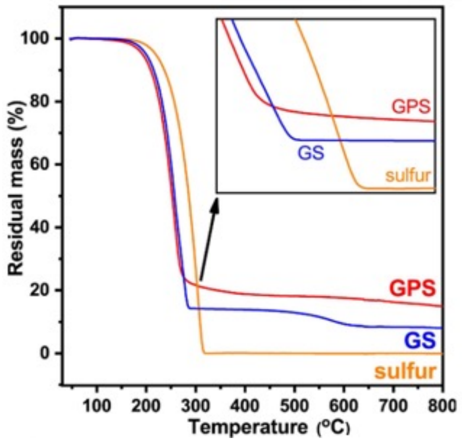
AVX PrizmaCap (4 Wh/L)

Skeleton SkelCap (16 Wh/L)

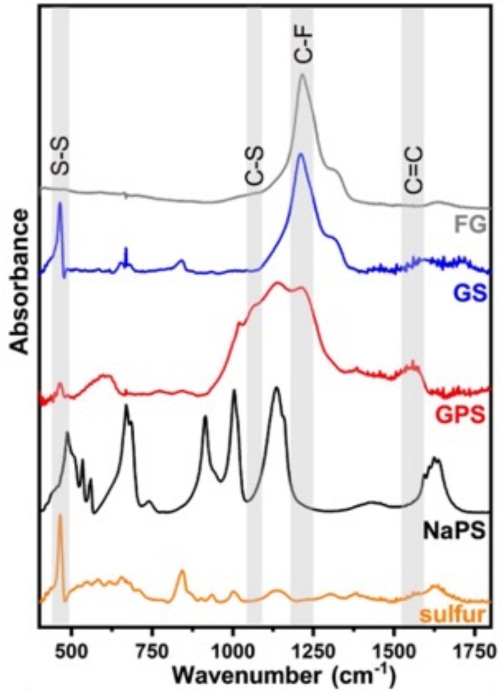
Background and characterization

- **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. %

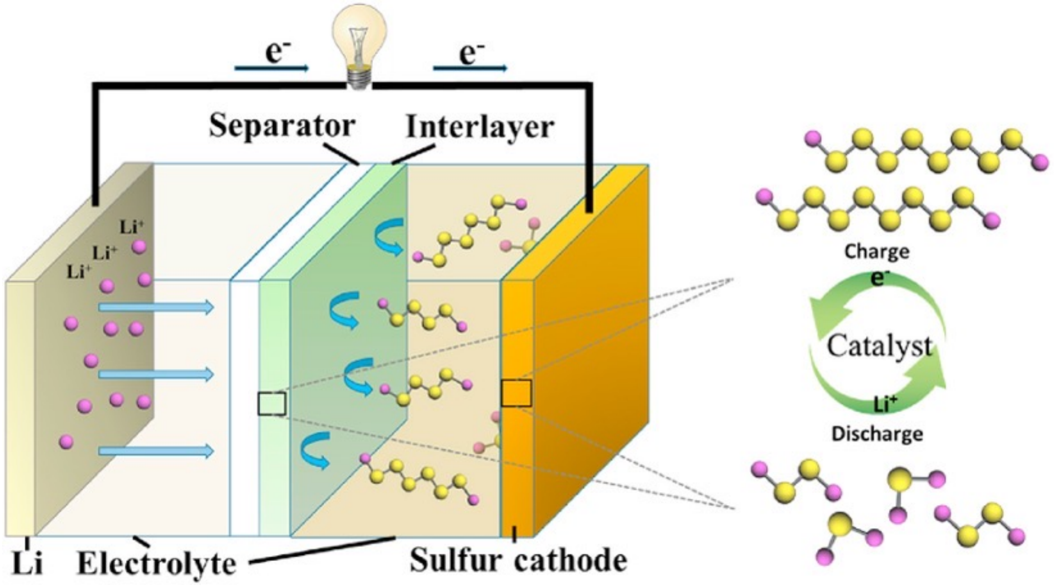


GPS: C–F at ~1200 cm^{-1} decreased (i.e., defluorination) 1580 cm^{-1} band emerged (graphene lattice formation).
The new band at ~1150 cm^{-1} demonstrates the development of covalent C–S bonds.

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

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

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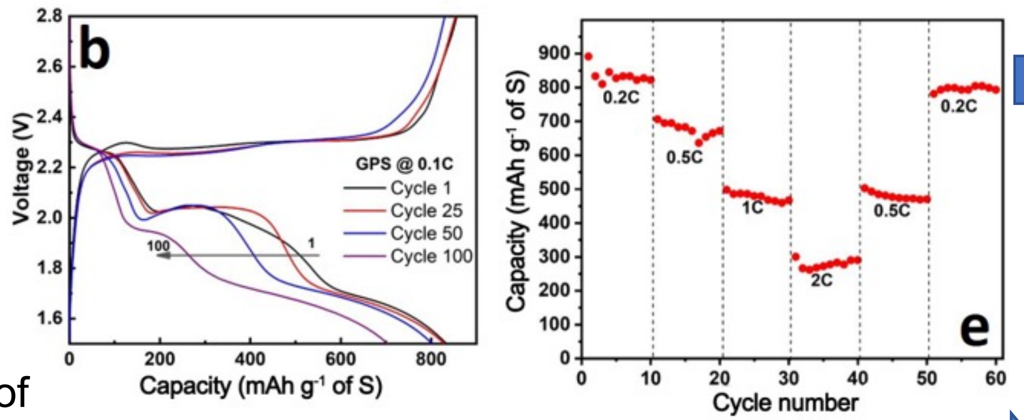
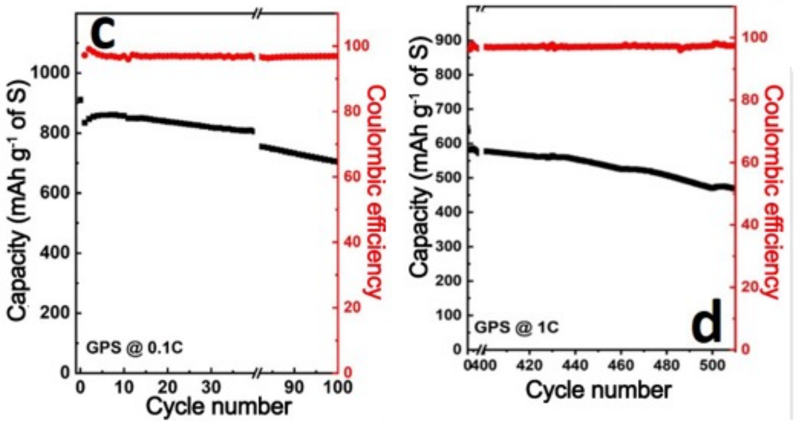
Electrochemical performance of the graphene-polysulfide cathode

