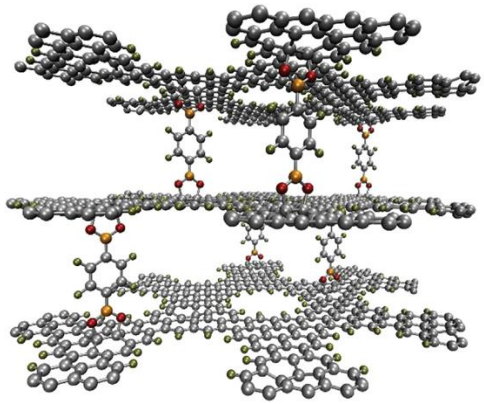
CHALMERS
UNIVERSITY OF TECHNOLOGY

Battery, supercapacitor, hydrogen storage



Graphene functionalization and composites

-Methods/Synthesis
-Properties
-Applications

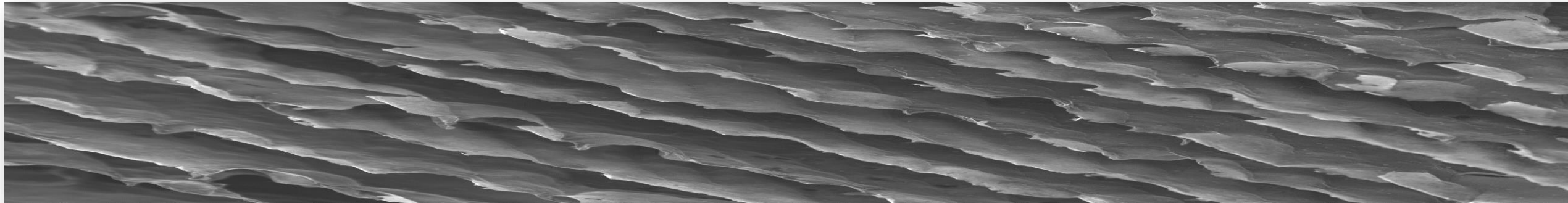
Associate Prof. Jinhua Sun

Department of Industrial and Materials Science

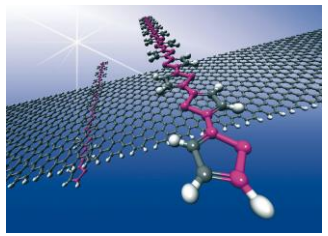
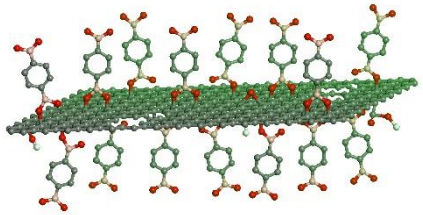
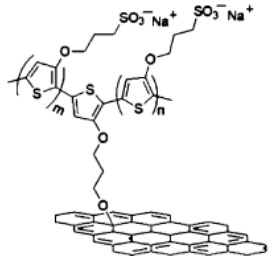
Chalmers university of Technology

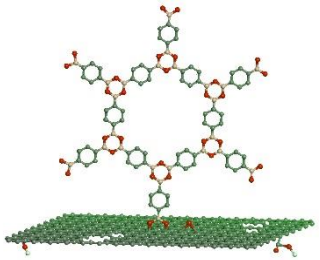
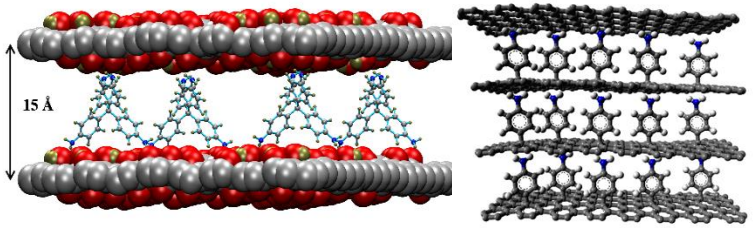
jinhua@chalmers.se

2025-06-17

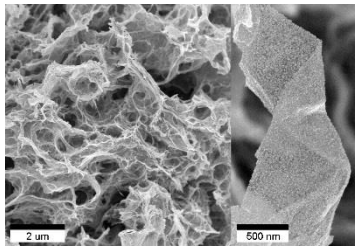


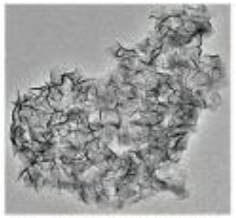
✓ **Chemistry of Graphene:** Surface modification and functionalization

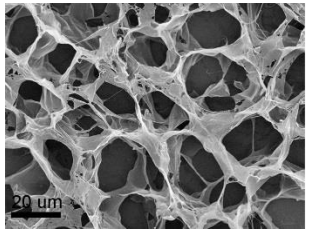




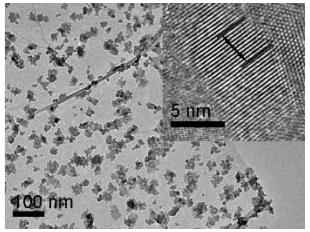



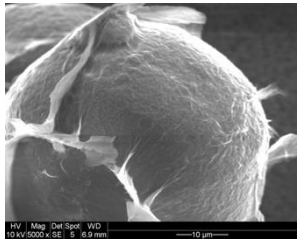
✓ **Graphene based composites:** design, synthesis, structure control, properties



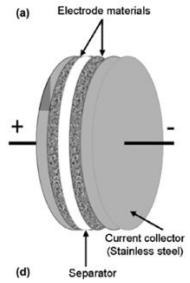


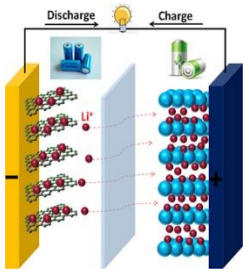


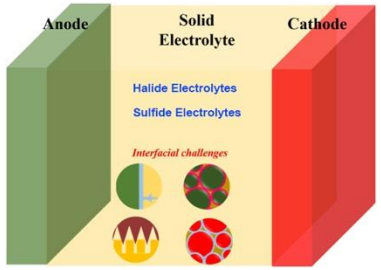


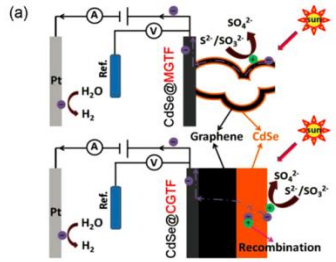


✓ **Energy related applications:** Catalysis, Supercapacitors, Li-/Na-ions battery, Li-sulfur battery, sensor









✓ **Industrial application:** 3d printing, coating, gas barrier, anti-corrosion




J. Mater. Chem., **2012**, 22, 18879
Chem. Commun., **2013**, 49, 5538
J. Mater. Chem. A, **2014**, 2, 5060
Adv. Funct. Mater. **2015**, 25, 4334
Chem. Mater. **2015**, 27, 4594
ACS Appl. Mater. Interfaces, **2016**, 8, 11711
Nature Commun. **2016**, 7, 10601
Carbon **2017**, 120, 145
Nanotechnology, **2017**, 28, 395404
Nanoscale, **2018**, 10, 21386
Angew. Chem. Int. Ed. **2018**, 57, 1034
APL Materials **2019**, 7, 020904
Angew. Chem. Int. Ed. **2019**
Science advances, **2021**

The research group

Research focus:

1) Design and synthesis of graphene based electrode materials and binders for Lithium-ion battery and future batteries.
2) Lithium-ion battery, Sodium ion battery, Li-S battery, Aqueous rechargeable battery.
3) Sensors for better battery management.
4) Advanced characterizations to understand the energy storage mechanism.
5) Development of advanced electrode processing and battery manufacturing technologies.

Research team:

- **4 Postdoc.**
- **5 PhD students**
- **Several Master students**

Labs and equipment

Labs and Equipment related to battery research

- Pouch cell
- Coin cell
- Swagelok cell
- In situ cell

Chemistry lab
Glove box

Materials synthesis

High speed centrifuge

Electrode preparation

Electrode coating

Heat roller press machine

4-Probe Station

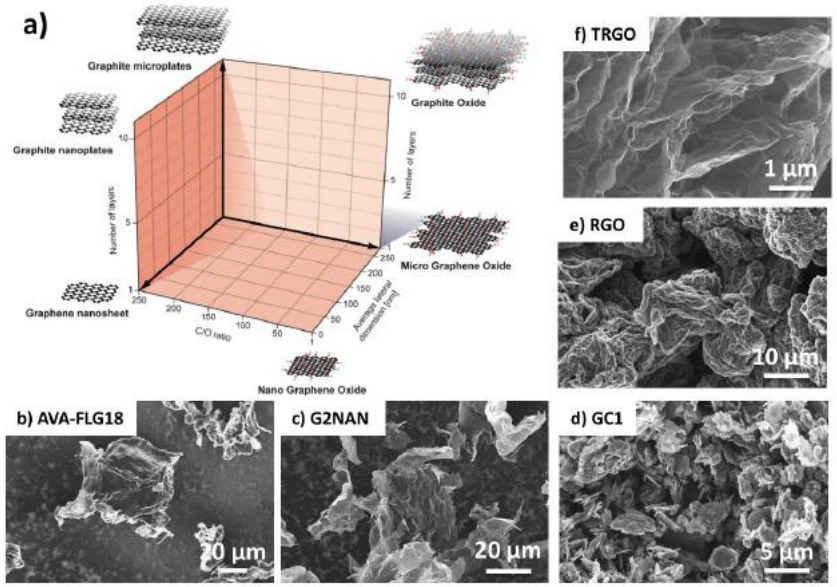
Battery characterizations ~200 channels

Biologic SP-300 Potentiostat

Biologic BCS-805 battery cycler

Commercial graphene in the market

Benchmarking of graphene-based materials



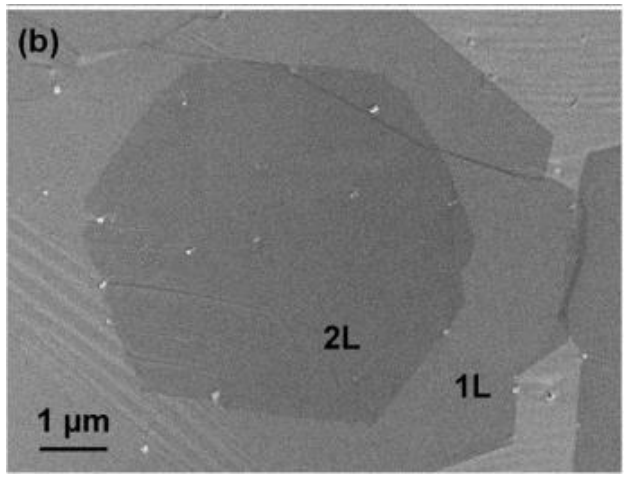
- Full characterizations
- Structure-property relationship
- Select the right graphene

Table 1. Summary of GRM properties measured using different techniques. Data reported by each GRM producer are also shown.

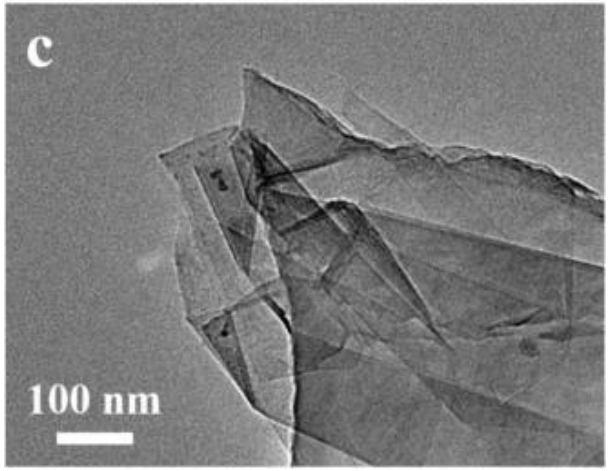
GRM commercial name	SSA ($m^2\ g^{-1}$)	SSA reported by producer	% oxygen (from XPS)	$\%sp^2$	Average bulk density ($mg\ ml^{-1}$)	Producer
Elicarb materials grade	10 ± 1	40	4.3 ± 0.5	96.3 ± 0.9	214 ± 1	Thomas Swan
AVA-FLG 18	22 ± 4	n.a.	1.7 ± 0.3	98.0 ± 0.9	44 ± 1	Avanzare
G2NAN	30 ± 3	30	2.1 ± 0.5	96.5 ± 0.9	18 ± 1	Nanesa
GC1	83 ± 5	60	3.6 ± 0.4	96.9 ± 0.9	126 ± 2	Graphene supermarket
XGnP M15	113 ± 10	135	4.0 ± 0.5	97.0 ± 0.9	55 ± 1	XG Science
Graphenit-OX	132 ± 10	n.a.	2.9 ± 0.4	95.1 ± 0.9	301 ± 1	Nanoinnova
AVA-FLG 23	190 ± 4	n.a.	4.2 ± 0.5	90.9 ± 0.9	12 ± 1	Avanzare
SE1430	195 ± 5	215	11.9 ± 0.5	77.8 ± 0.9	43 ± 1	Sixth element
SE1231	234 ± 5	170	2.8 ± 0.3	89.6 ± 0.9	39 ± 1	Sixth element
RGO	486 ± 35	461	14.2 ± 0.5	57.8 ± 0.9	—	Graphenea
XGnP C750	745 ± 50	750	6.3 ± 0.5	85.0 ± 0.9	207 ± 2	Xg Science
TRGO	1154 ± 30	n.a.	8.5 ± 0.5	86.1 ± 0.9	6 ± 1	Universitat Freiburg

A. Kovtun, V. Palermo, et al, *2D Mater.* **2019**, 6, 025006

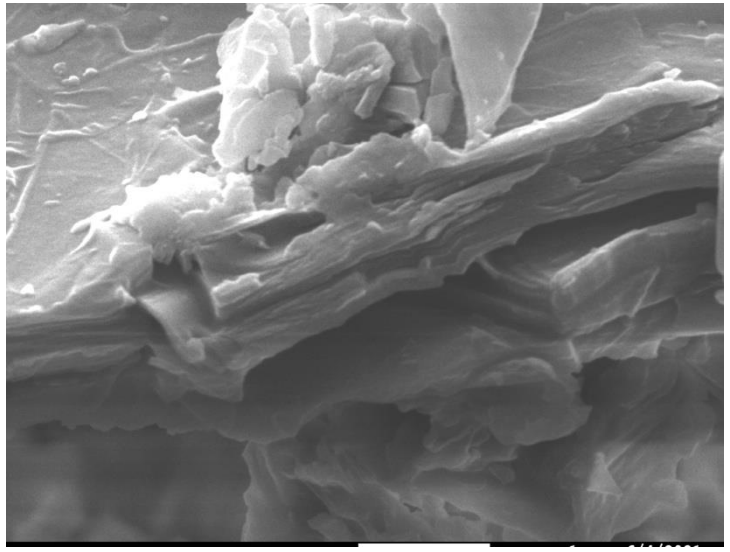
Different graphene used in metal reinforcement



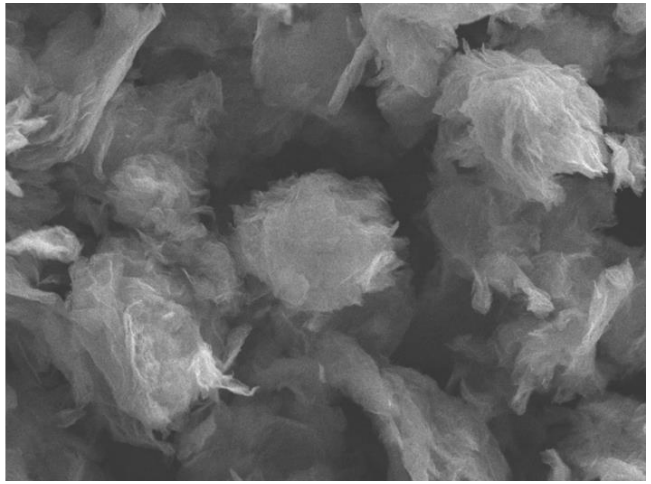
CVD graphene



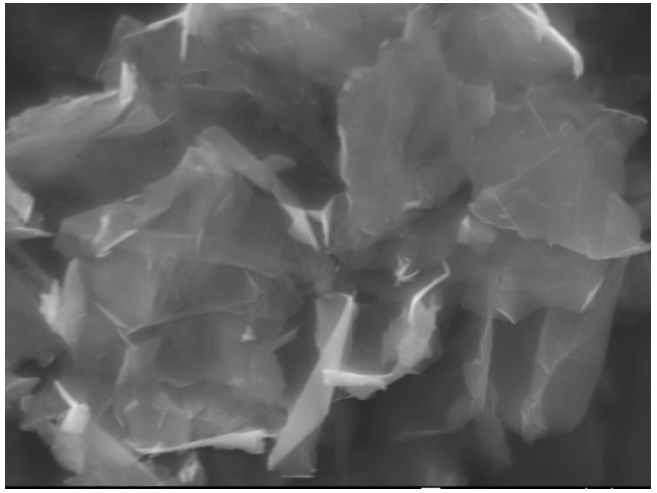
multilayer graphene
graphite nanoplatelet



Graphite oxide/Graphene oxide



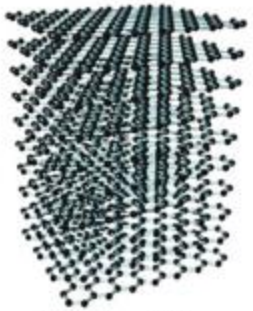
Reduced graphene oxide particles



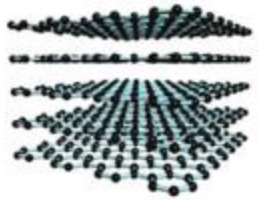
Mechanically exfoliated graphene

Possible applications

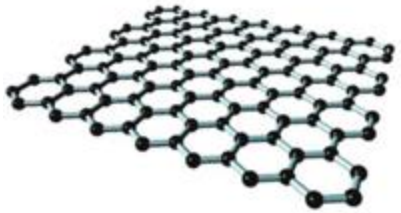
Selection of right graphene



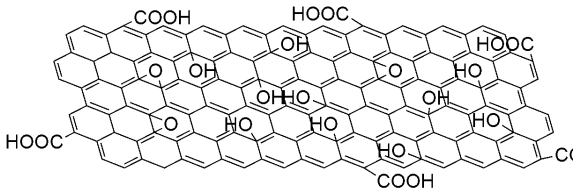
(C) Graphite



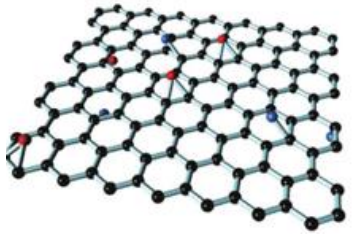
(B) Few-layer graphene



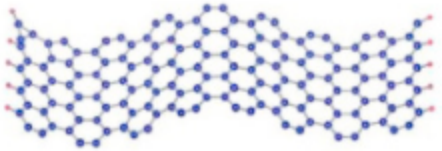
(A) Graphene



Graphene oxide



(D) Reduced graphene oxide (rGO)

