Perspectives on graphene based materials for PTOLEMY

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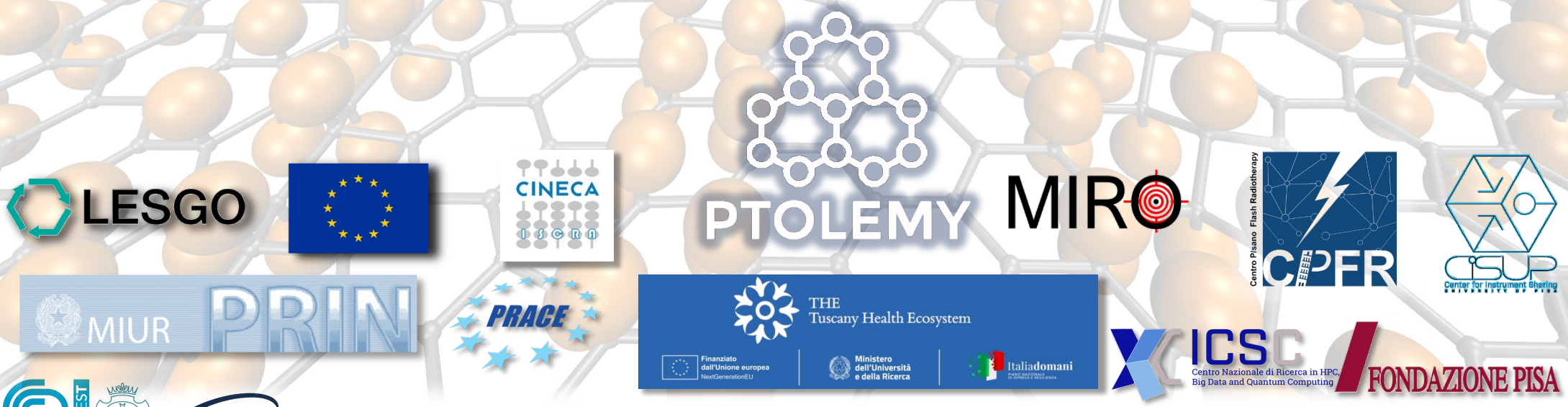
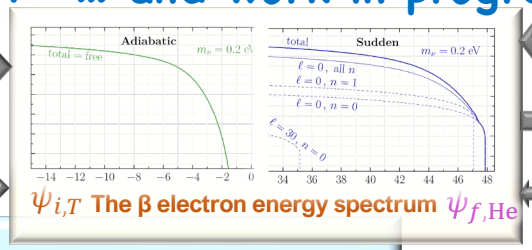


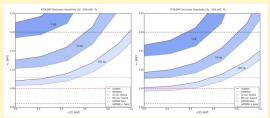
State of the art … and work in progress

What is done

In progress

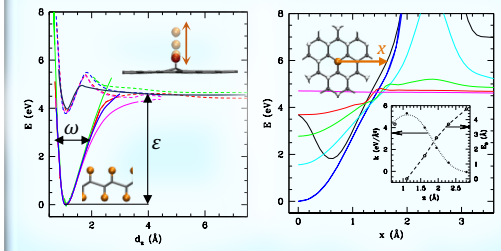


Sensitivity curves

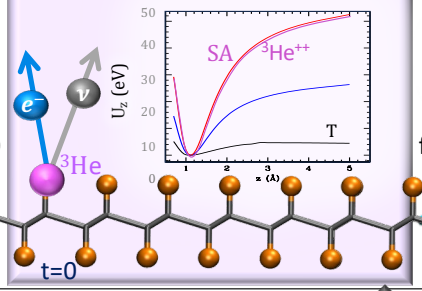


Substrate heating up / consumption / degradation…

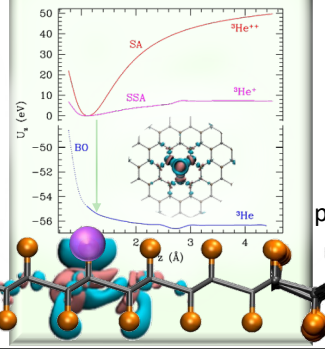
T bonded to graphene, steady state



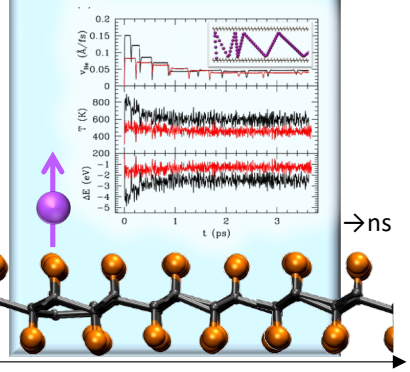
Sudden Approximation for He



Electronic relaxation



He release and interaction with the substrate



t<0 fs ps →ns

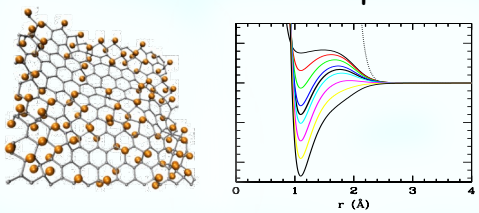
T@gr

T@gr → e^- + $\bar{\nu}$ + ^{3}He*@gr

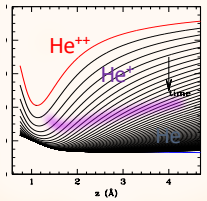
^{3}He*@gr → ^{3}He@gr

^{3}He@gr → ^{3}He + gr

The true substrate is not ideal
Graphene architecture, T loading/distribution and external fields **modulate the T potential**