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

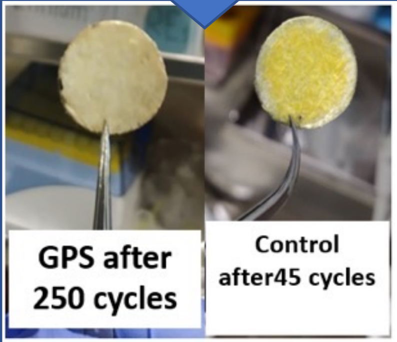


Good rate capability for both high and low specific currents

- ✓ 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**



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



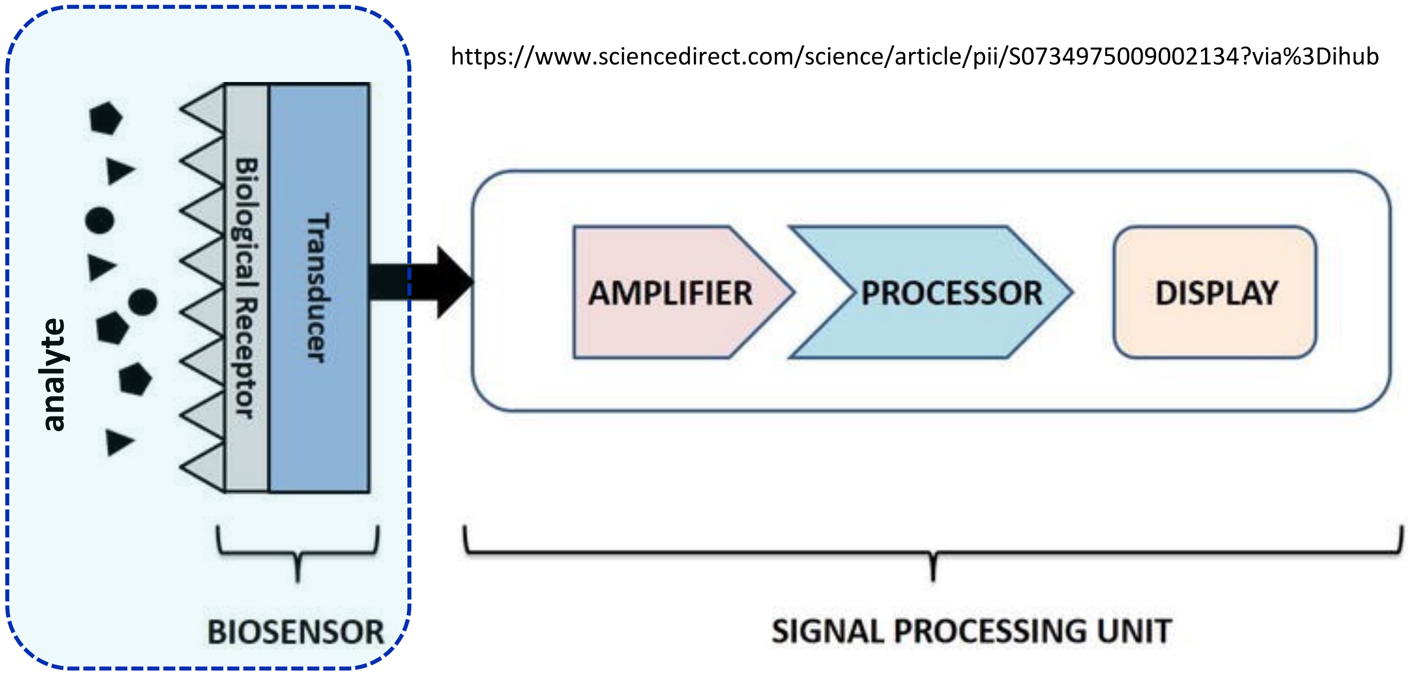
Glass fiber separator after cycling showing the dissolution of sulfur at the control material