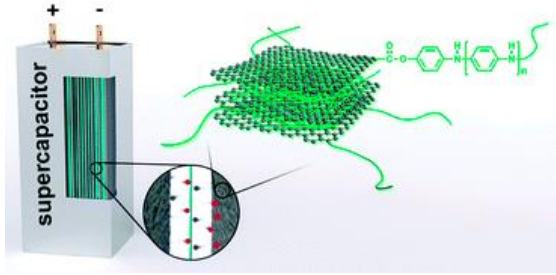


Graphene nanoribbon

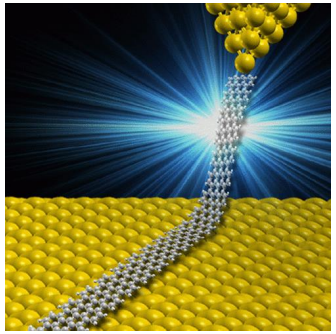
Graphene/polymer

electronics

Membrane



Energy storage

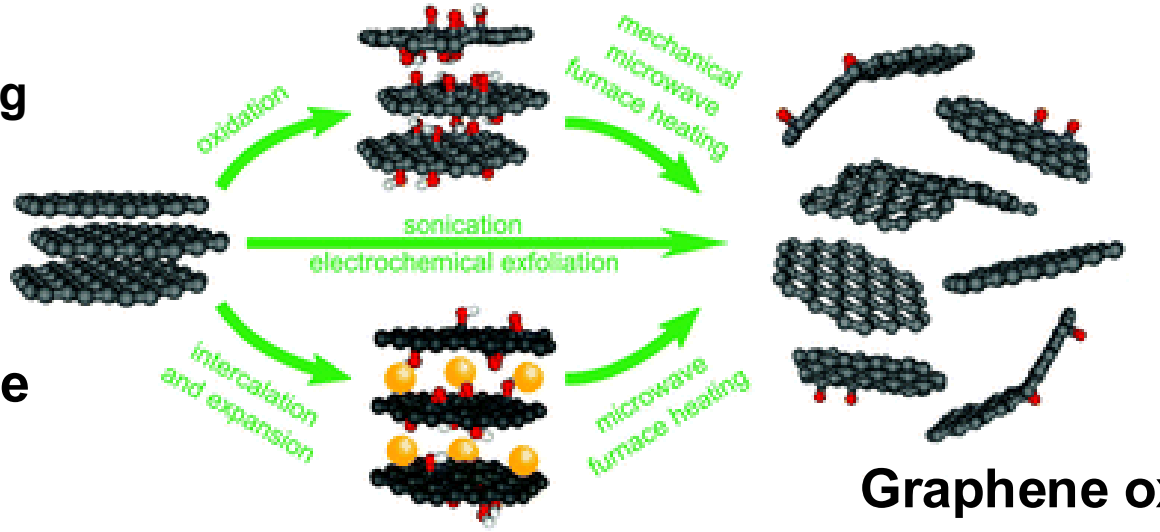


Transistor

Exfoliation and restacking of graphene

AB stacking

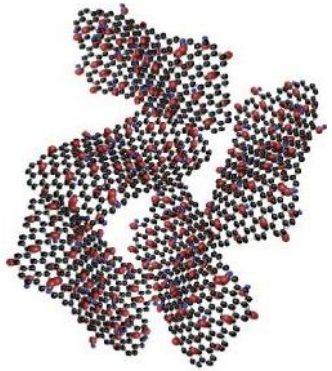
Graphite



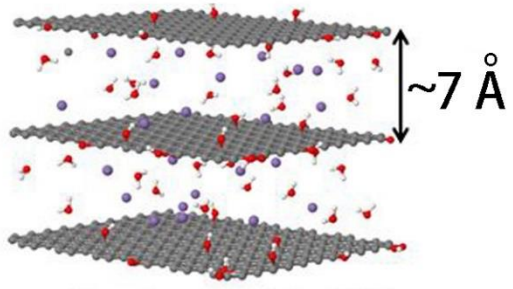
Graphene oxide (GO)

- Water dispersible
- Single layer
- Easy process
- Self-assembling

Radom structure



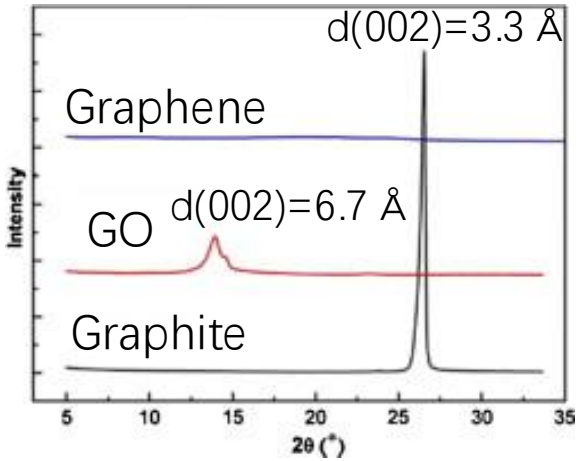
Aligned structure



GO

- **Interlayer structure**
- **Surface chemistry**

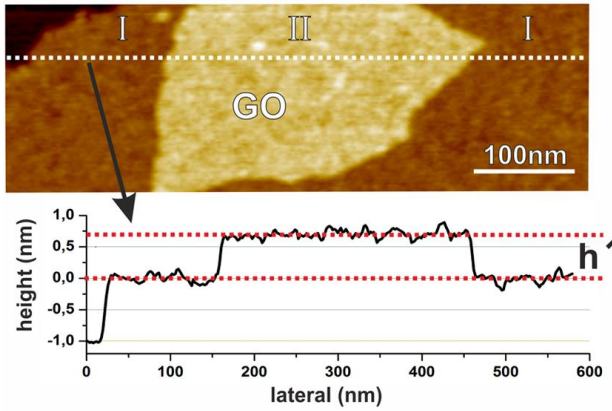
Interlayer distance



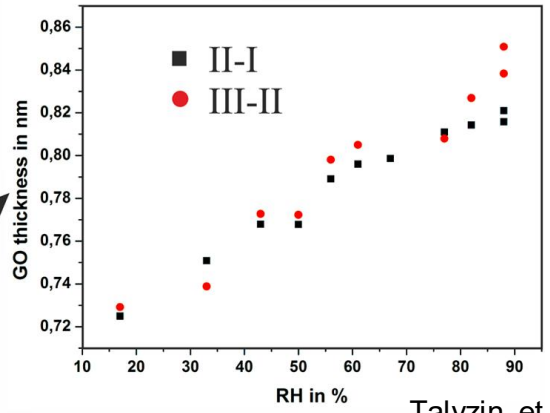
Control of interlayer distance

Intercalation of solvent molecules

Scanning force microscopy (SFM)



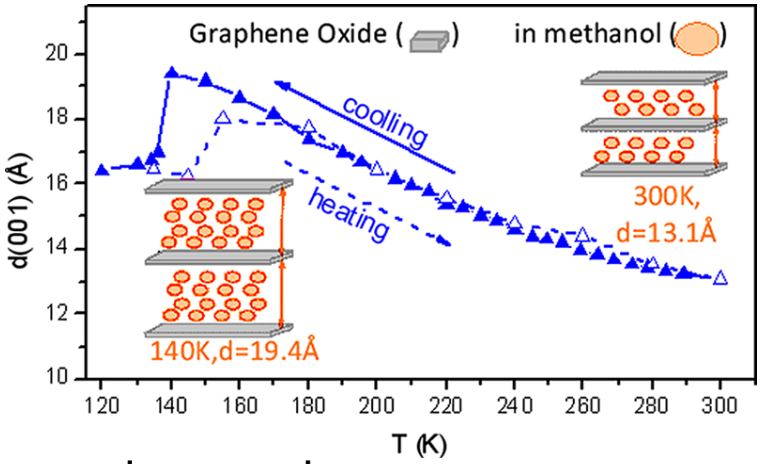
Water: 12 Å



Swell in water

Talyzin, et al., ACS Nano **2013**, 7, 1395

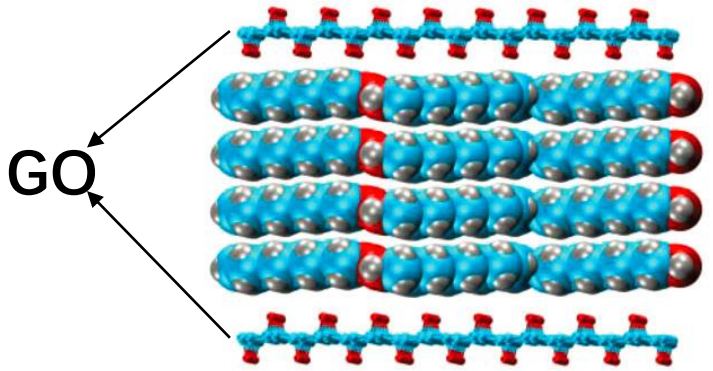
Methanol: 19.4 Å



Negative thermal expansion

Talyzin et. al., Nano Lett. **2014**, 14, 3993

1-octanol: 28.0 Å upon cooling



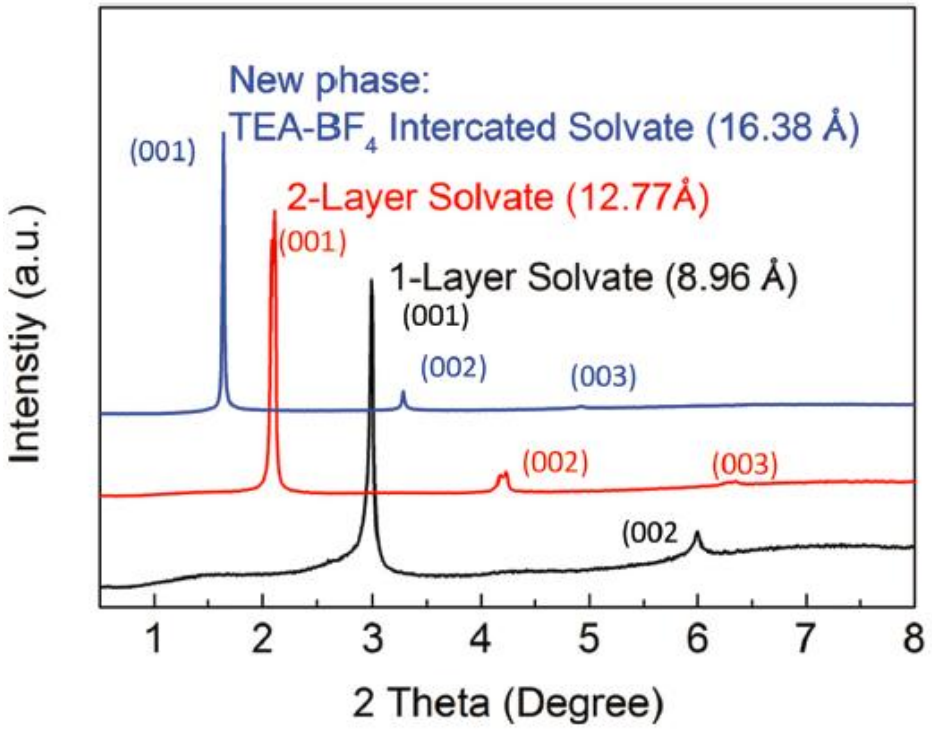
ca. -60 °C

4 layers 1-octanol

Talyzin, Sun. et al., Nanoscale, **2017**, 9, 6929

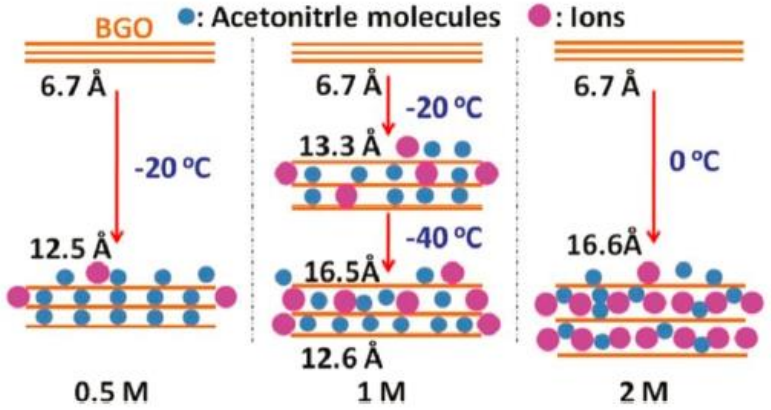
Control of interlayer distance

◆ Intercalation of ions

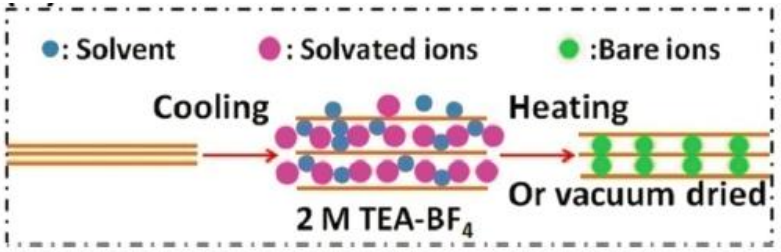


XRD patterns representing three different phases of BGO immersed in electrolytes with different concentrations

Tetraethylammonium Tetrafluoroborate (TEA-BF) in acetonitrile



Temperature- and concentration dependent intercalation of solvated $TEA\text{-}BF_4$ ions into BGO.



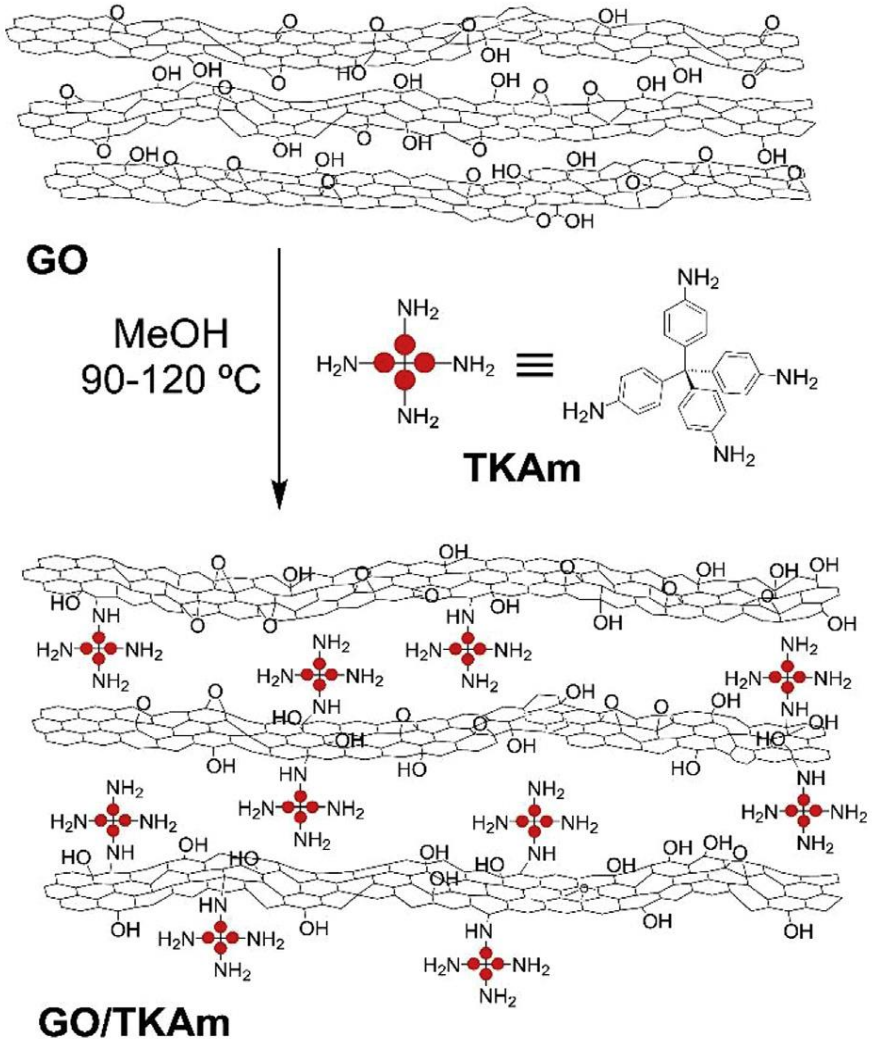
Intercalation of TEA-BF4 electrolyte ions into the BGO interlayer space

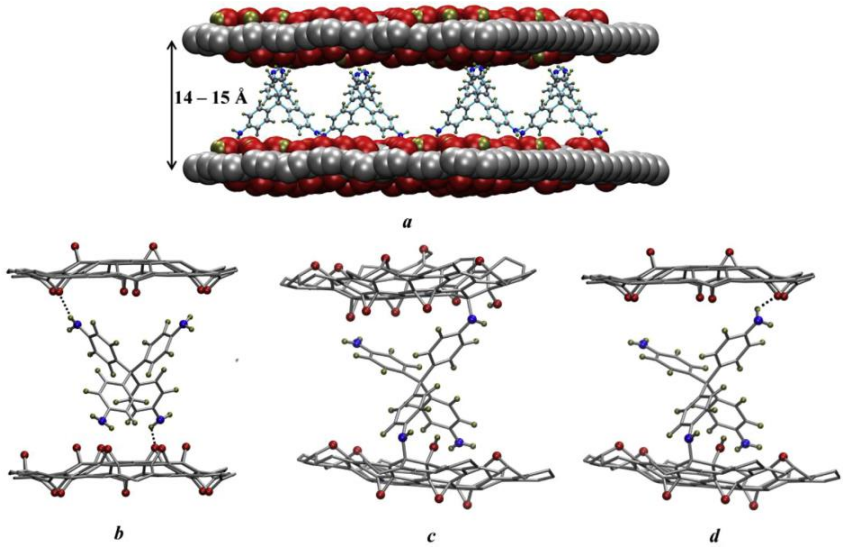
Temperature- and concentration dependent intercalation

Sun. et al., Nanoscale, **2018**, 10, 21386

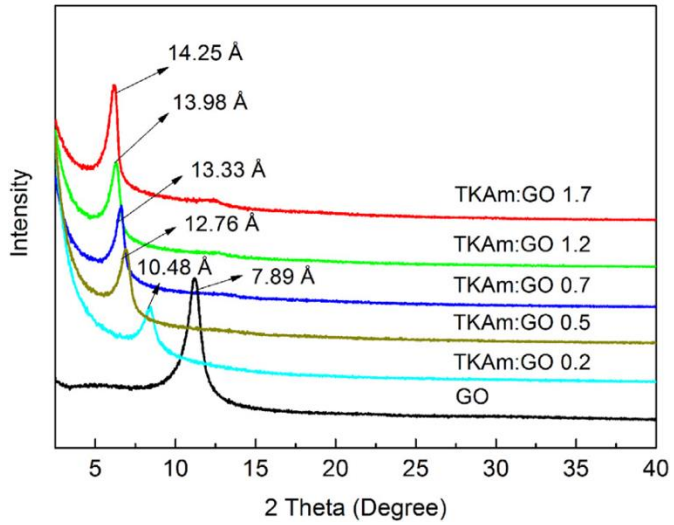
GO pillared with tetrapod-shaped molecules

Tetrakis(4-aminophenyl)methane (TKAm)





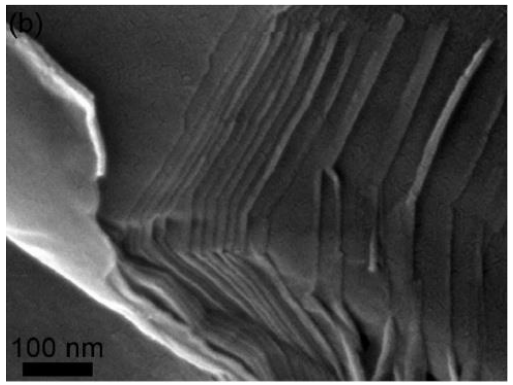
A model of the pillared GO/TKAm structure



XRD of TKAm:GO with variation of loading TKAm:GO.

- **Rigid structure**
- **3D structure**
- **Steric effect**
- **Controllable distance**

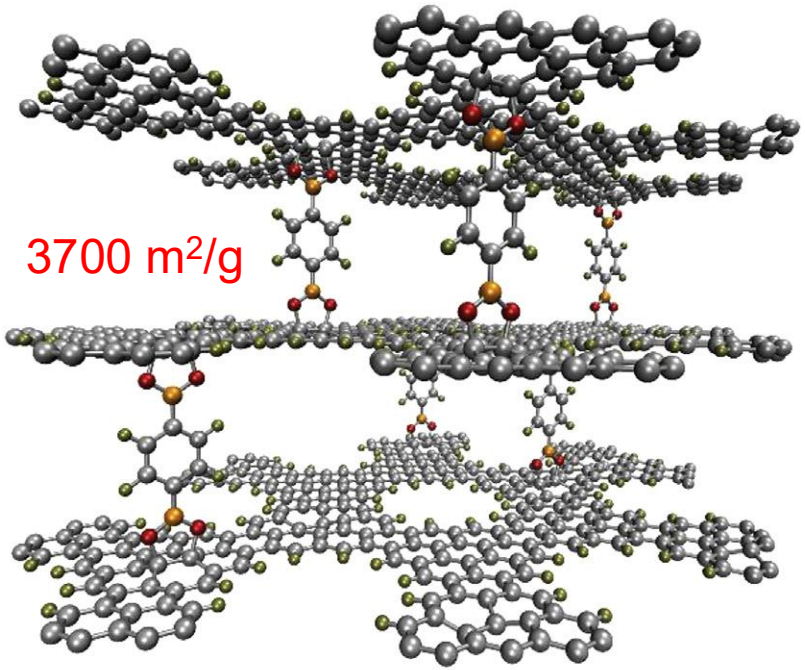
Surface area: 700 m^2/g

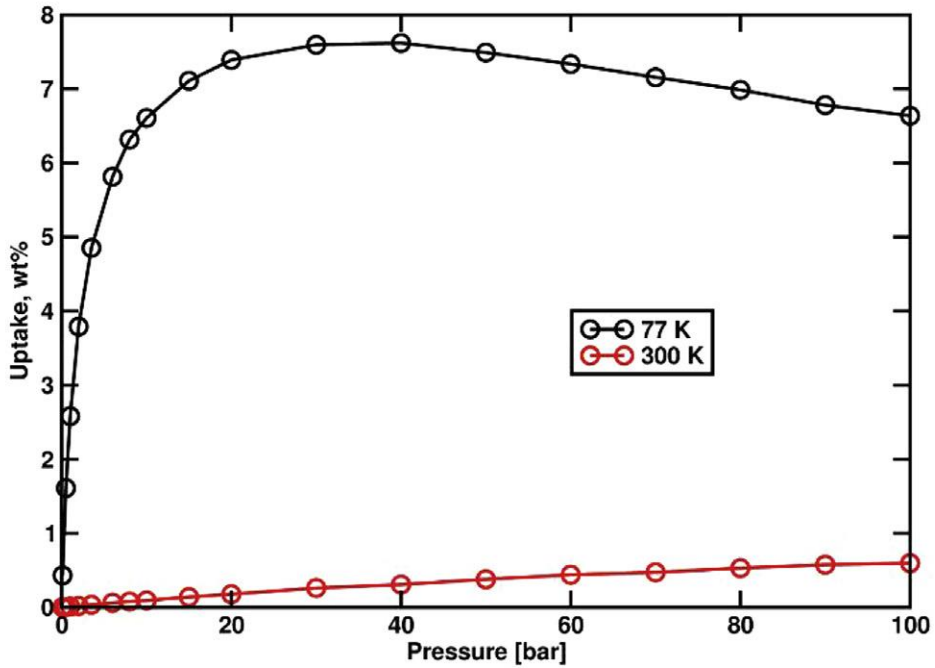


Sun. et al., Carbon **2017**, 120, 145

Pillared graphene for energy storage

The surface area is about 700 m^2/g, higher than most of other reported pillared graphene

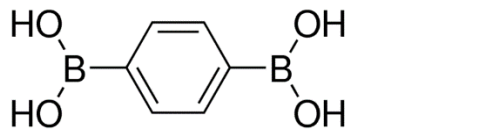




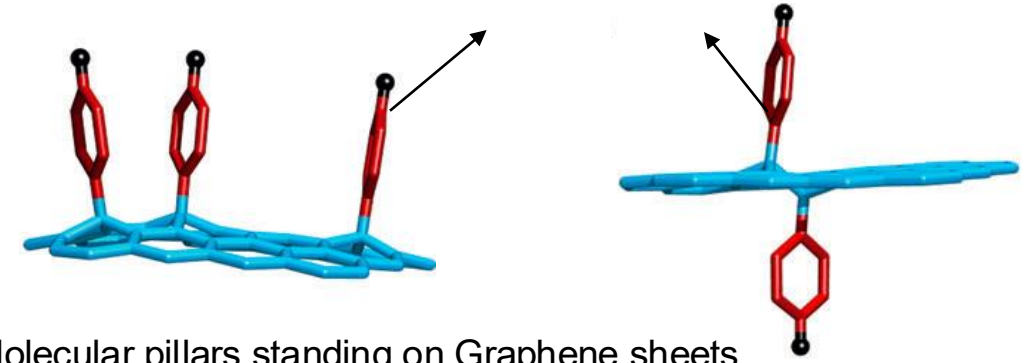
A structural model of pillared perforated GO with surface area of 3700 m^2/g and simulated hydrogen adsorption isotherms.

Molecular pillars on graphene oxide

DBA molecular pillars

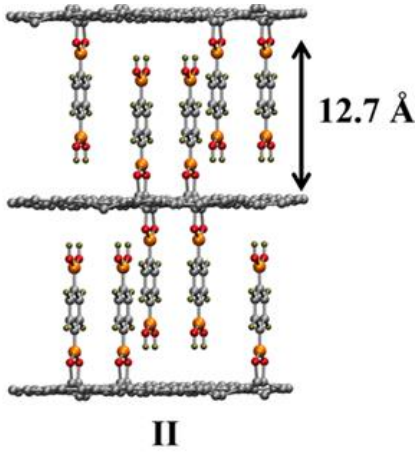


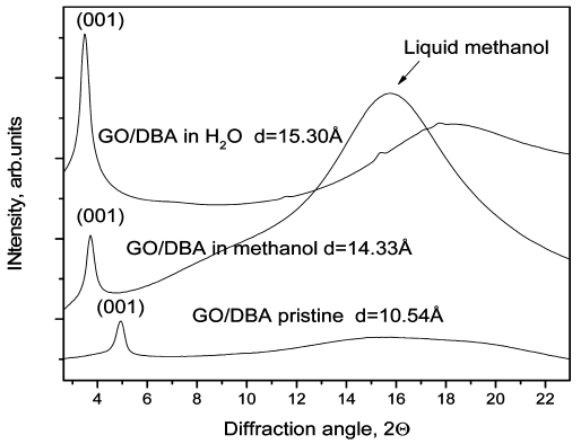
Benzene-1,4-diboronic acid (DBA)



Molecular pillars standing on Graphene sheets

Evidence of only one side of DBA grafted on GO





Interlayer distance of GO/DBA:

1. In air :10.54 Å
2. In methanol: 14.33 Å
3. In water: 15.30 Å

The pristine state is recovered after solvent evaporation at ambient temperature.

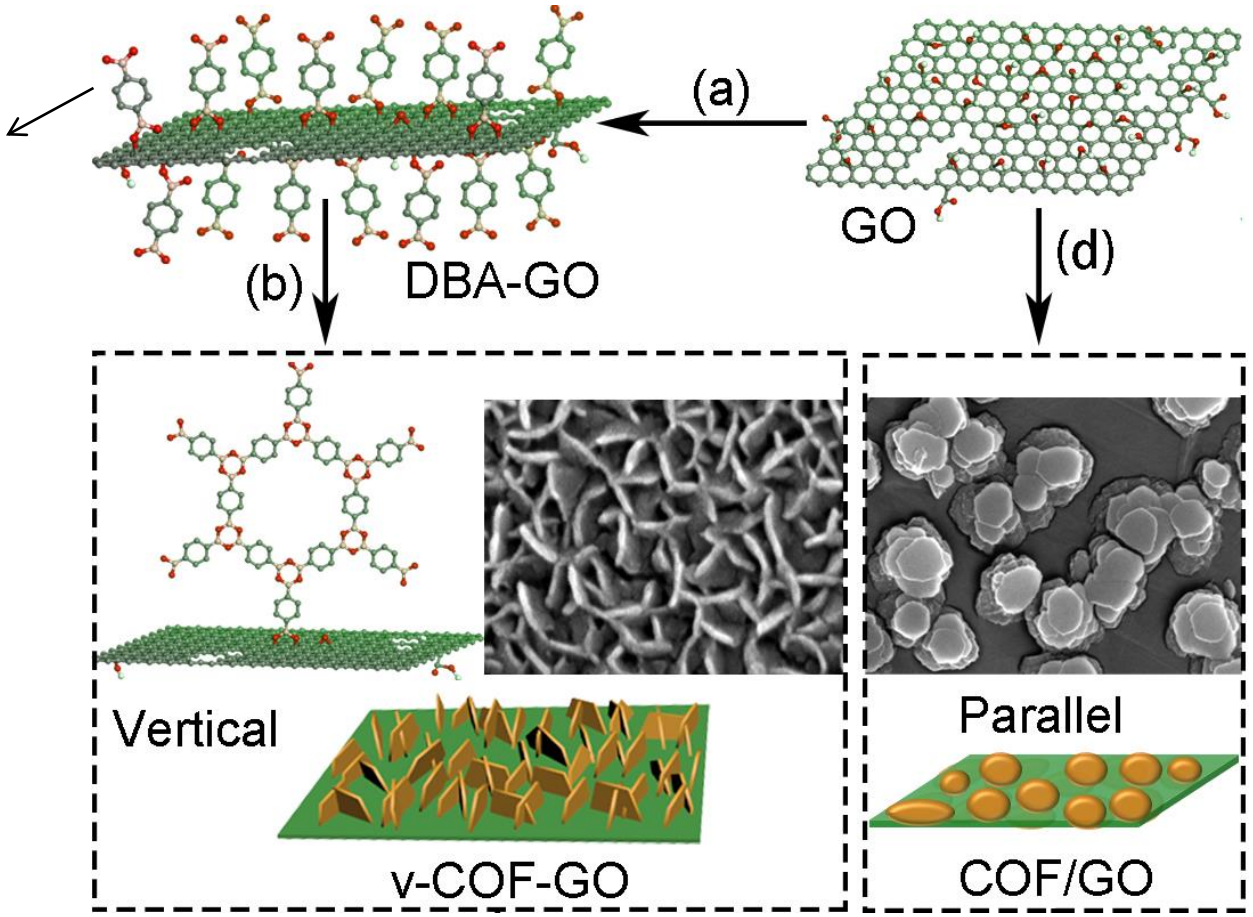
J. Phys. Chem. C **2015**, 119, 27179

Molecular pillar approach to grow vertical COF on graphene

Highlight of this work: **Control the orientation of COF on the surface of graphene**

Molecular pillars

Covalent organic framework (COF)



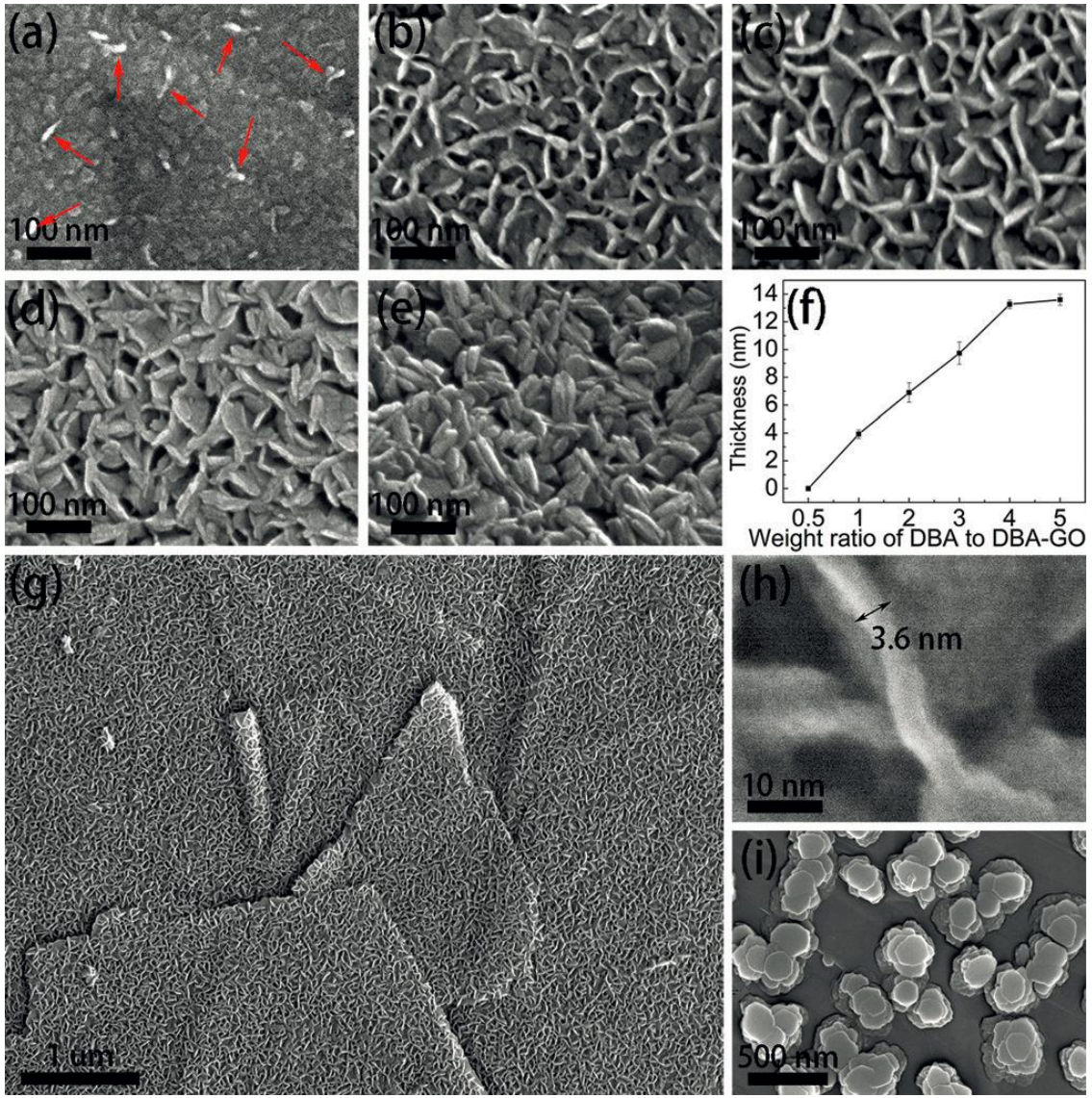
Growth of vertical COF-1 nanosheets using DBA as molecular nucleation sites grafted on GO

Sun. et al., Angew. Chem. Int. Ed. **2018**, 57, 1034 –1038

Morphology of vertical COF on graphene

Controllable:

1. **Thickness**
2. **Density**



Thickness:
from 3nm to 15nm

Uniform distribution of orientated COF on graphene nanosheet

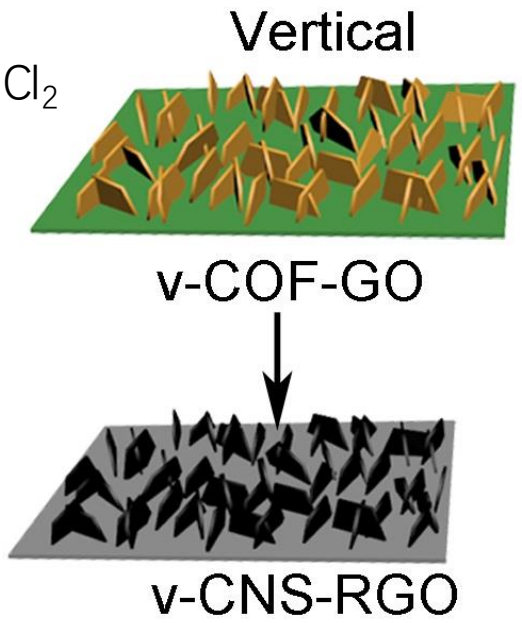
Random
COF platelets

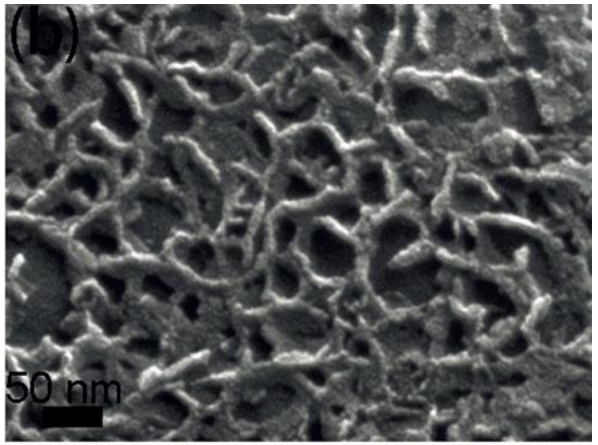
Morphology control of vertical porous carbon nanosheet

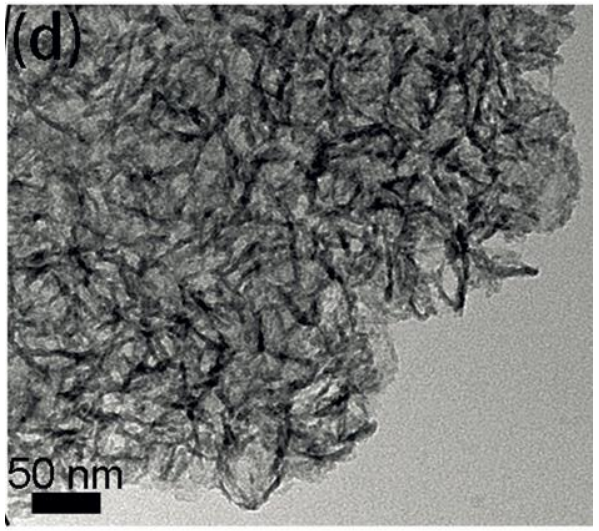
Vertical porous carbon nanosheet on Graphene

Vertical COF ⟶ Vertical porous Carbon

Molten salt method Using $ZnCl_2$

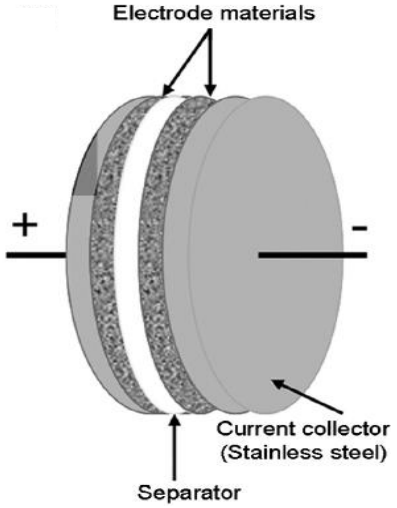




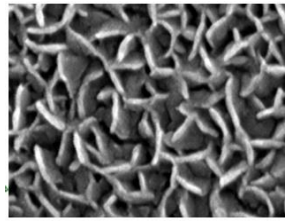


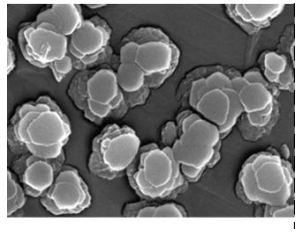
Application: Supercapacitors

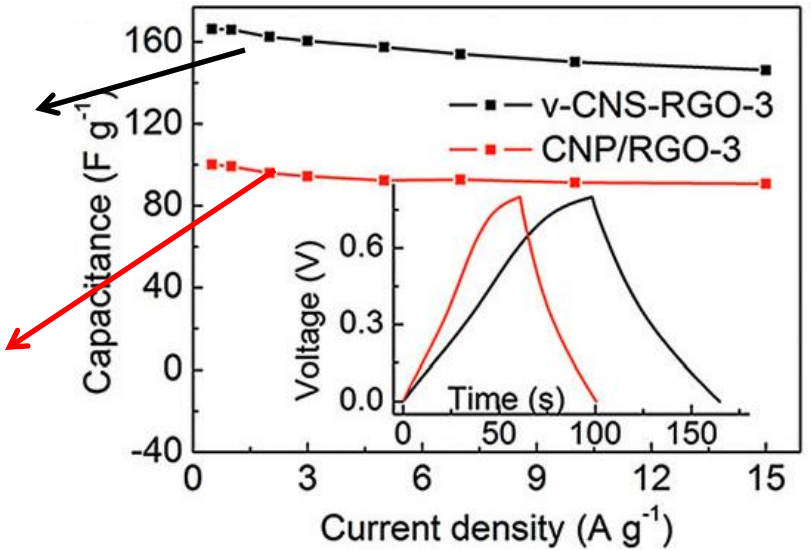
- Porous structure
- High surface area
- High conductivity
- Unique structure