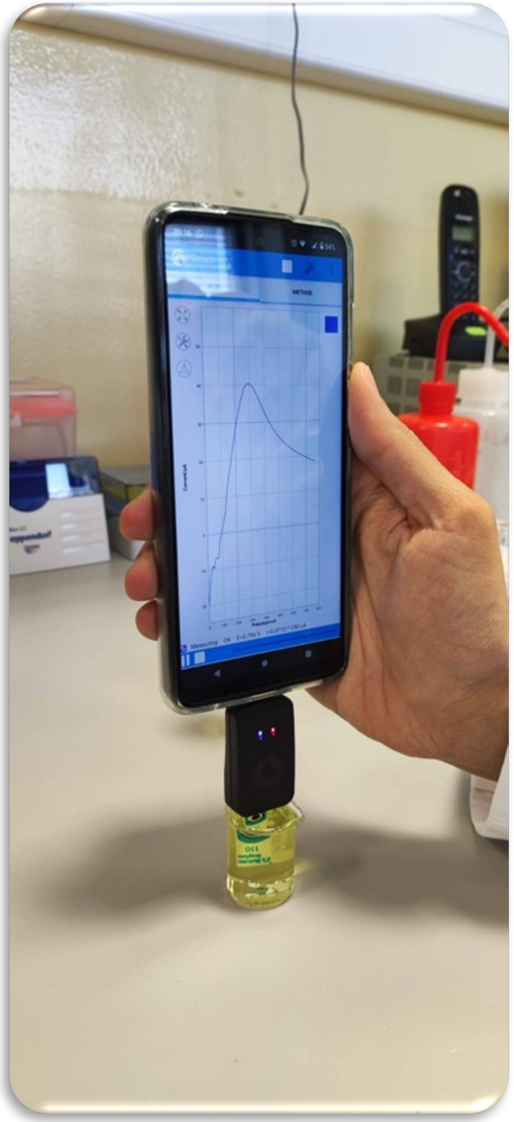
Supported by ERC PoC

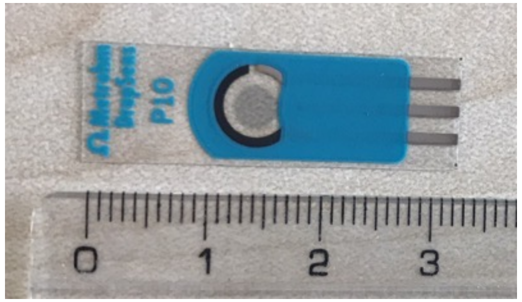
EP 3978431
Tantis et al. Adv. Funct. Mater. ***2021****, 2101326*

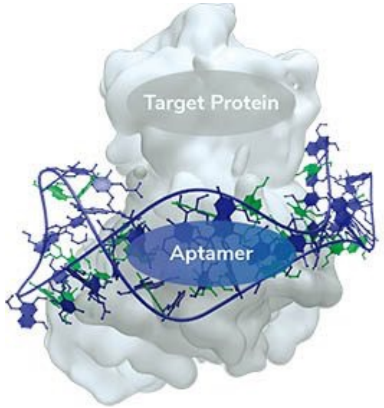
Biosensors – general overview

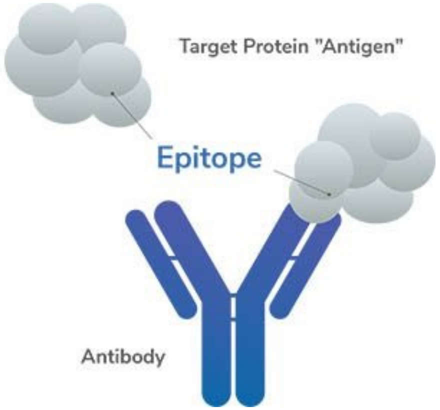
https://www.sciencedirect.com/science/article/pii/S0734975009002134?via%3Dihub







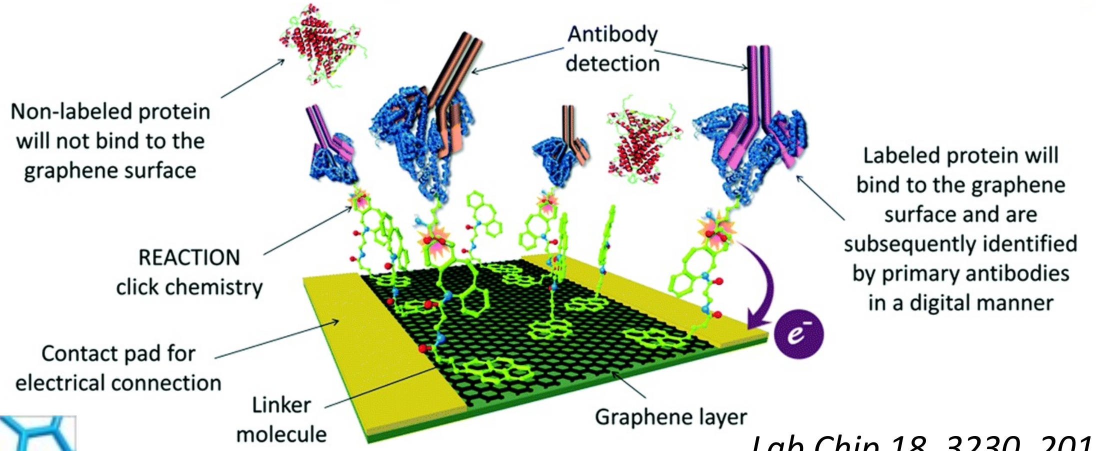




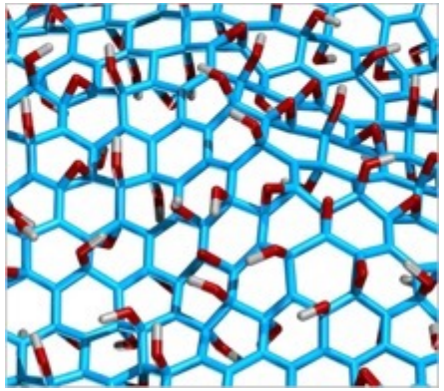
Graphene based (bio)sensors

- Noncovalent functionalization
  - functionalized anchor (e.g., based on pyrenebutyric acid)
  - Risk of leakage/disintegration

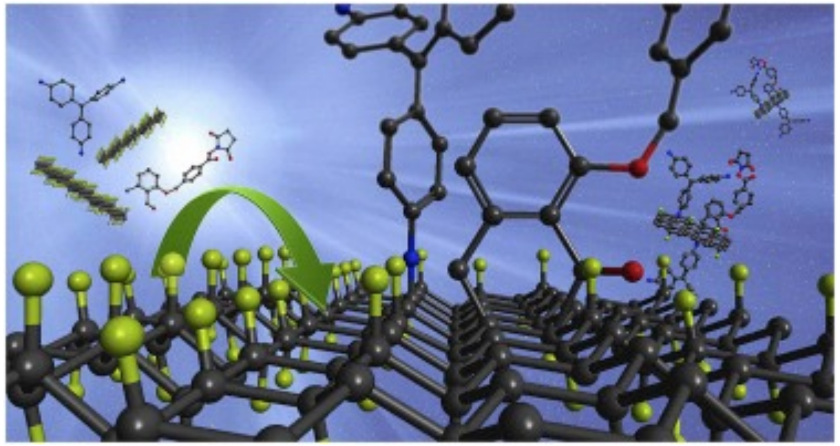
- Covalent functionalization
  - Graphene oxide
    - Great water dispersibility
    - Enables covalent functionalization
    - Complex chemistry
    - Nonconductive
    - Standardization challenge
  - Reduced Graphene oxide
    - Conductivite
    - Limited water dispersibility
    - Hard covalent functionalization
  - Fluorographene derived graphene derivatives
    - Precise chemistry
    - Reasonable conductivity