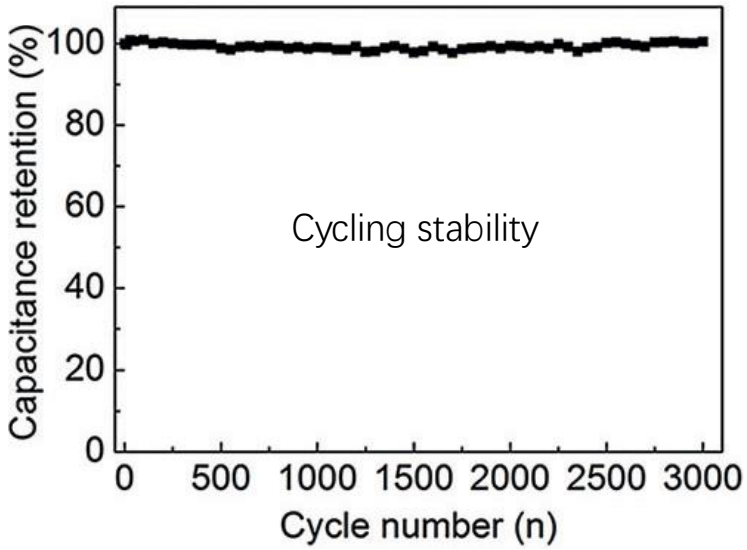


Electrons transfer from carbon nanosheet to high conductive graphene



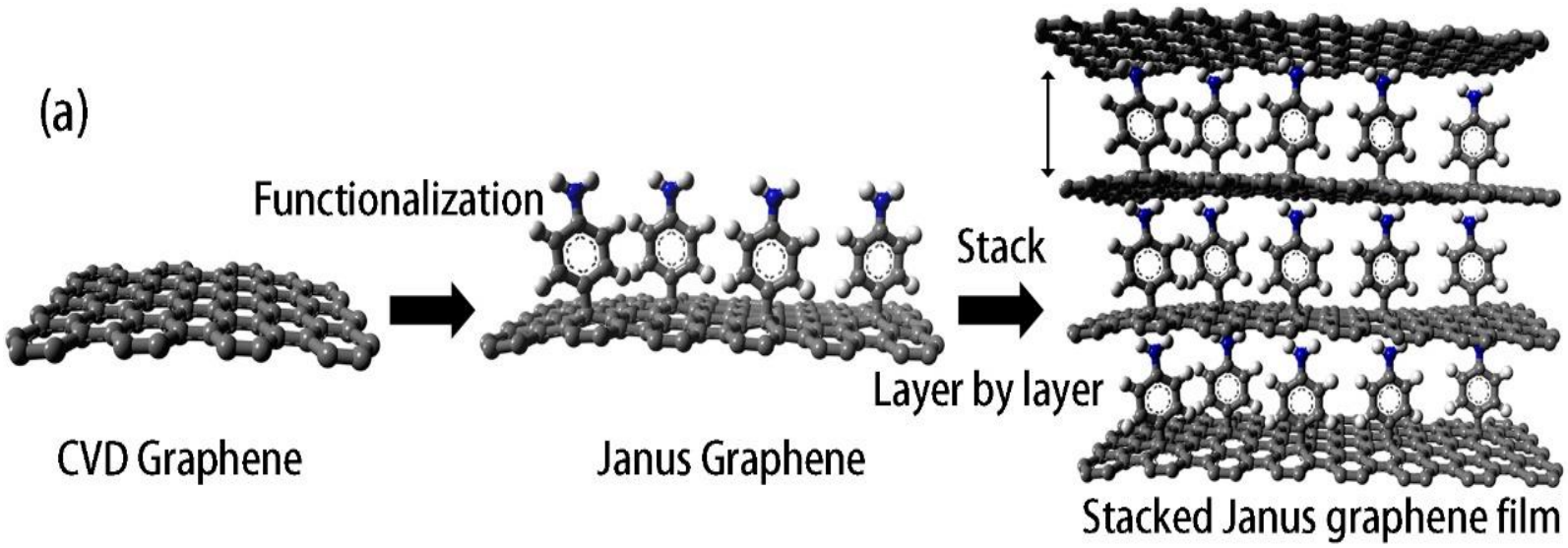


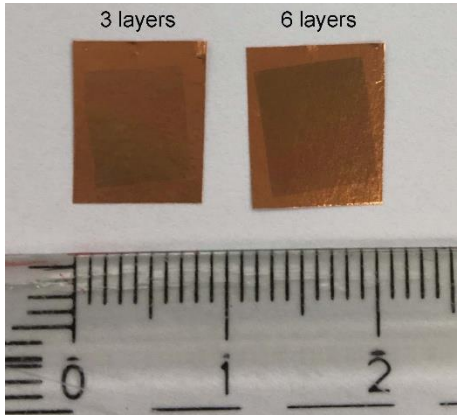




Janus graphene for sodium ion battery

Janus graphene: asymmetric functionalization

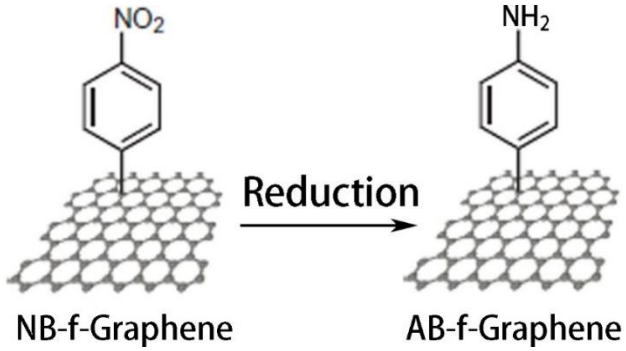


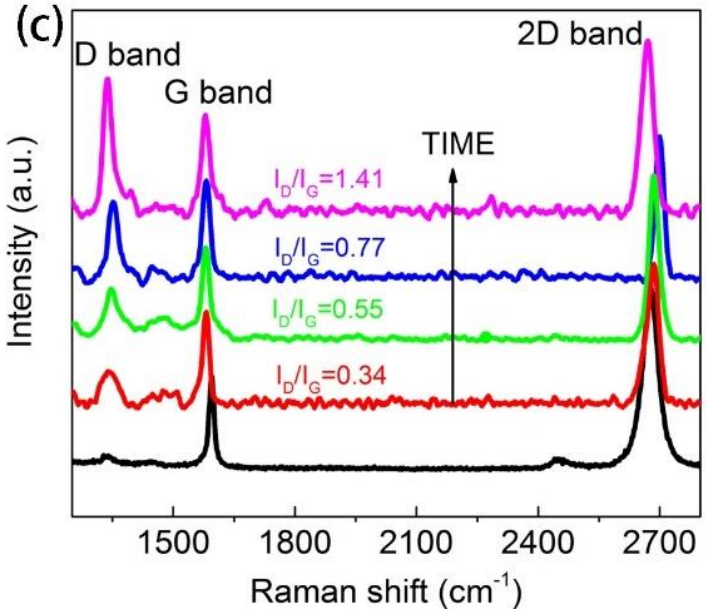


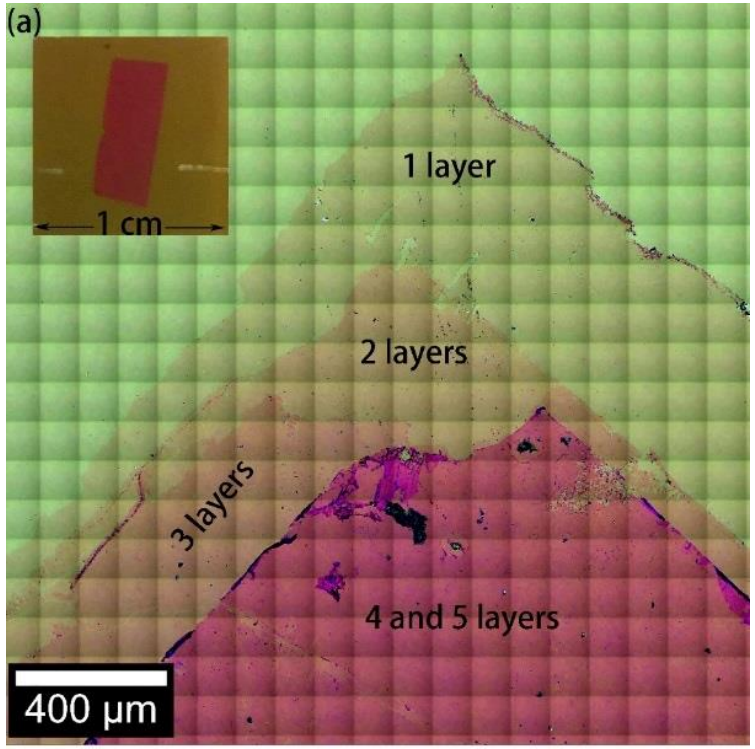
- **Vertical molecules**
- **Covalent bond**
- **Variable chemical groups**
- **Controlled density**

Sun. et al., ***Sci. Adv.*** **2021**, 7, eabf0812

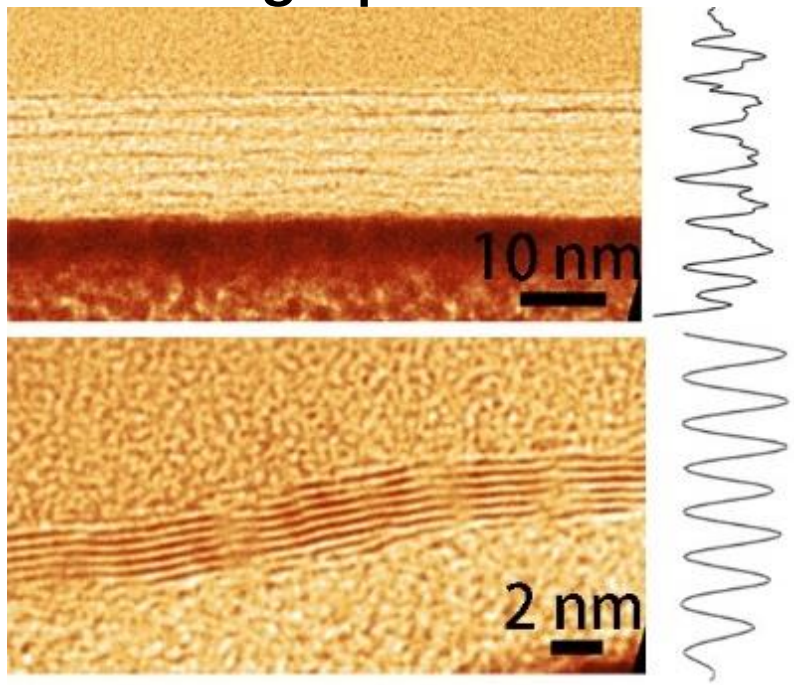
Janus graphene film







Janus graphene film

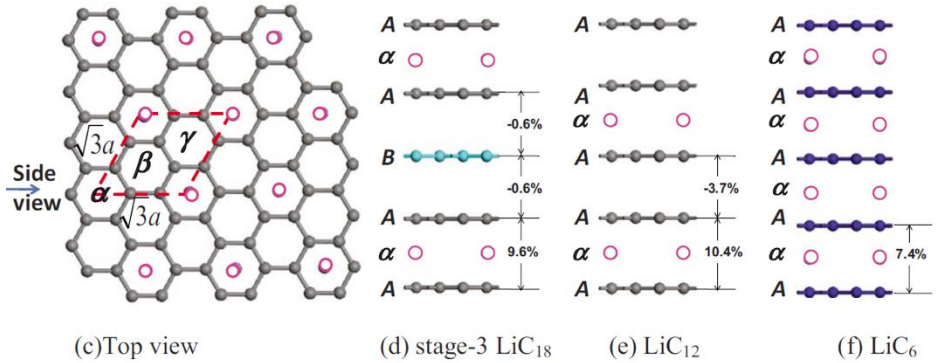


Stacked CVD graphene film

Sodium ion battery

Why graphite doesn't work for sodium ion battery

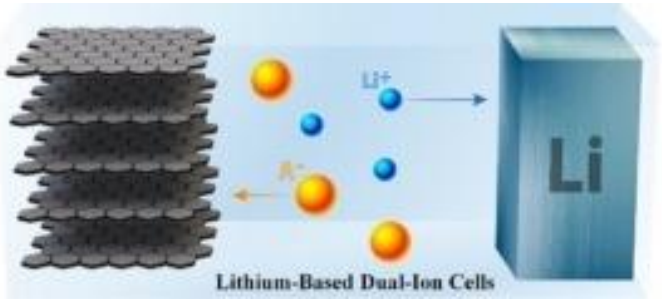
Graphite for Li vs. Na



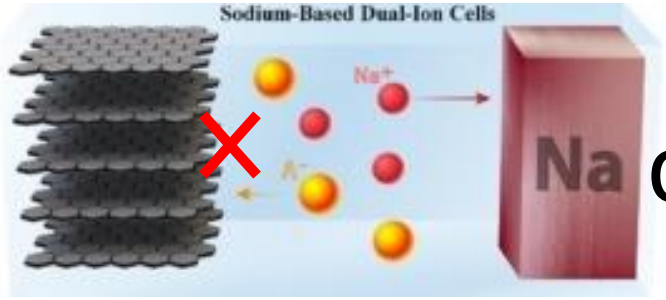
(c)Top view (d) stage-3 LiC_{18} (e) LiC_{12} (f) LiC_6

stage-I binary intercalation compound

Li-ion Battery (LIB)



C_6Li



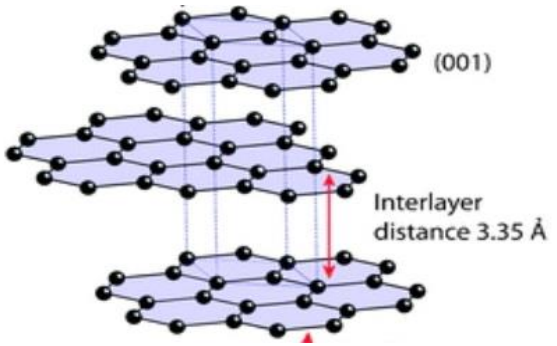
$C_{64}Na$

Sodium-ion Battery (SIB)

Hypothesis

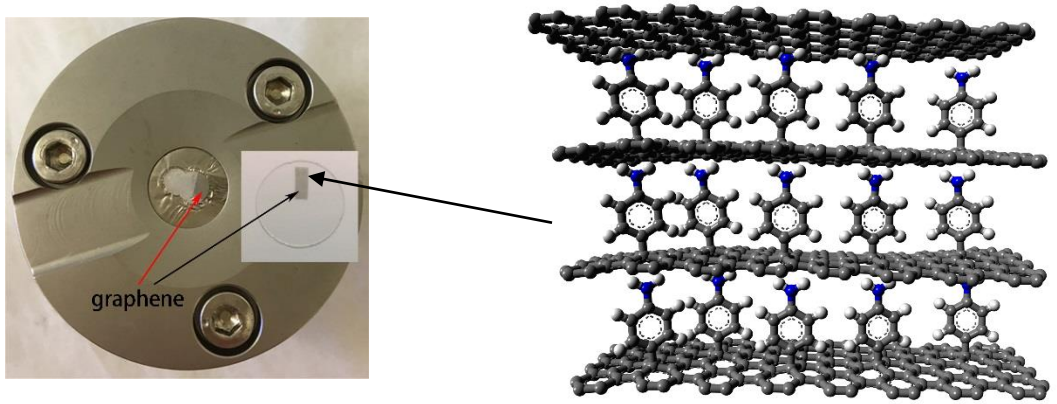
Reason: Na^+ > Li^+

0.97 Å 0.68 Å

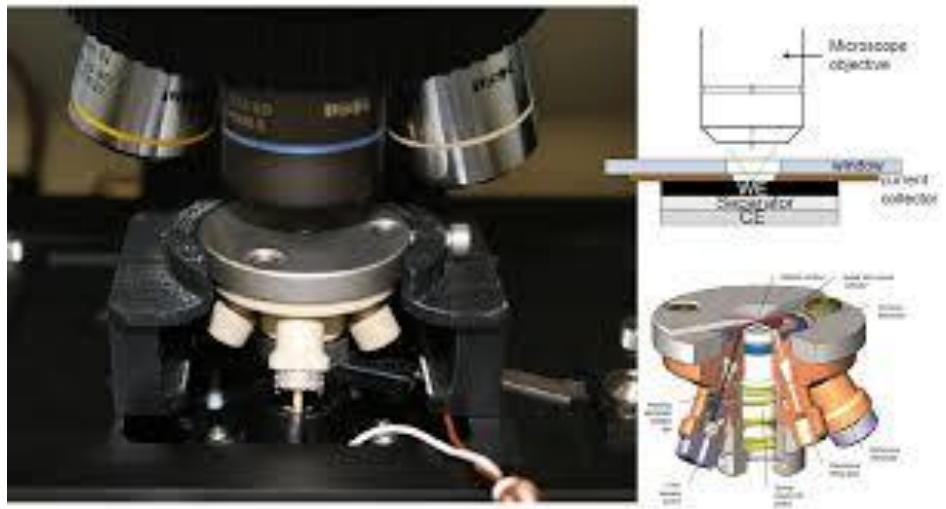


Large size

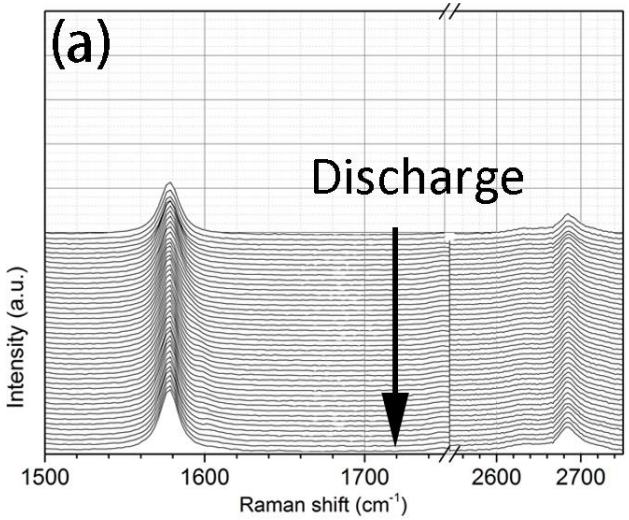
Operando Raman

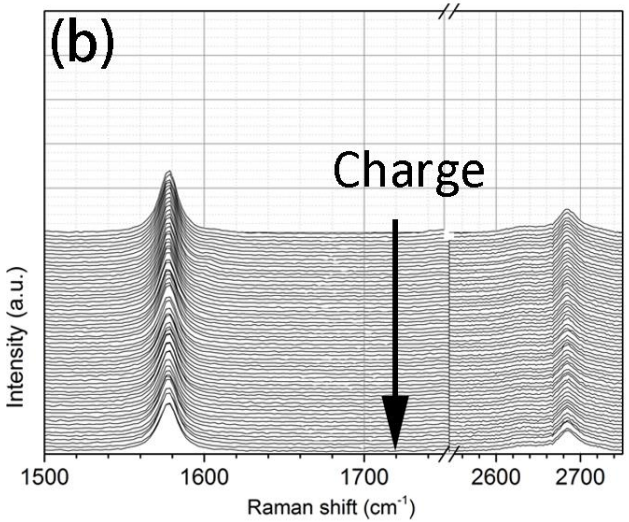


Operando Raman



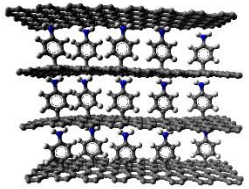
HOPG (Graphite) for Na ions

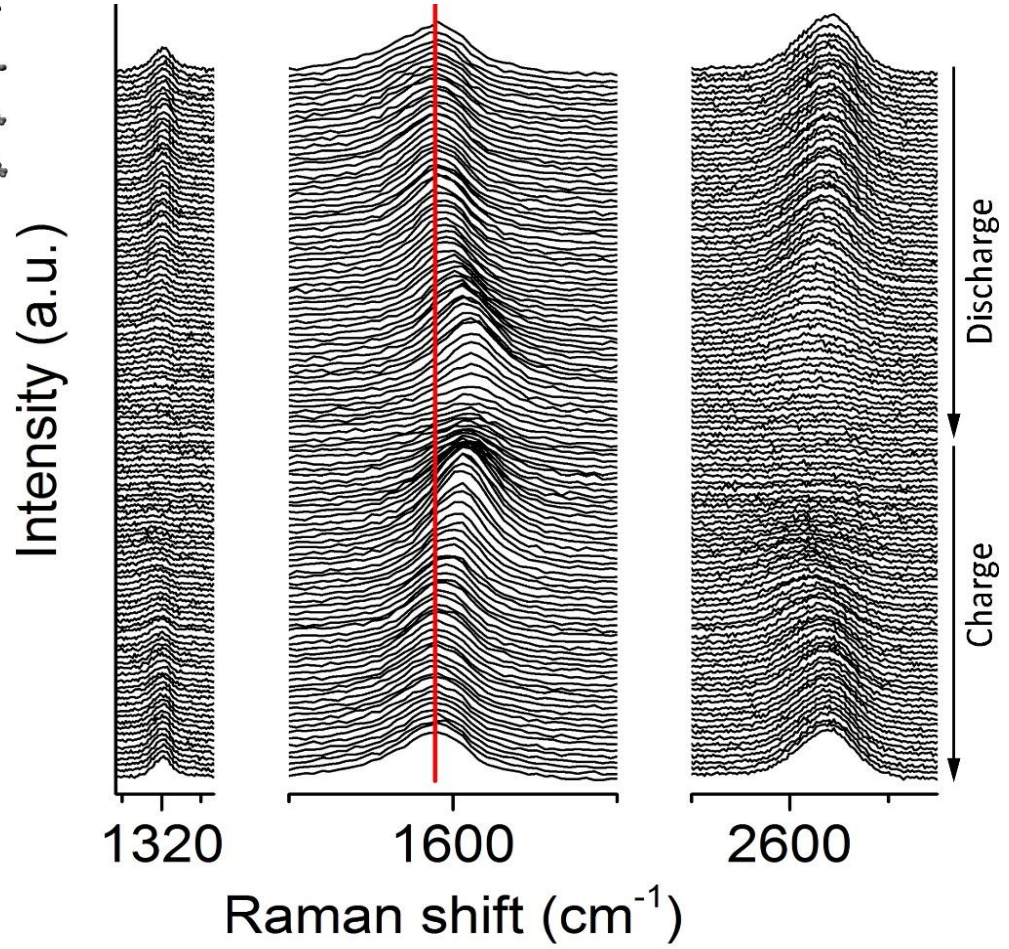


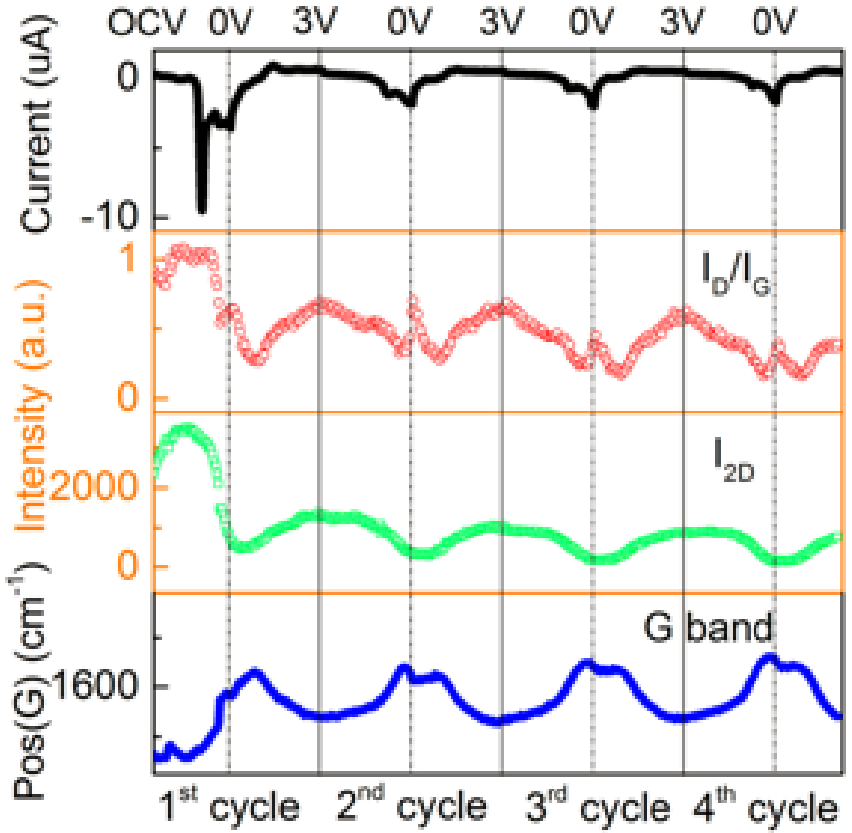


Monitoring Na ions intercalation

Janus graphene for Na ion battery

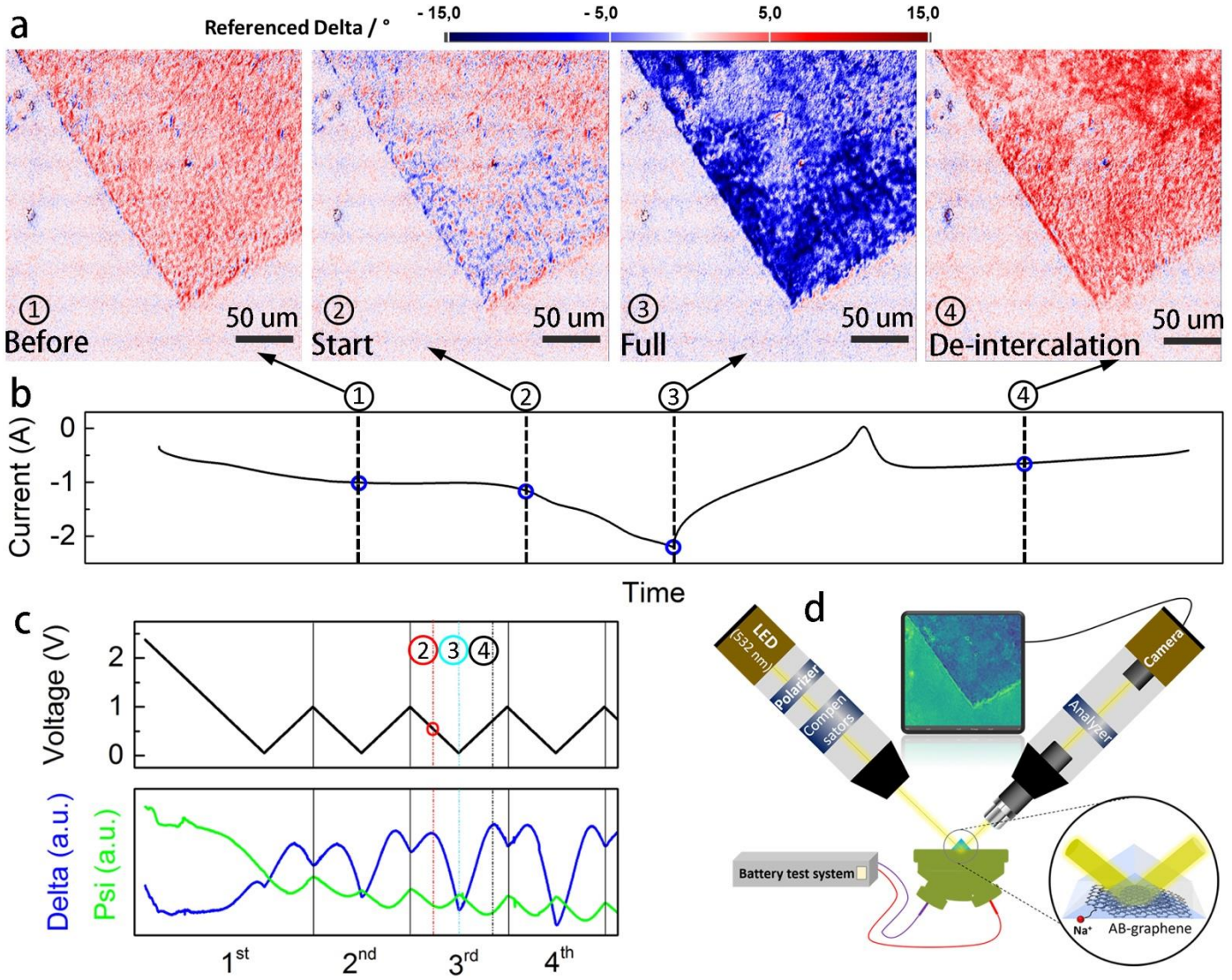






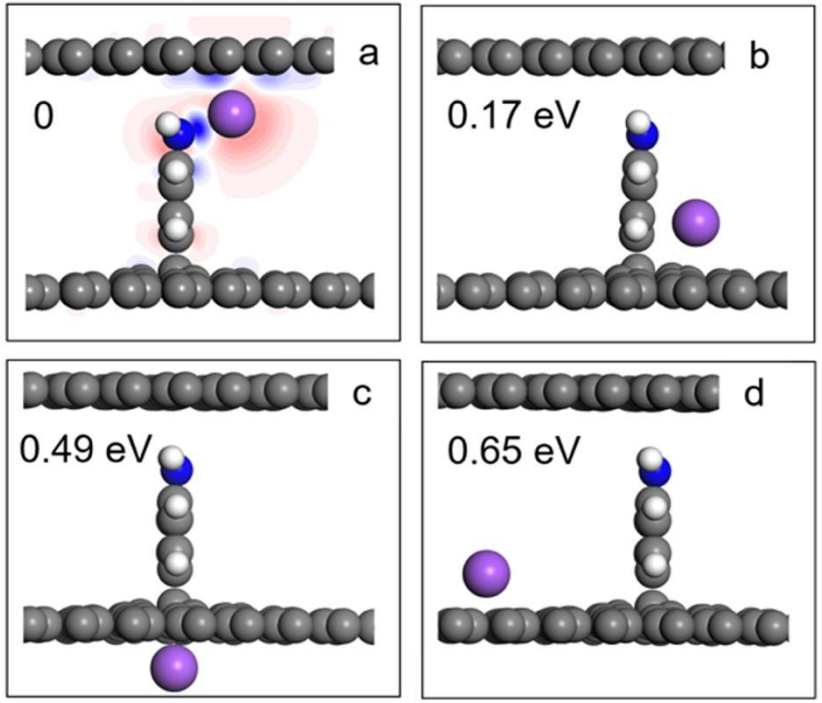
Intercalation/Deintercalation

Ellipsometry imaging

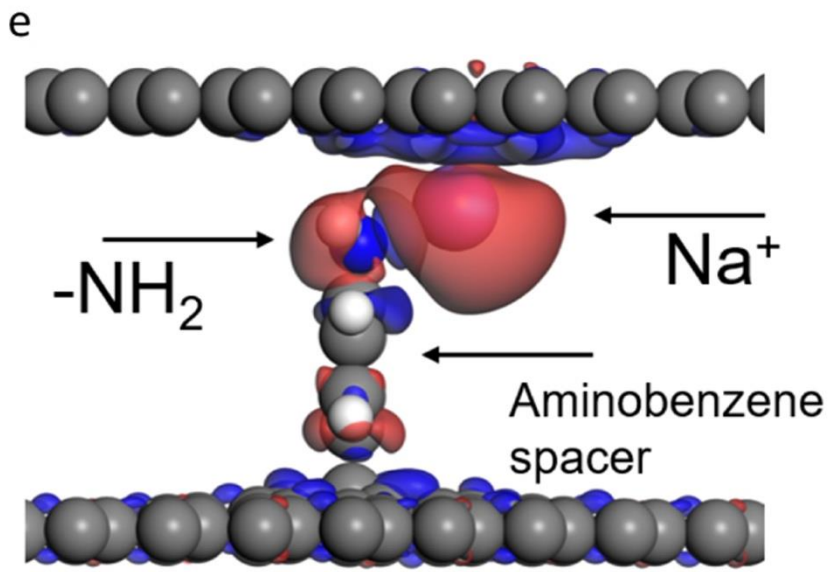


DFT calculation

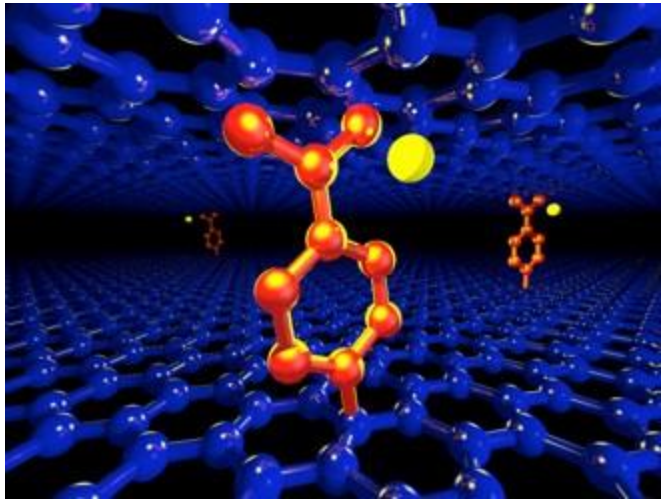
Understanding the intercalation mechanism of sodium ions



- Active sites
- Functional groups
- Defects



Synergic ionic bonds

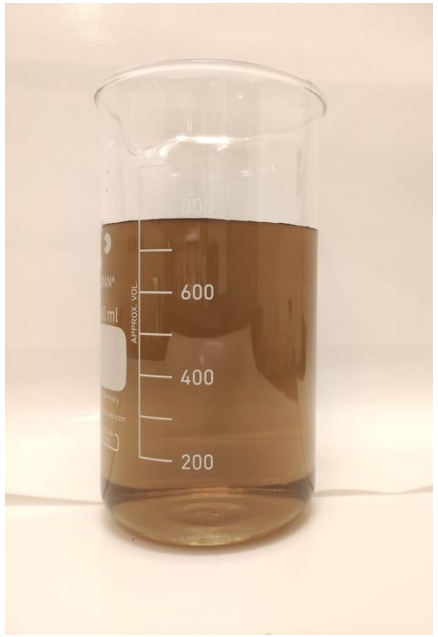


$C_{6.9}Na$

The interaction process is energetically favorable.

Large scale synthesis

Large scale synthesis of Janus graphene powder with different surface chemistry



Janus graphene collection

Janus graphene for Sodium ion battery

Coin cell result

Other applications

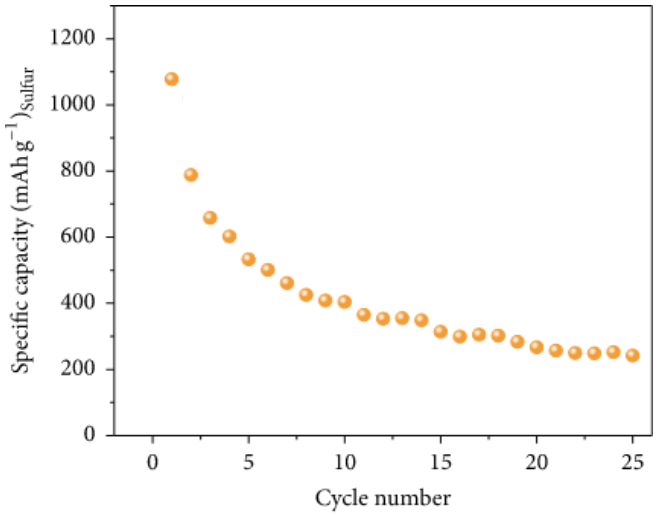
- **Energy storage**
- **Surfactant**
- **Additives**
- **Electronics**
- **…….**

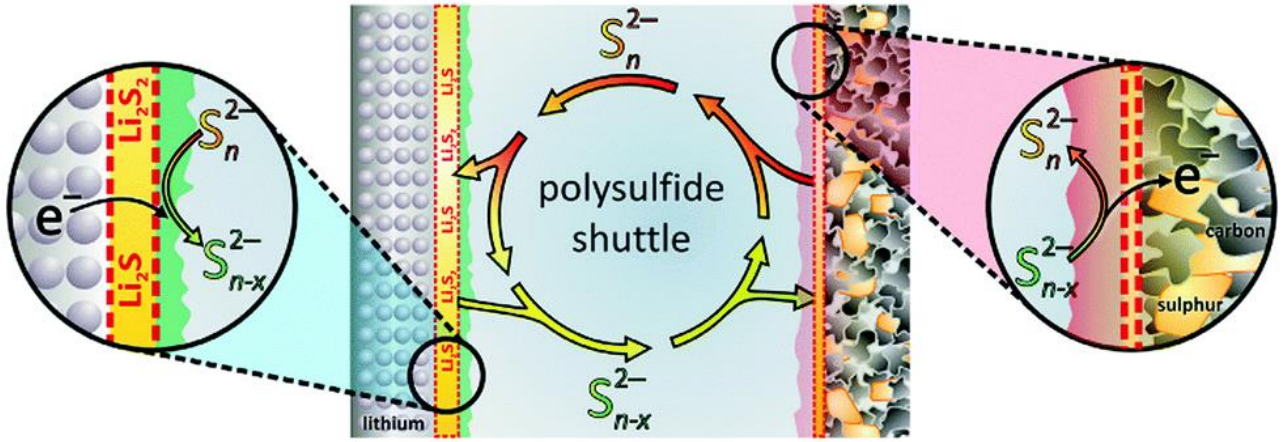
Issues of Li-S batteries： shuttle effect

Graphene for Li-Sulfur battery

$$2Li^+ + S_8^{2-} \Leftrightarrow Li_2S_8$$
$$2Li^+ + S_4^{2-} \Leftrightarrow Li_2S_4$$
$$2Li^+ + S_2^{2-} \Leftrightarrow Li_2S_2$$
$$2Li^+ + S^{2-} \Leftrightarrow Li_2S$$

$$2Li^+ + S + 2e^- \Leftrightarrow 2Li_2S$$





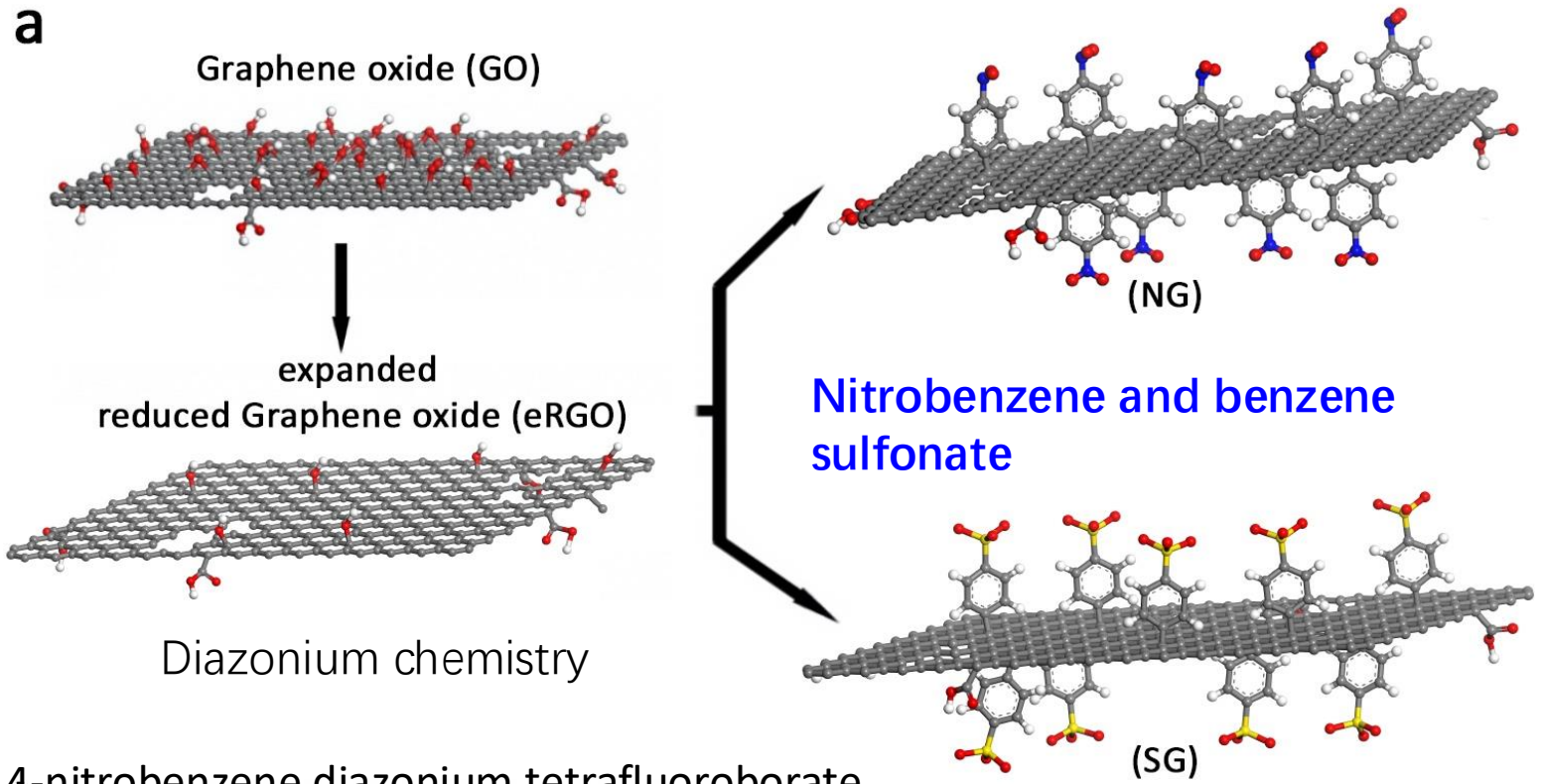
Parasitic polysulfide shuttle effect

Yang et. al., Chem. Soc. Rev., 2018, 47, 2020

- Low utilization of sulfur
- Poor cycling stability
- Low capacity
- Low coulombic efficiency