Lab Chip 18, 3230, 2018



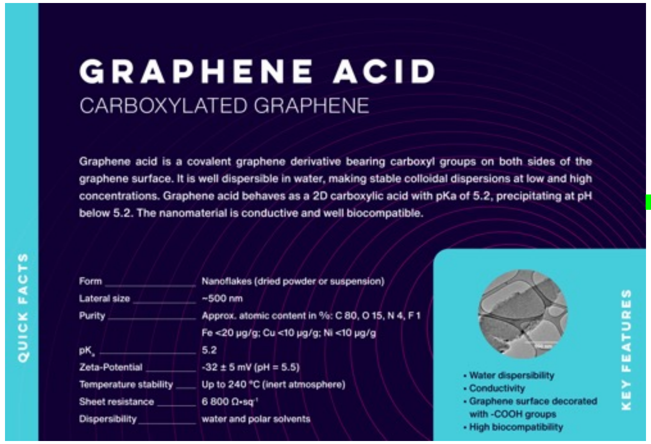
ChemNanoMat 4, 244, 2018



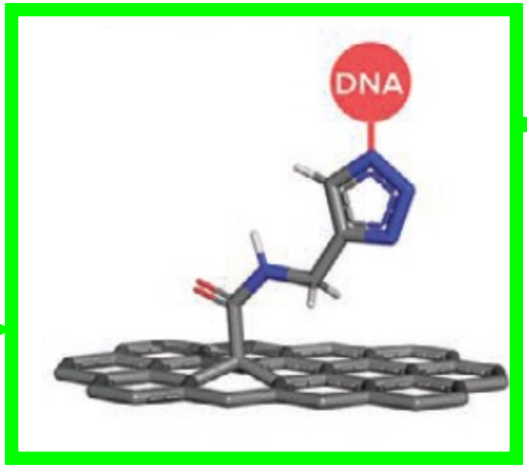
Carbon 145, 251, 2019

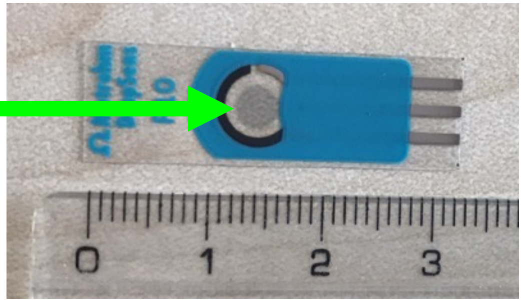
Biosensors – Detection of antibiotic ampicillin

Graphene acid (GA)
graphene-derivatives.com



aptamer functionalization





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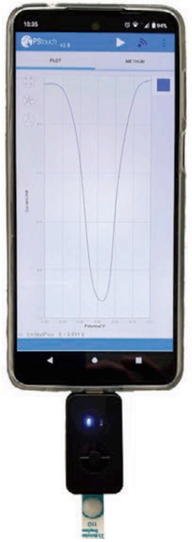
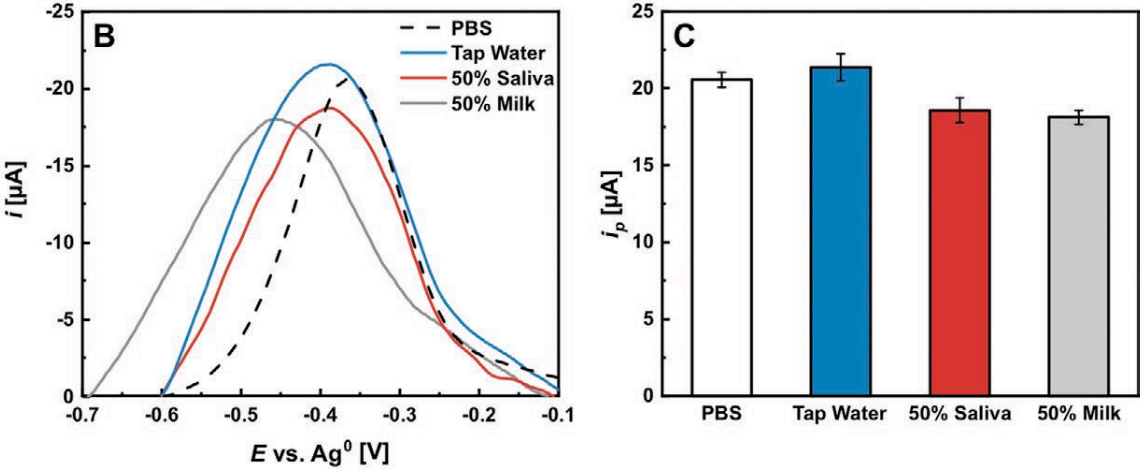


Highlights

- using click chemistry, an aptamer is immobilized and used as a platform for the **selective determination of antibiotic ampicillin** in real samples
- **detection limit of 1.36 nM** eight-fold lower than the European maximum residue limits in milk (4 µg L−1)
- the **storage stability of 4 weeks**, high selectivity among other antibiotics



Real sample detection. B) Voltammograms were recorded in different samples. C) Bar chart of the current response in different samples.