Synthesis of functionalization graphene

Functionalize graphene

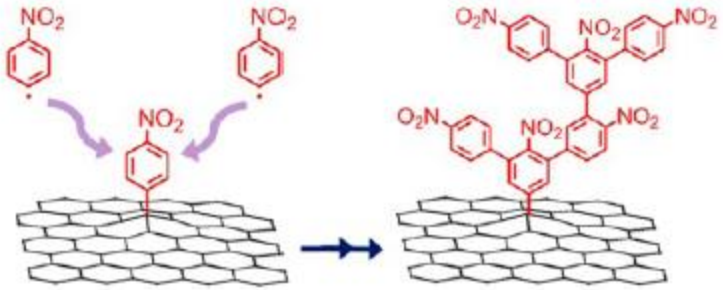


Diazonium chemistry

4-nitrobenzene diazonium tetrafluoroborate

4-sulfonic acid phenyl diazonium tetrafluoroborate

Diazonium chemistry



ACS Nano **2015**, 9, 5520

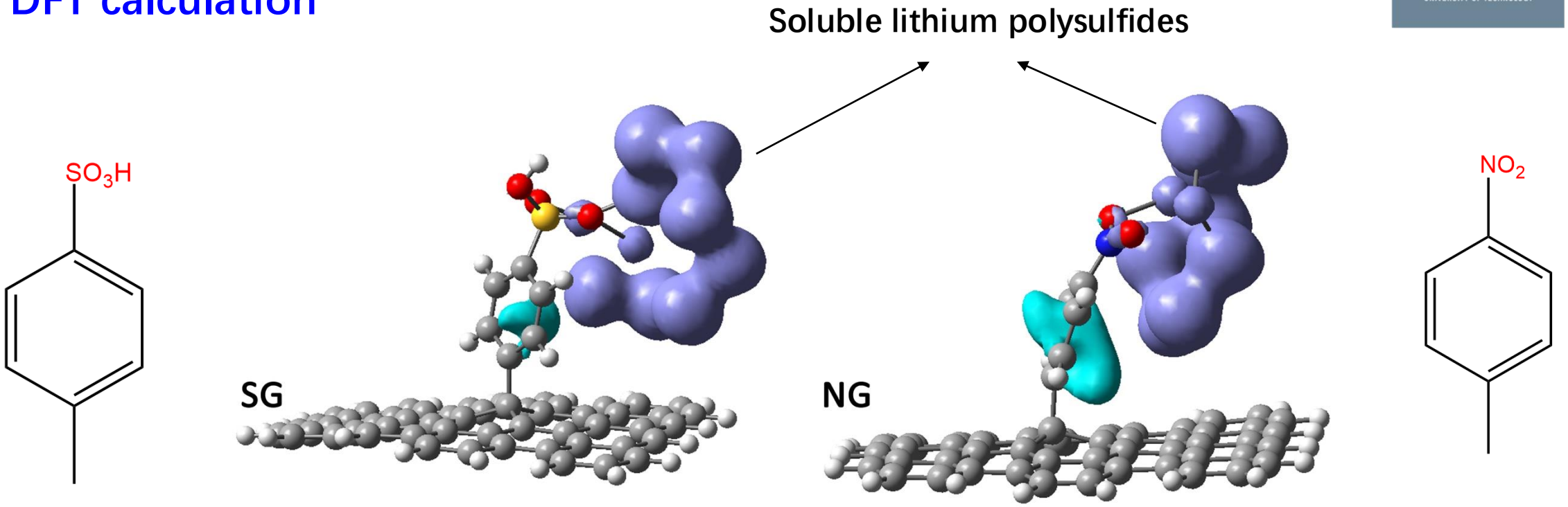
Self-polymerization

High reactivity of aryl radicals

Sun. et al., Small 2021, 2007242

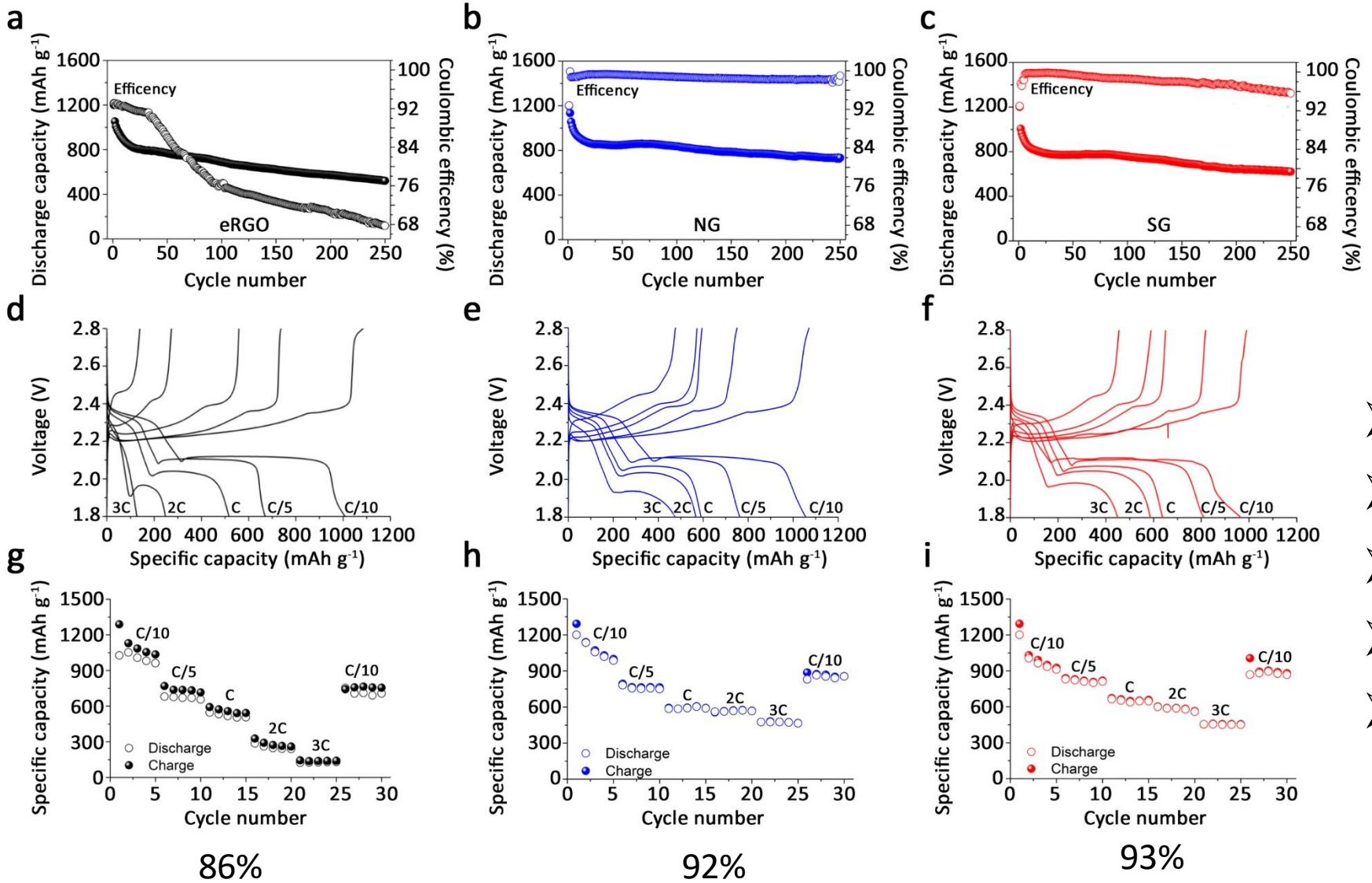
Exfoliation and restacking of graphene

DFT calculation



Fukui functions of the electron density

Electrochemical performance



High sulfur loading

Li_2S_n polysulfides

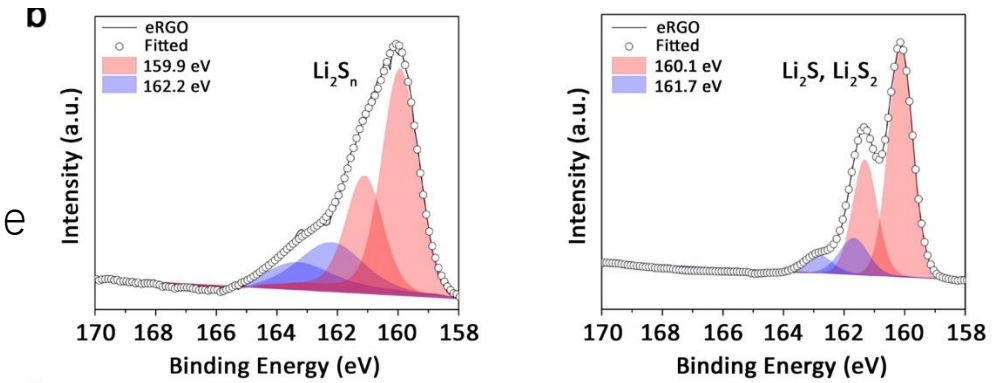
Low sulfur to electrolyte (S/E) ratio (i.e., 1:5)

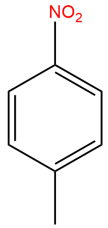
- High utilization of S
- High specific capacity
- Better rate performance
- Long cycling stability
- High energy density

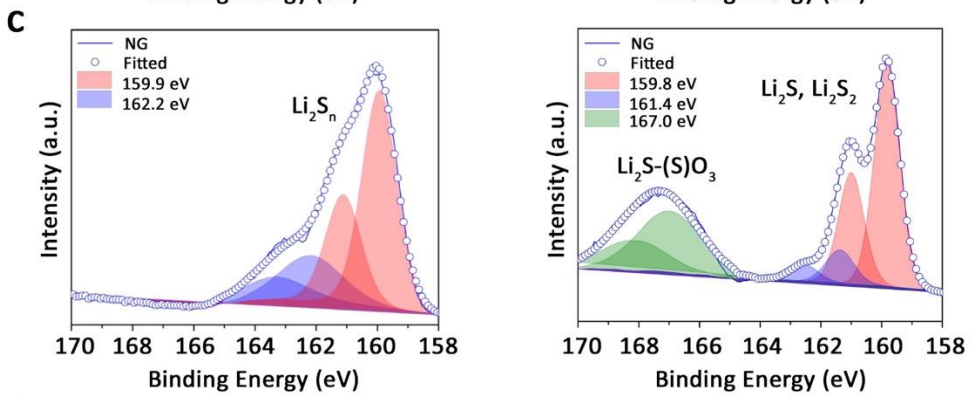
Polar-polar interaction

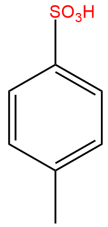
Interaction: XPS evidence

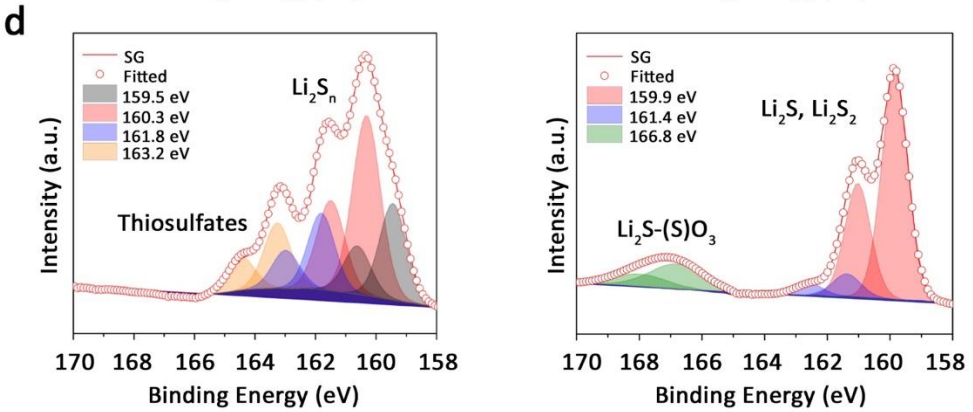
Pristine Graphene

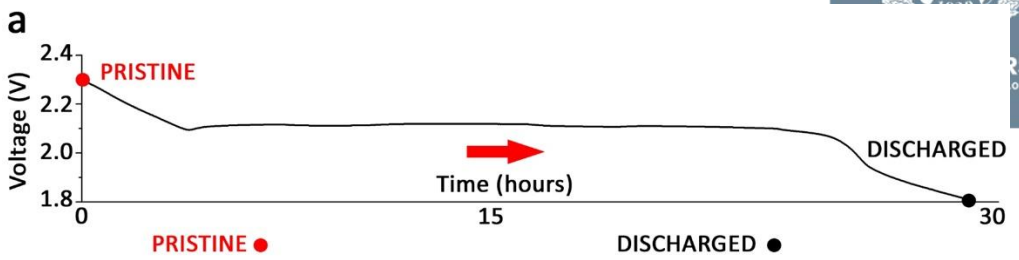








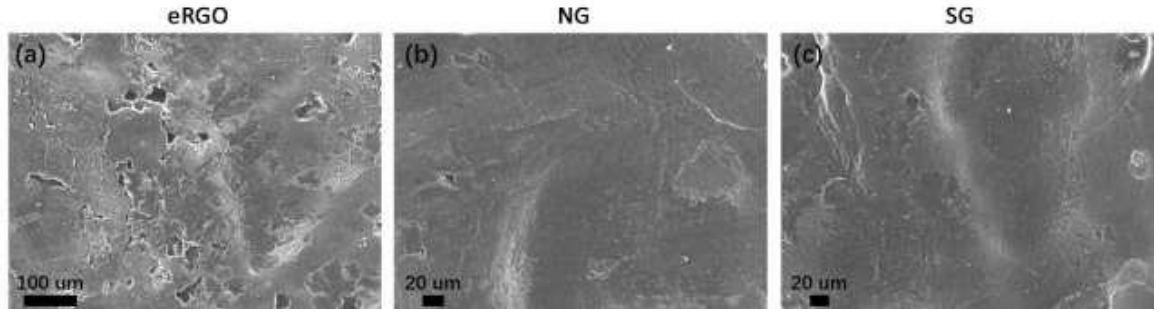




Evolution of lithium polysulfides on graphene surface

Formation of Li_2S-$(S)O_3$ and S-O bonds

NG has better stability then SG due to the formation of more bonds

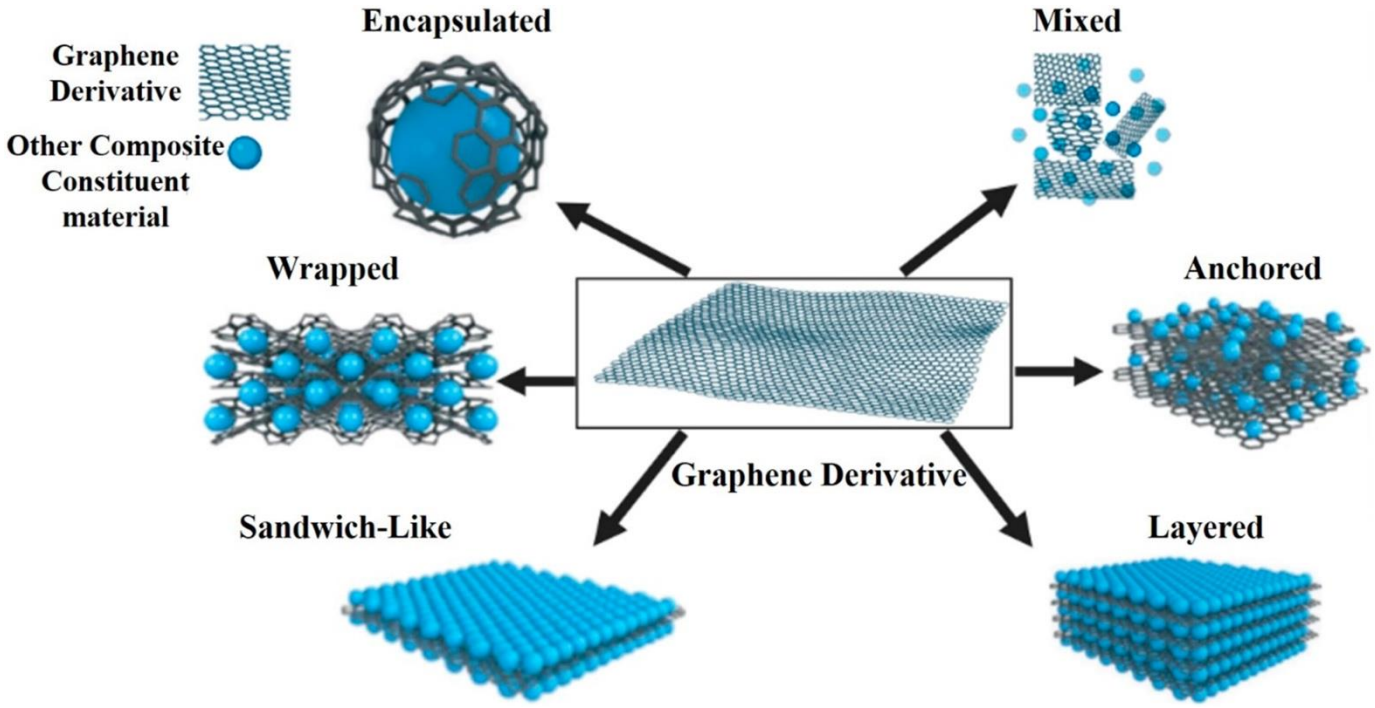


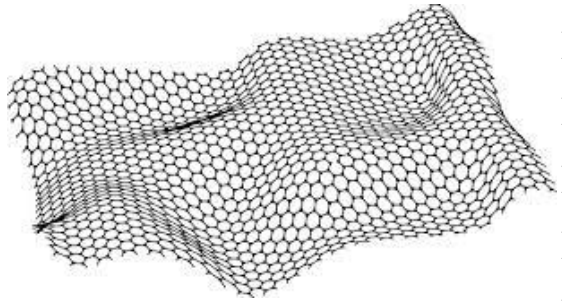
Lithium surface after cycling

Graphene for lithium ion battery

- Graphene coating
- Graphen conductive additives

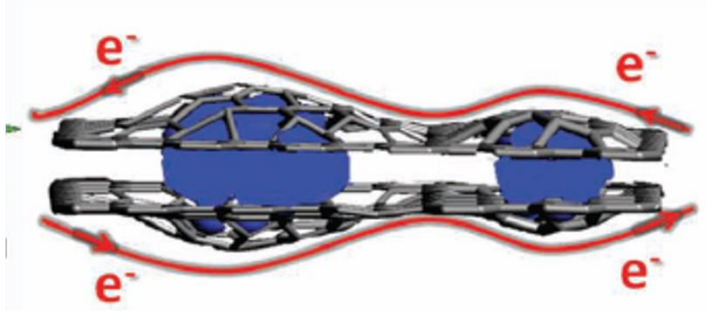
Graphene to solve problems of silicon electrode





- Flexible
- Large surface area
- Conductive
- Stable
- Accommodate lithium

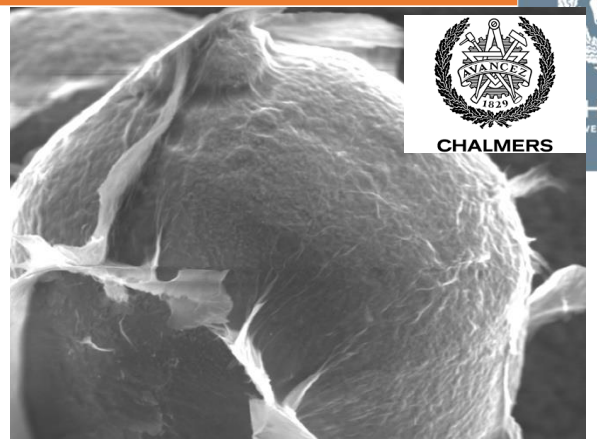
Graphene coated electrode materials



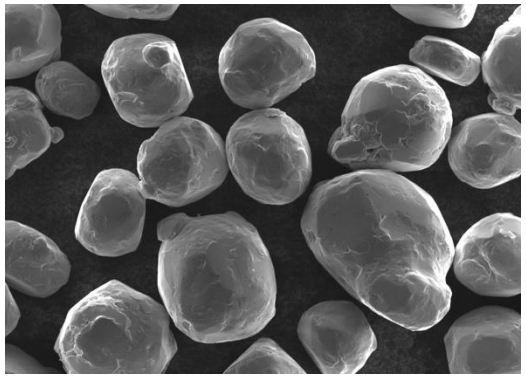
Fast lithium-ion diffusion inside the electrode

Our Strategies:

1) Surface coating.



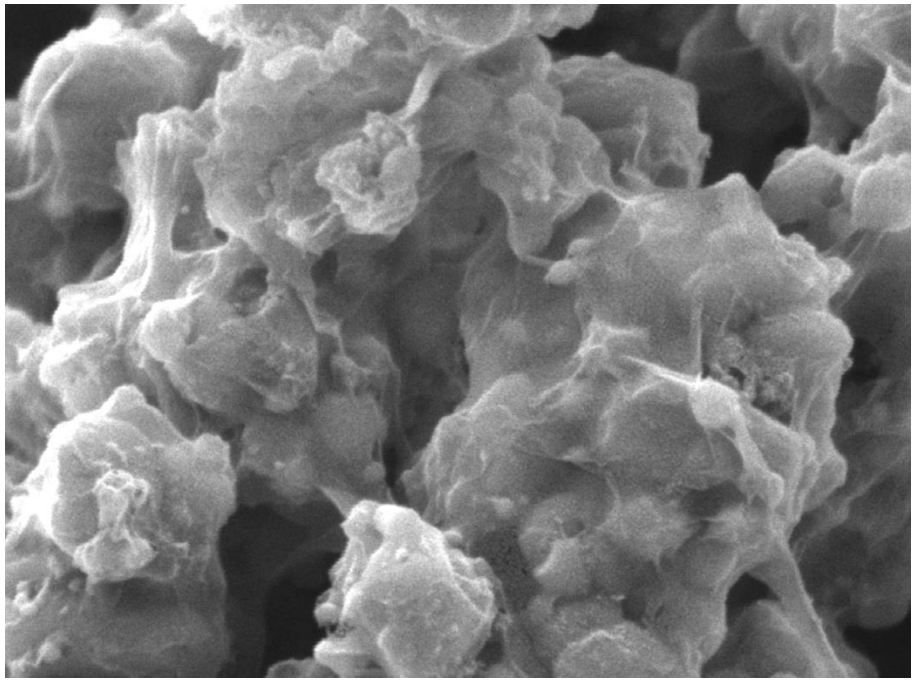
- NMC
- NCA
- LFP
- Si



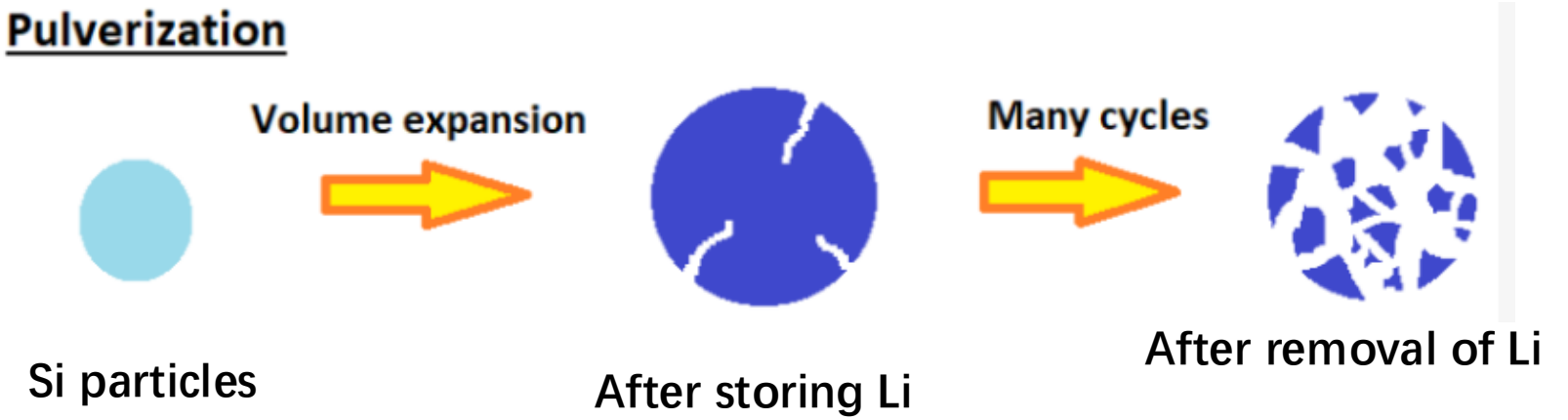
Surface modification

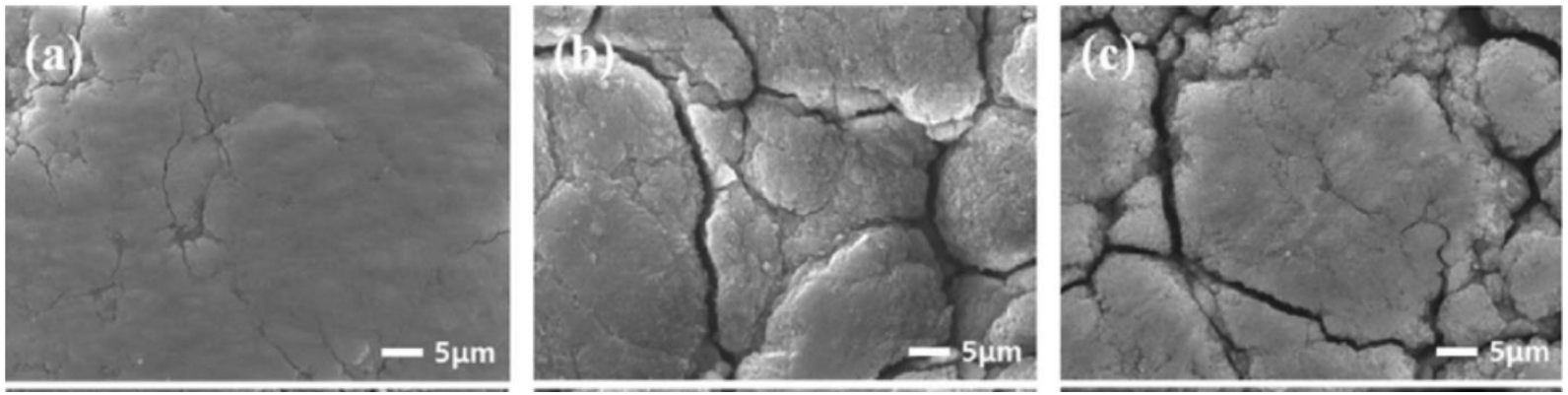
→

Coating graphene



Issues of Silicon electrode



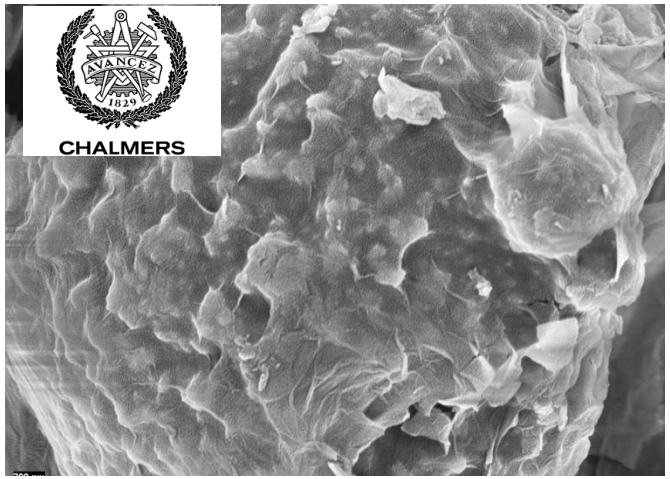


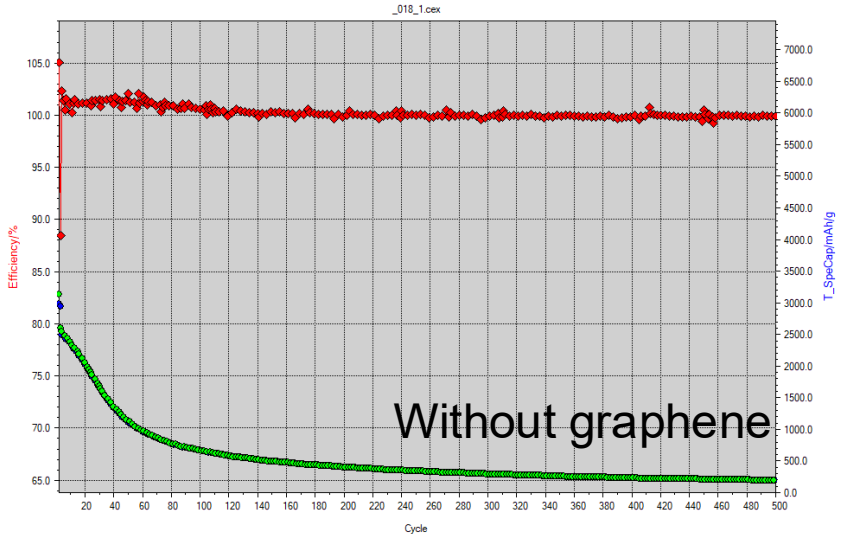
Silicon (5wt%)/graphite

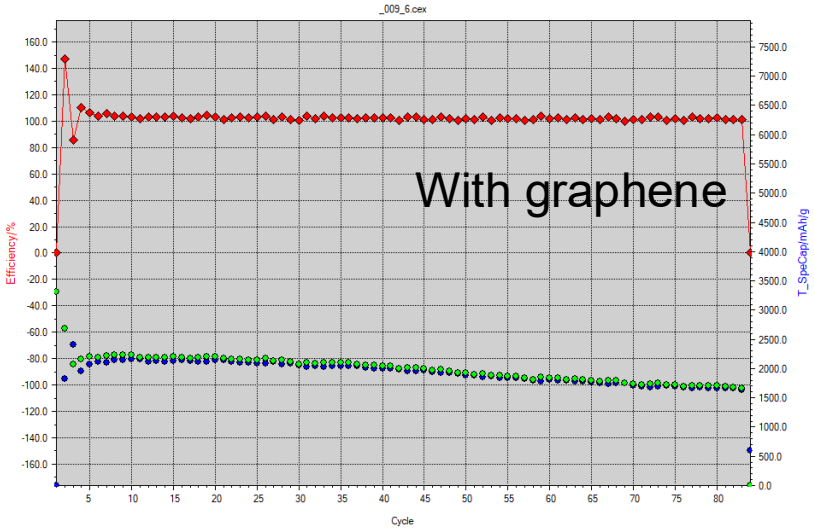
High Silicon mass loading

- Poor cycling stability
- Low rate capability (can not fast charge)

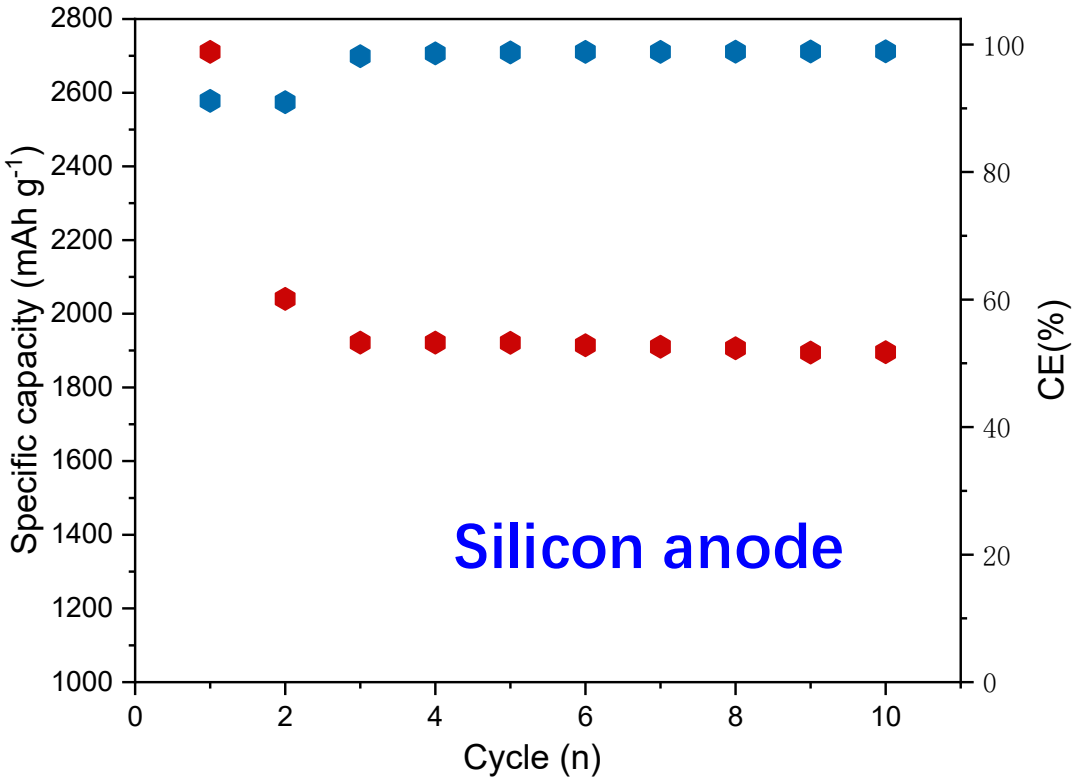
Coat graphene on silicon particles







Graphene as conductive additives



LFP
LFMP
NCM

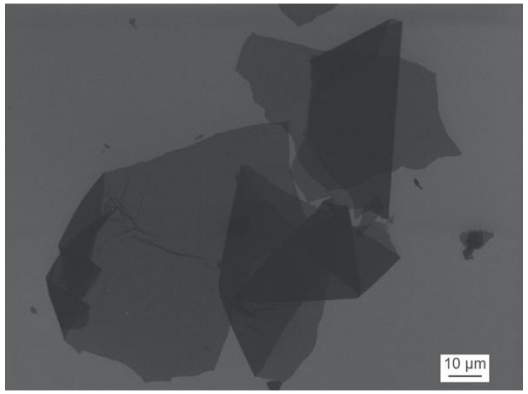
Graphene based composites

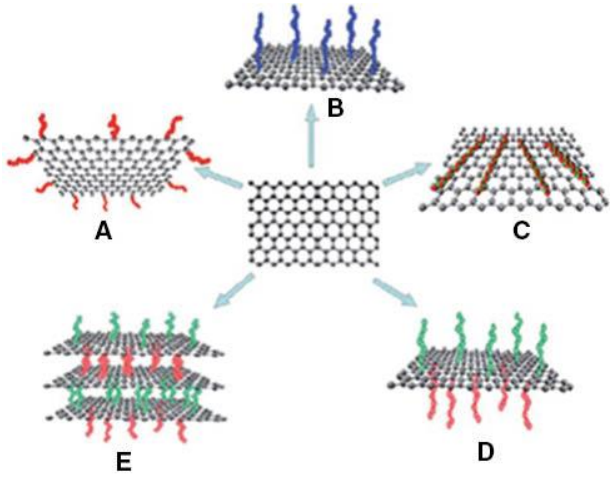
Metal and Polymer

Graphene investigation and modification

Different graphene derivatives

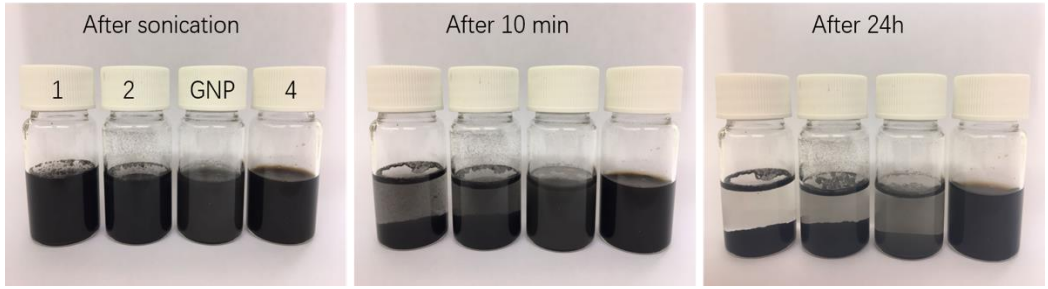
- Grphene
- Graphene oxide
- Reduced graphene oxide
- Graphite nanoplatelet





Modify the surface chemistry of graphene in order to have better interaction with matrix materials

Surface modification, and stabilize the graphene in solvents



1 kg graphene paste

1 mg/ml

Overnight

Graphene investigation and modification

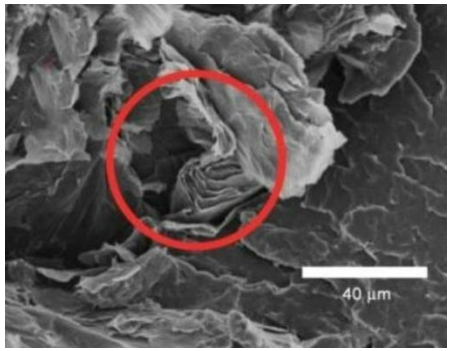
Issues to be addressed in the processing