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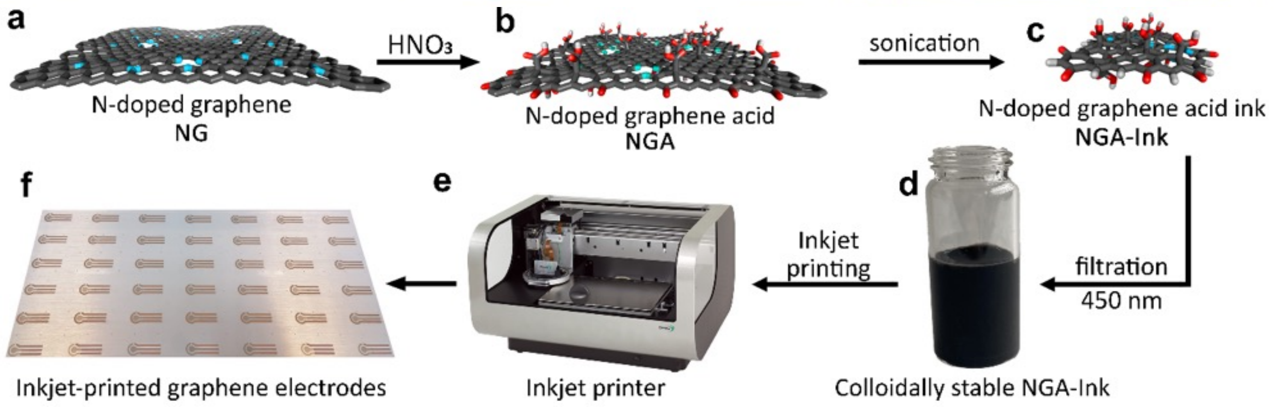
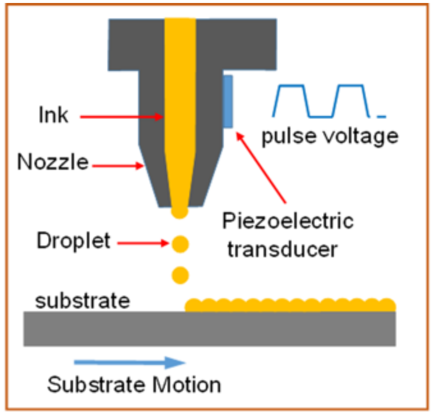
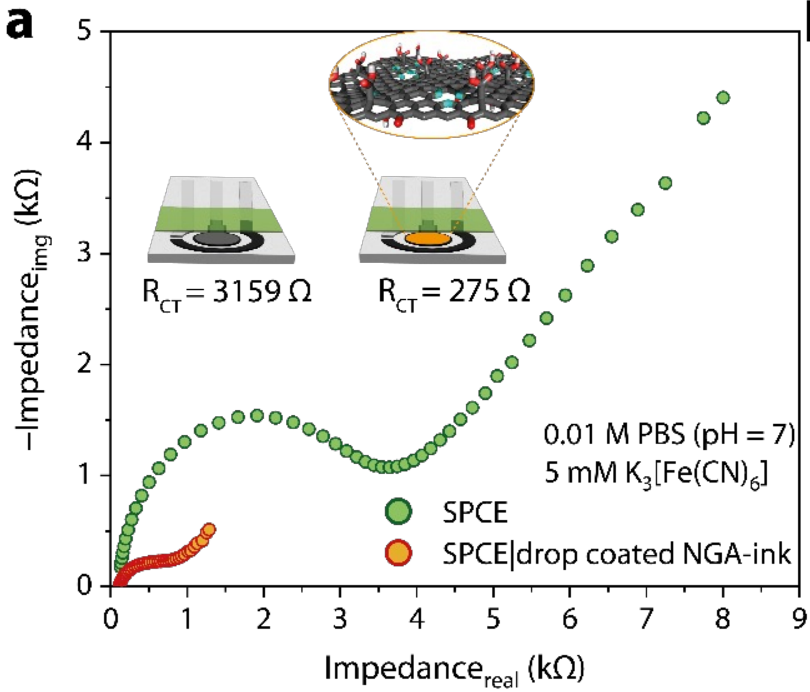
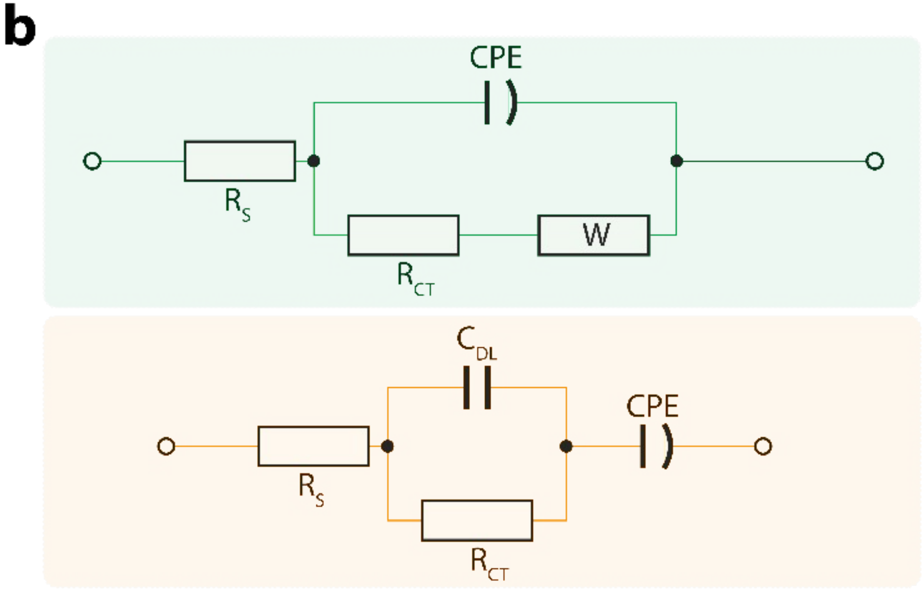
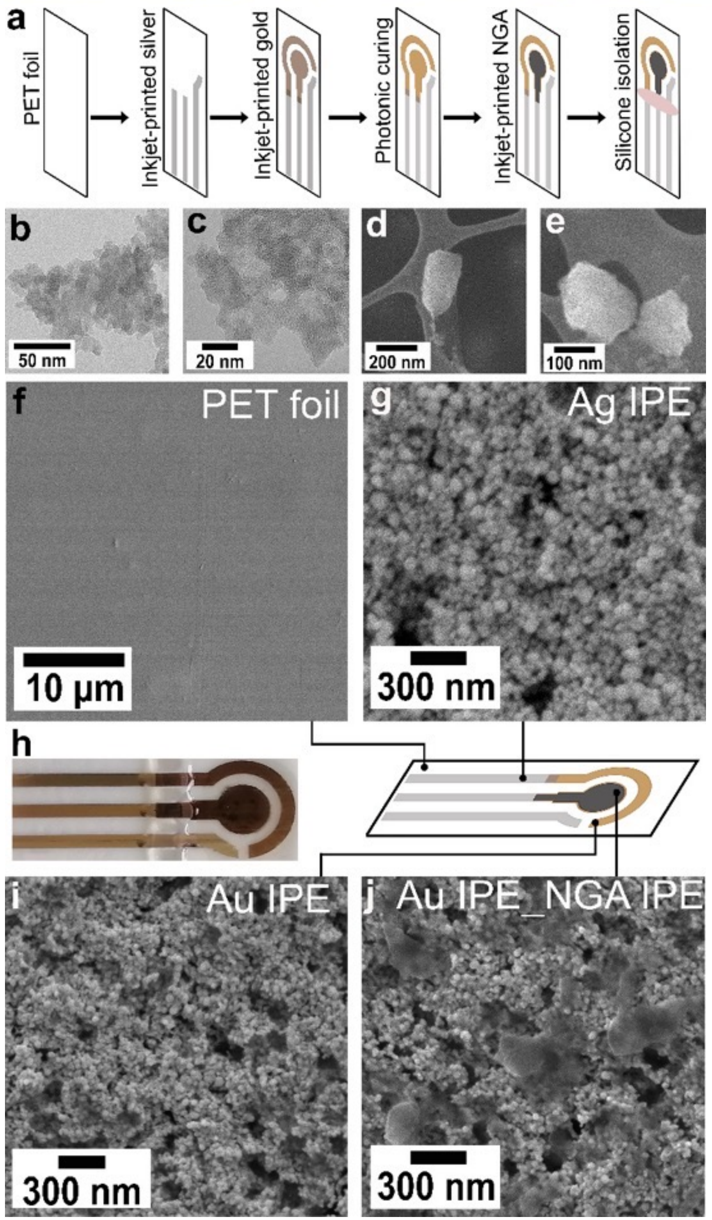
Biosensors – Inkjet Printing











Biosensors & Bioelectronics 256, 116277, 2024

Fluorograhene reacts at mild conditions

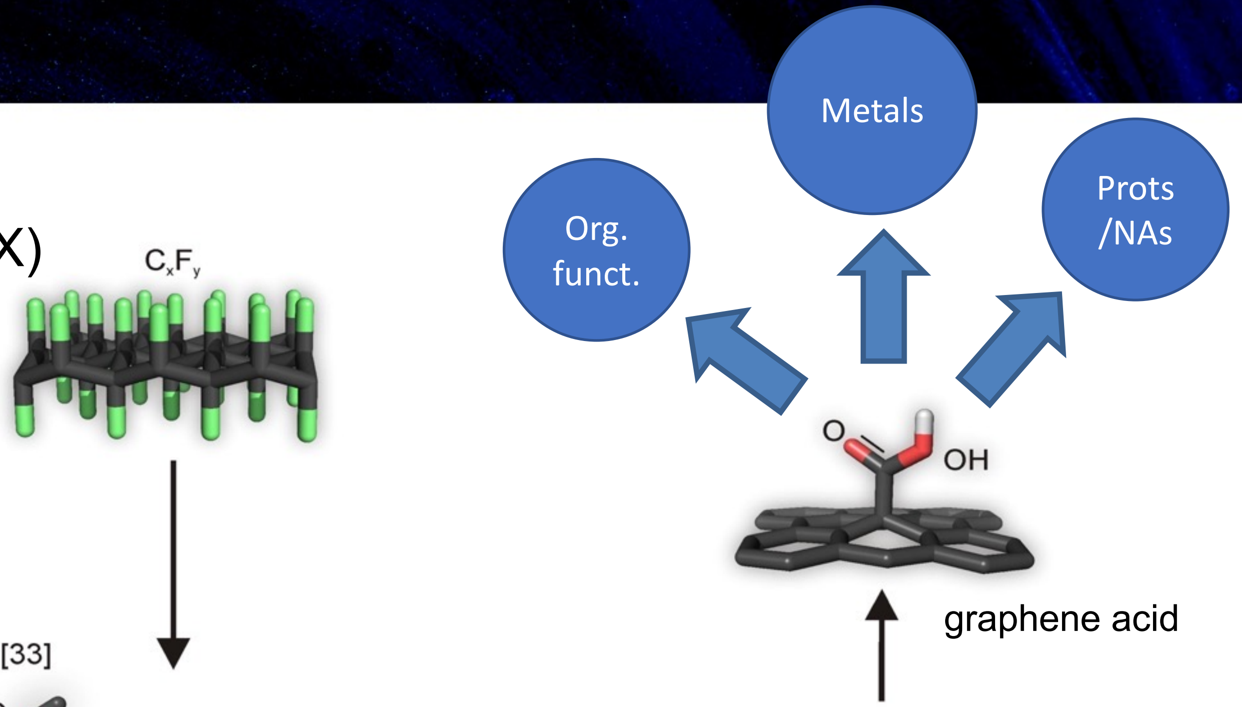
elimination (C_{sp3}-F → C_{sp2}) + substitution (C-F → C-X)