Agglomeration of graphene in metal and polymers

Graphene in metal

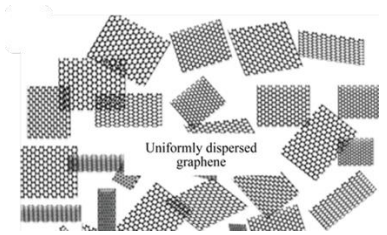
Melton metal on graphene

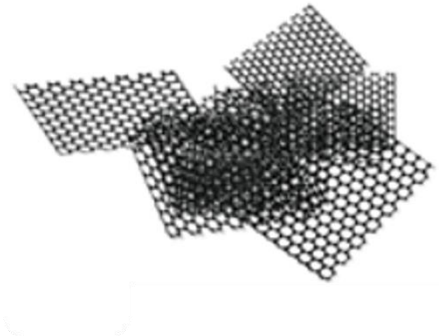
Graphene in polymer



Graphene aggregate

Agglomerate

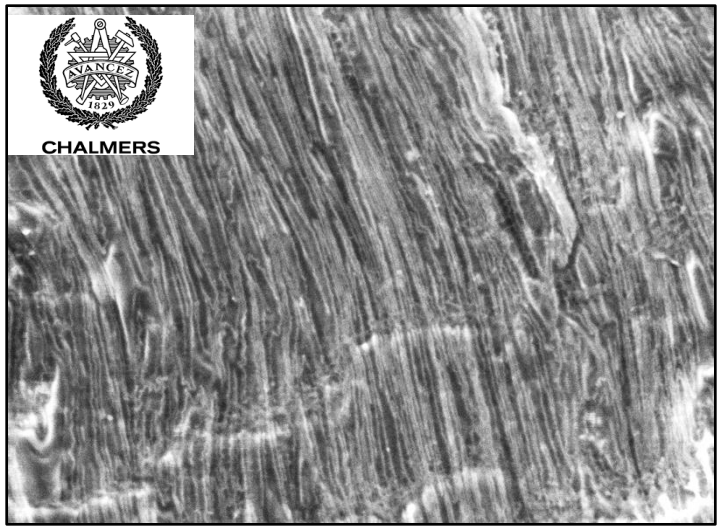




- **Large surface area**
- **High surface energy**
- **Pai-pai interaction**

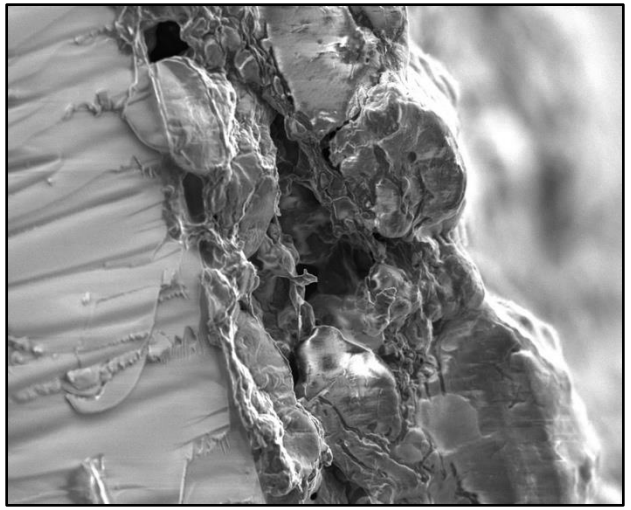
Development of graphene/polymer dispersion and coating

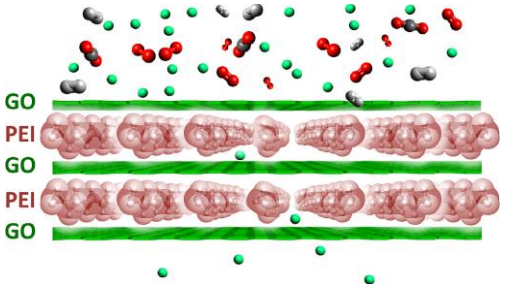
Cryofractured cross-section (25 um)



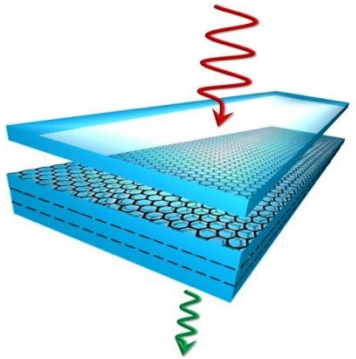
VS

Aggregated cross-section (25 um)





Gas barrier
Gas separation



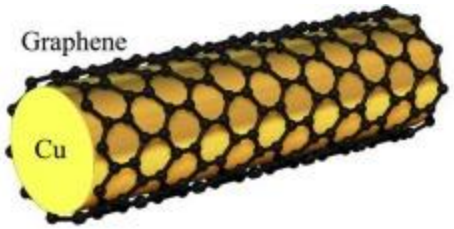
EMI Shielding

Thermal conductivity

Graphene enhances contacts/switches in electricity and tribology

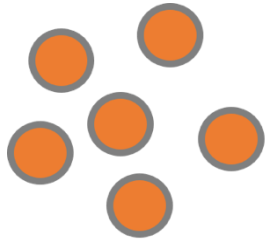
Solutions: coating graphene

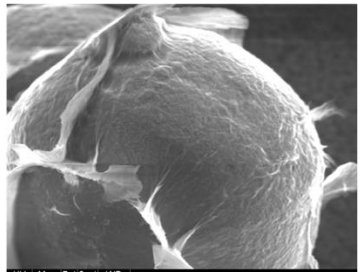
Graphene on metal top surface



Graphene coated metal bulk

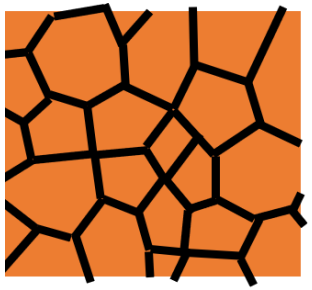
Graphene in metal matrix





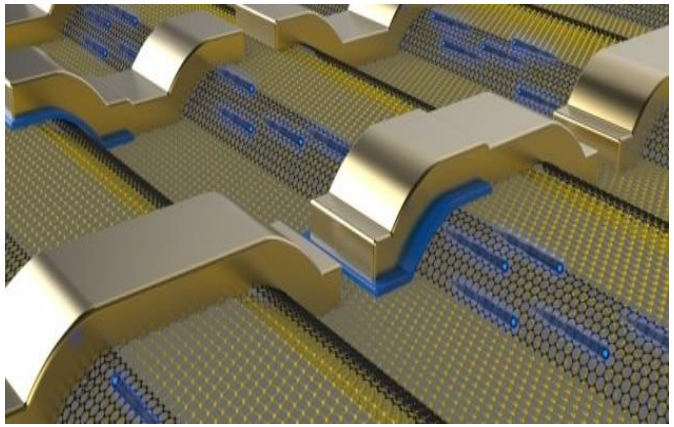
Graphene coated metal particles

3D printing



Graphene/metal matrix

- Anti-friction
- Anti-wear
- Self-lubricate

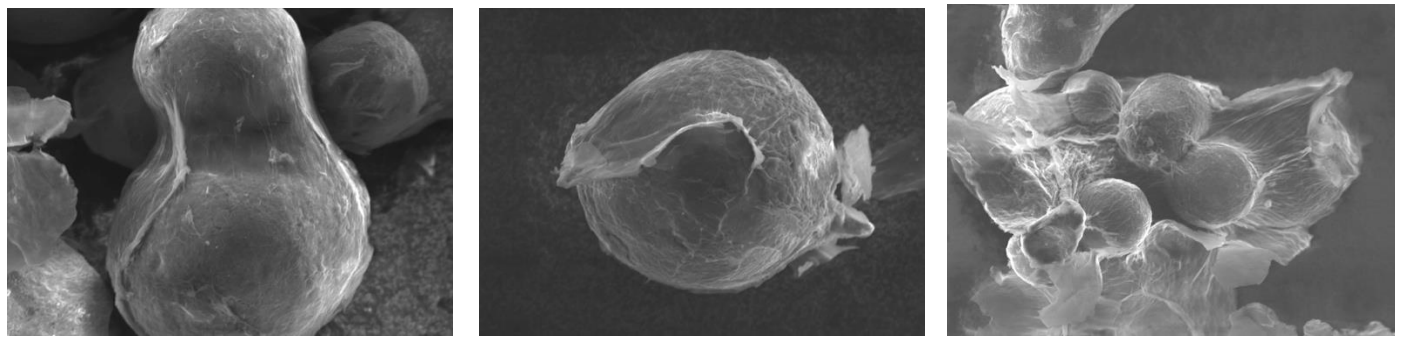


Low voltage circuit breakers

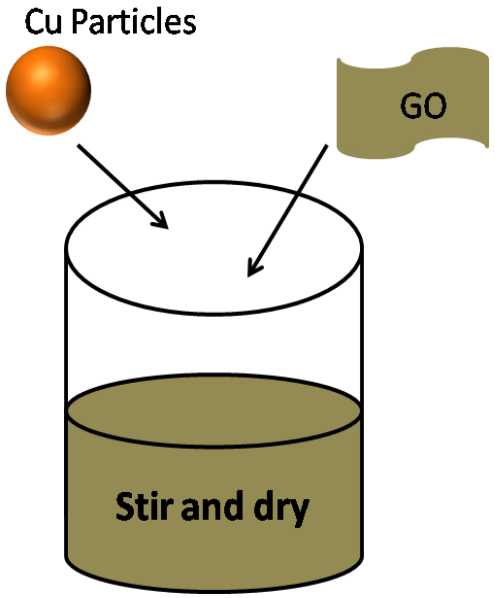
- High electrical conductivity
- High chemical resistance
- Anti-corrosion
- High thermal conductivity

Coating graphene on Cu particles

Increased thickness of coated graphene

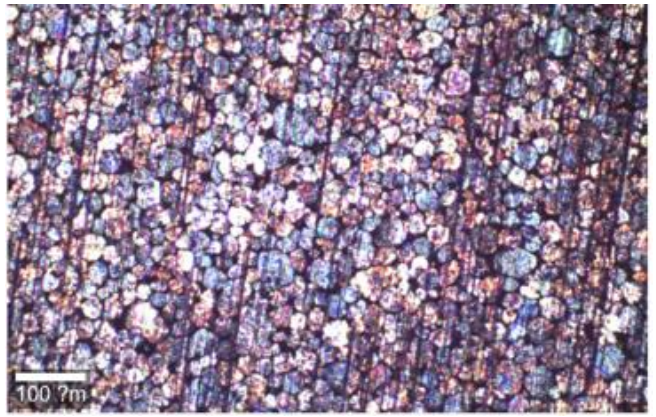


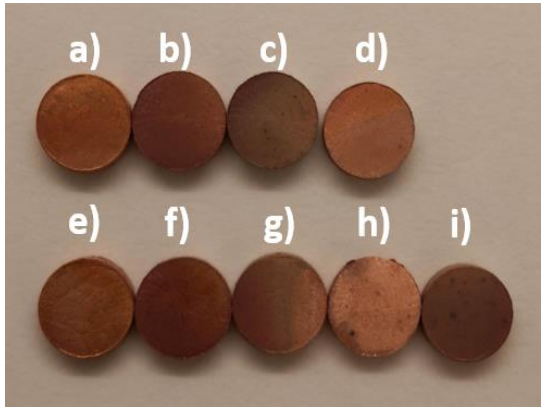
Surface modification



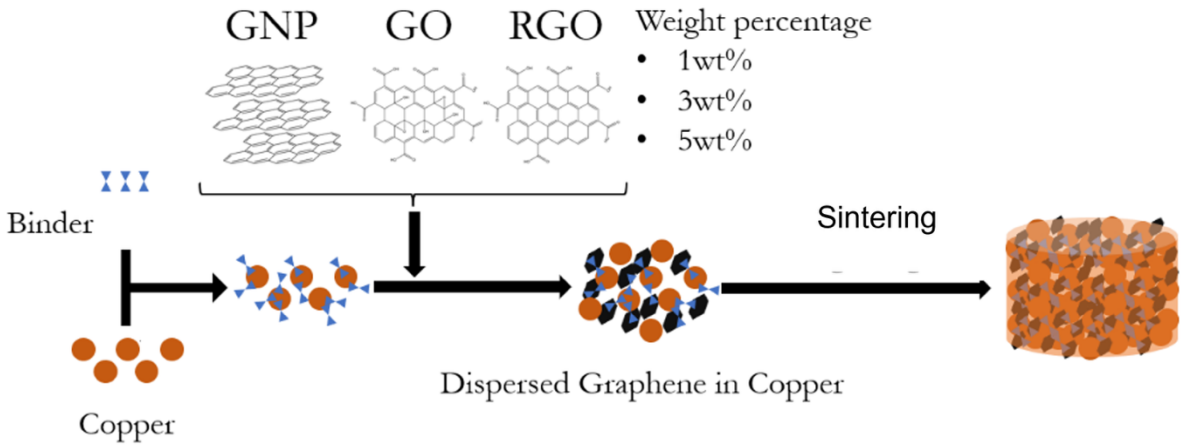
Mixing GO and Cu powder in water

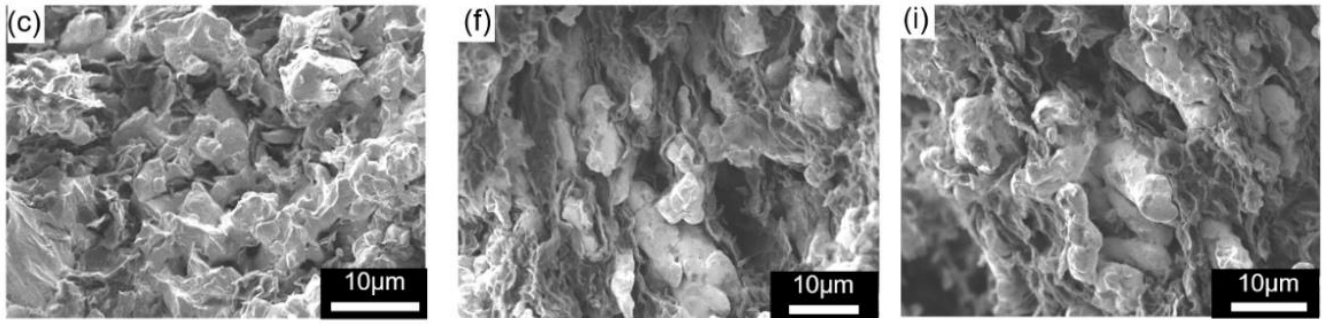
Thermal conductivity, anticorrosion



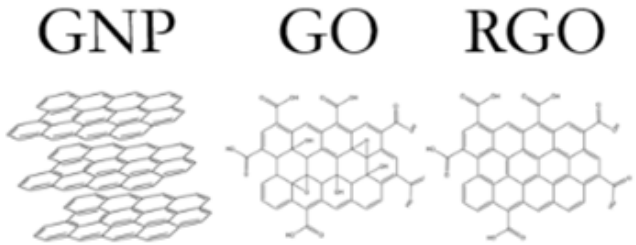


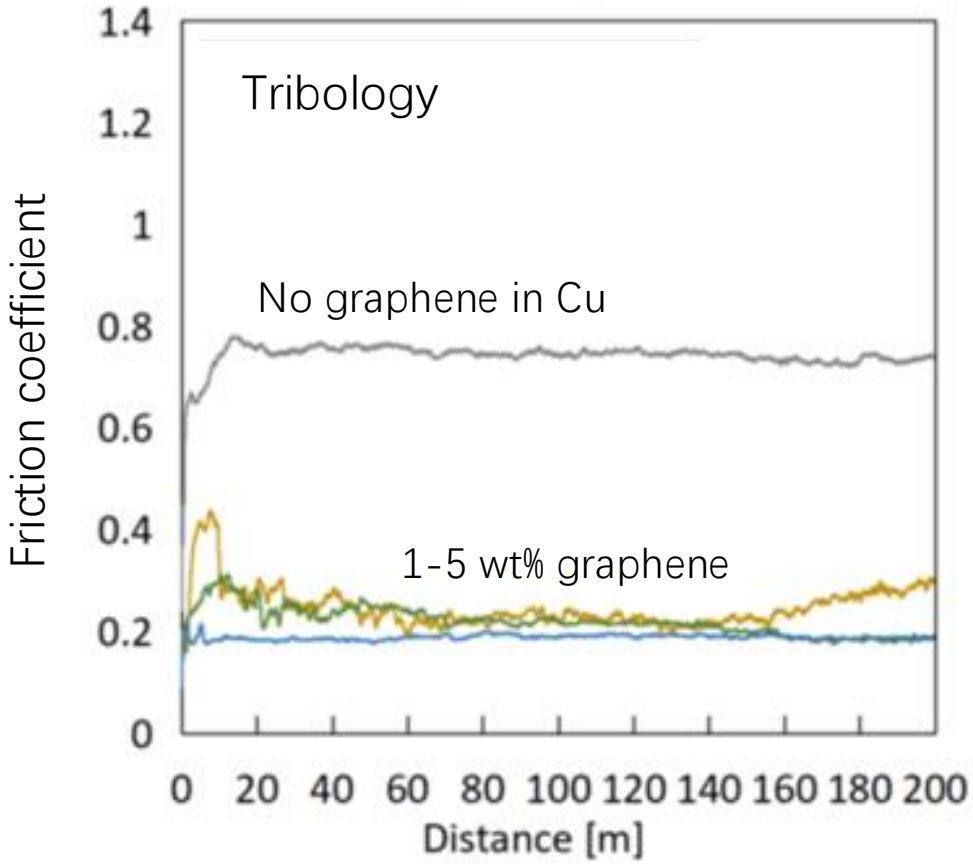
Tribology



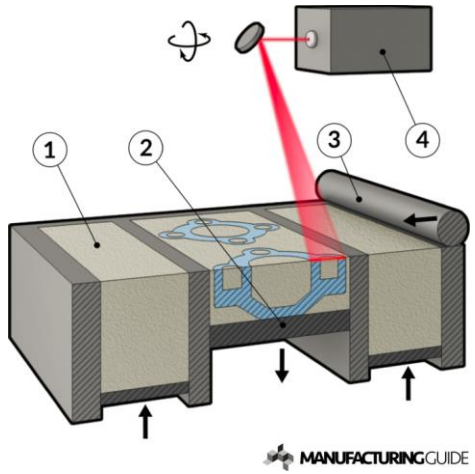


Comparison

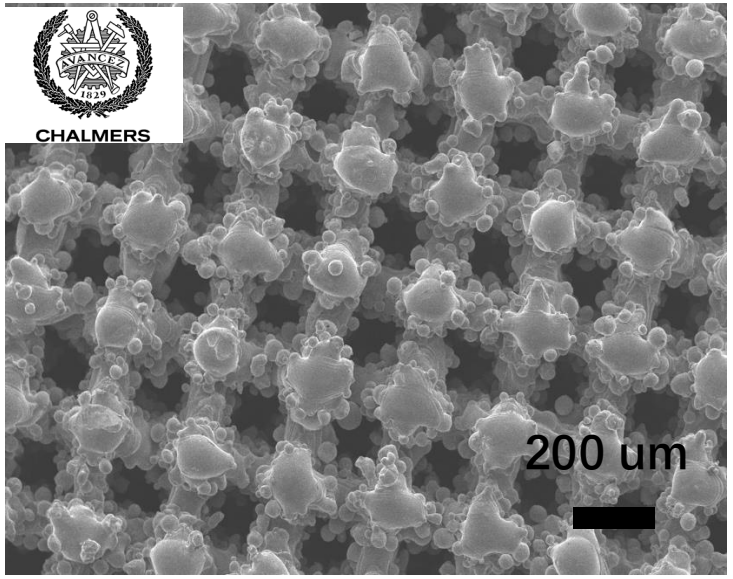


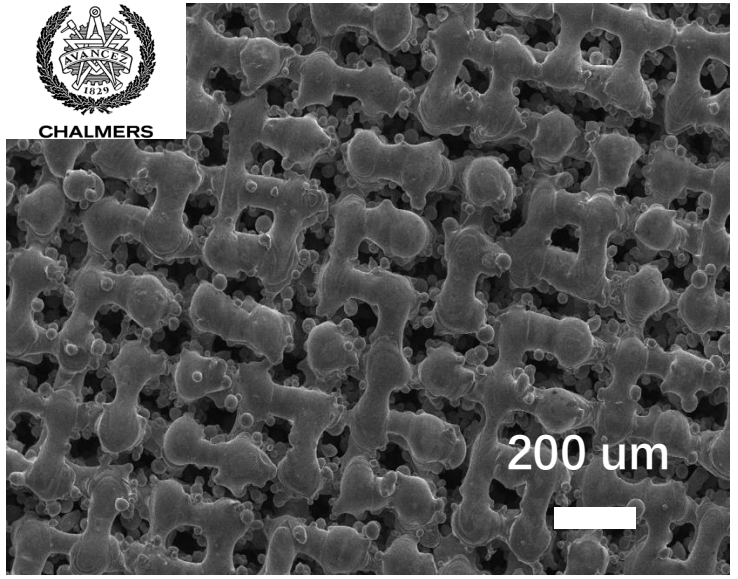


Additive Manufacturing



Porous Cu substrate with regular and controllable pore structures





- Controllable pore size
- Porous structure with high density
- Graphene coating
- Better interaction with deposited lithium

Thanks for your attention !

Jinhua Sun
Jinhua@chalmers.se