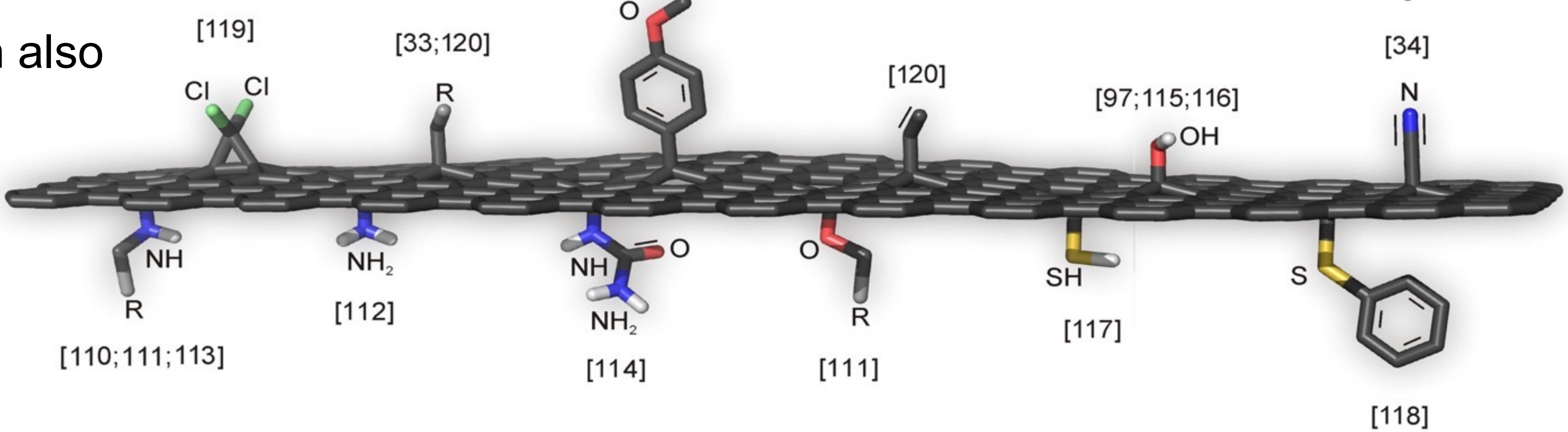
reaction is triggered by point defects, which behave like el-philes

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

dual functionalization is possible

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]

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Graphene derivatives based on fluorographene chemistry

FLUOROGRAPHENE

C-F

AMINES
GRIGNARD
CYANIDES
AMIDES
AZIDES
…

I. GENERATION
of
GRAPHENE
DERIVATIVES

C-X

CDI
CLICK CHEM

METAL IONS

II. GENERATION
of
GRAPHENE
DERIVATIVES

C-X-Y
C-X-M

Graphene derivatives based on fluorographene chemistry

FLUOROGRAPHENE

C-F

AMINES
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…

GRAPHENE ACID

CARBOXYLATED GRAPHENE

Graphene acid is a covalent graphene derivative bearing carboxyl groups on both sides of the graphene surface. It is well dispersible in water, making stable colloidal dispersions at low and high concentrations. Graphene acid behaves as a 2D carboxylic acid with pKa of 5.2, precipitating at pH below 5.2. The nanomaterial is conductive and well biocompatible.

QUICK FACTS

Form	Nanoflakes (dried powder or suspension)
Lateral size	~500 nm
Purity	Approx. atomic content in %: C 80, O 15, N 4, F 1 Fe <20 μg/g; Cu <10 μg/g; Ni <10 μg/g
pK_a	5.2
Zeta-Potential	-32 ± 5 mV (pH = 5.5)
Temperature stability	Up to 240 °C (inert atmosphere)
Sheet resistance	$6\,800\ \Omega \cdot sq^{-1}$
Dispersibility	water and polar solvents

KEY FEATURES

- Water dispersibility
- Conductivity
- Graphene surface decorated with -COOH groups
- High biocompatibility

APPLICATIONS

- Conductive support for enzyme (electro)catalysis (ACS Appl. Mater. Interfaces, 12, 250-259, 2020)
- Carbocatalysis (metal free catalysis) (Chem. Sci., 10, 9438-9445, 2019)
- Arene CH insertion (Carbon, 143, 318-328, 2019)
- Electrochemical sensing (ChemElectroChem, 6, 229-234, 2019)
- Hydrogen peroxide electrochemical sensing (ACS Omega, 4, 19944-19952, 2019)
- Metal ions sorption (ACS Nano, 15, 3349-3358, 2021)
- Gas sensing (J. Mater. Chem. A, 9, 17434-17441, 2021)
- Genosensing (Biosens. Bioelectron., 195, 113628, 2022)
- Lithium-ion batteries (Adv. Energy Mat., 12, 2103010, 2022)

SALES INFO

Package available
Powder – 50 mg, 100 mg, 1 g, 5 g, 10 g
Dispersion – 1 ml, 5 ml, 10 ml, 50 ml

+420 585 631 447
sales@graphene-derivates.com
graphene-derivates.com

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METAL IONS

II. GENERATION
of
GRAPHENE
DERIVATIVES

C-X-Y
C-X-M

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Applications explored in our labs for graphene-derivatives

erc erc erc erc

Environment
Detox-monitoring

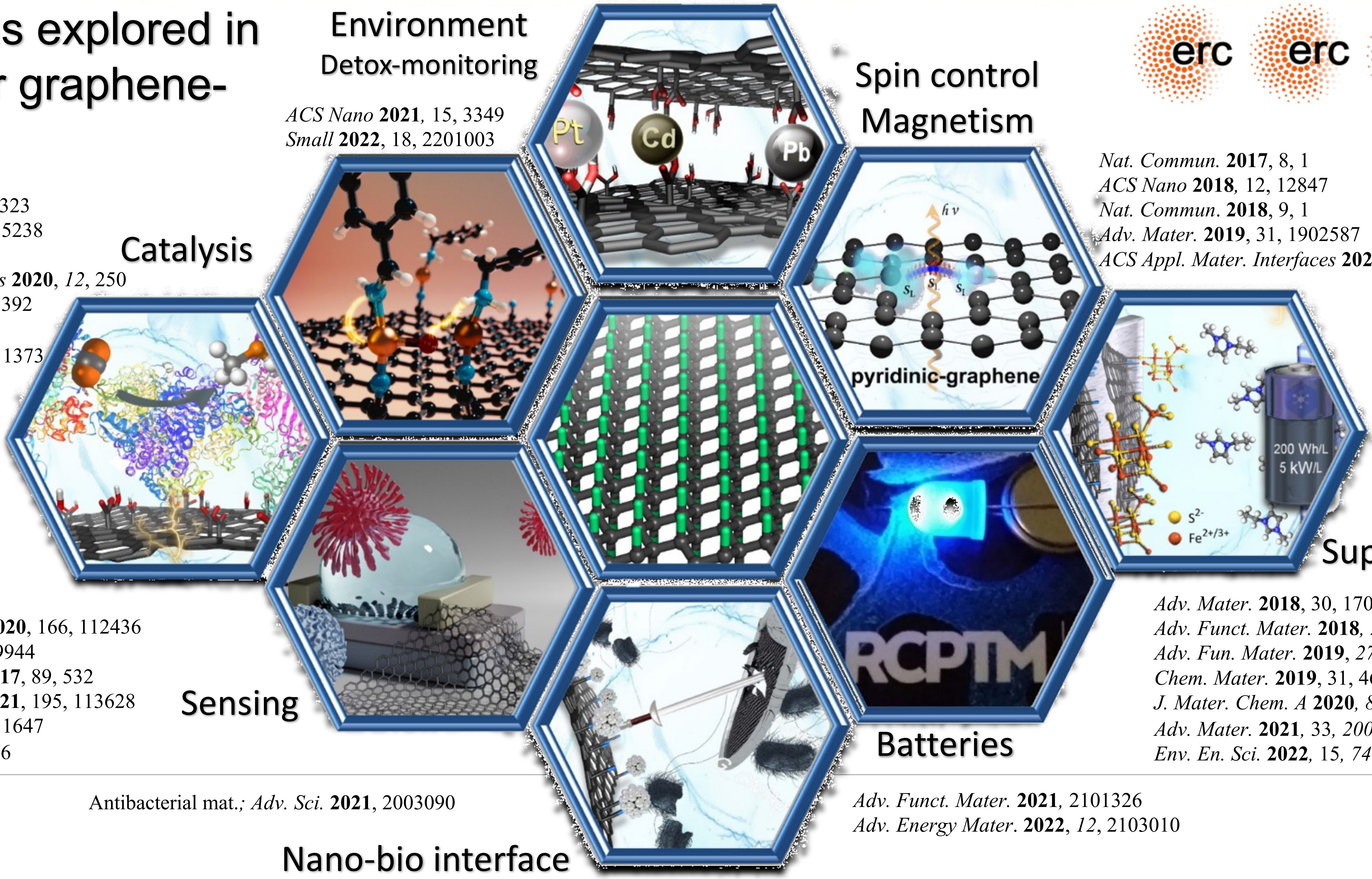
ACS Nano **2021**, 15, 3349
Small **2022**, 18, 2201003

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

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**, 19, 2207216

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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Petr Lazar
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Rostislav Langer
Michal Langer

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European Research Council

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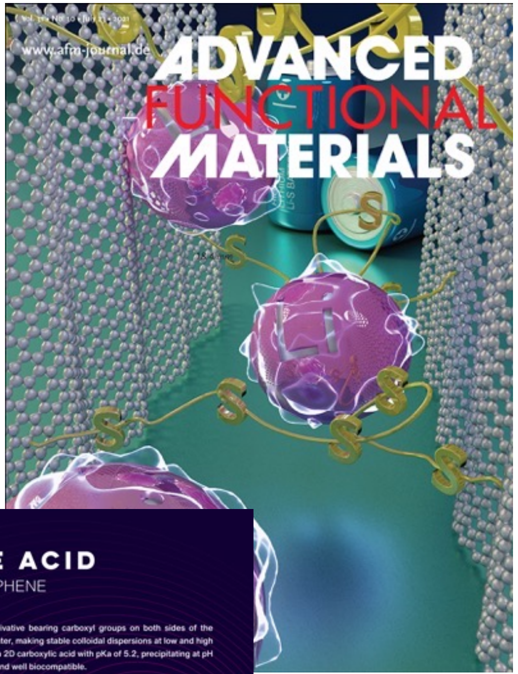
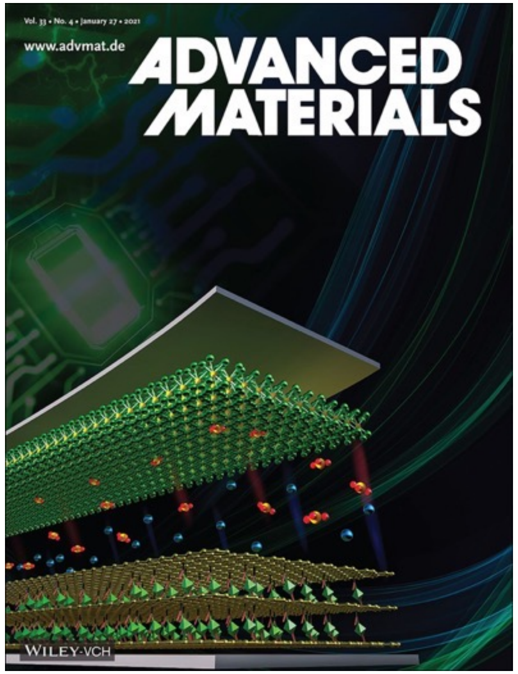
SUSNANO
SUSTAINABLE NANOSENSORS





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Contact: michal.otyepka@upol.cz