Beyond the sudden approximation
He potential after decay **changes with time**, determining different probabilities for different final charge states of He
⇒ **Non adiabatic dynamics** for electrons



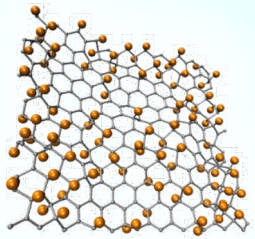
The post-reaction substrate dynamics
- ✓ Vibrational modes
- ✓ Flexural phonons

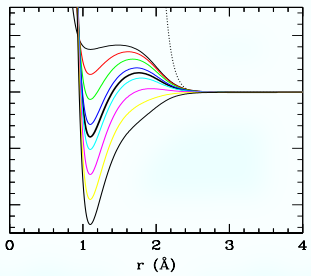
Full quantum He + substrate dynamics and non adiabatic electron dynamics

Outline

The true substrate is not ideal

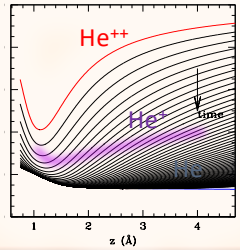
Graphene architecture, T loading/distribution and external fields **modulate the T potential**





Beyond the sudden approximation

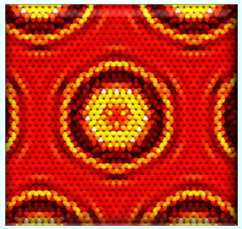
He potential after decay changes with time, determining different probabilities for different final charge states of He



The post-reaction substrate dynamics

✓Vibrational modes

✓Flexural phonons



Material structure and its effects

→ Dependence of T potential on the structure and loading and feedback to β spectrum

→ Dependence of loading on the material

→ Adsorption of β by the substrate

→ Electronic mechanic[illegible] properties of the substrate

WORK IN PROGRESS

Non adiabatic dynamics for electrons

WORK IN PROGRESS

→ Corrections to He potential

→ Distribution of final charge states of He

→ Feedback to the β spectrum

Molecular dynamics of the substrate

WORK IN PROGRESS

→ Recoil and corrections to the β spectrum

→ Detectable signals from the substrate

Material structure and its effects

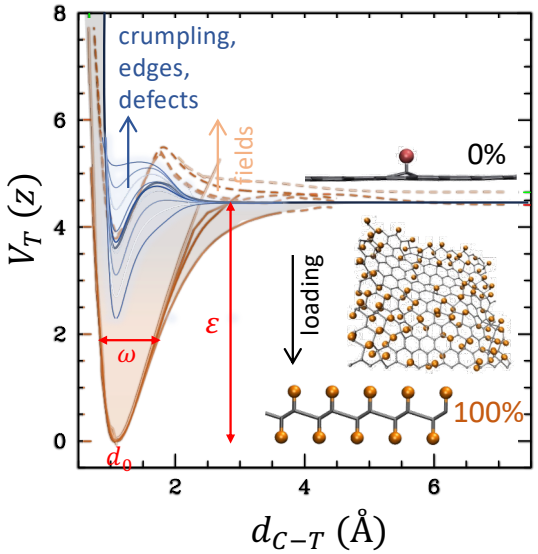
1. T Binding potential **is modulated by**

- → External fields/temperature, **F**
- → T **loading** (and distribution), **L**
- → **Structure** (curvature/defects/edges), **S**

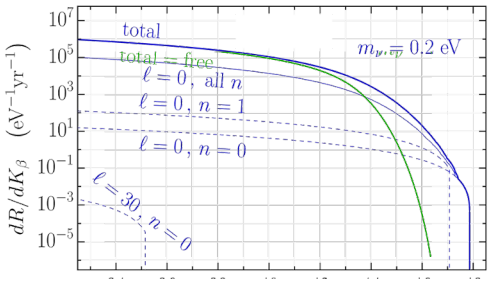
The potential is basically described by three parameters:

- → well location d_0
- → well depth ε
- → well width ω

} all depending on F,L,S



3. The β spectrum depends both on T and He potentials

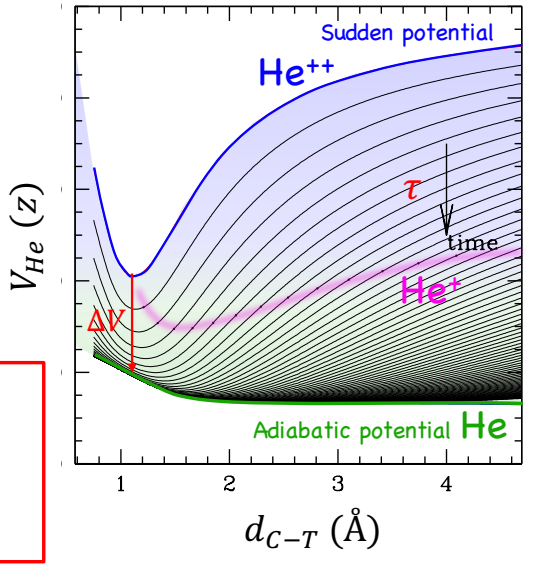


$$Sp = Sp(\varepsilon, \omega, d_0, \Delta V, \tau)$$
$$= Sp(F,L,S)$$

i.e. ultimately the spectrum depends on S, L and F via ε(F,L,S), ω(F,L,S) , τ (F,L,S) "solid state effects"

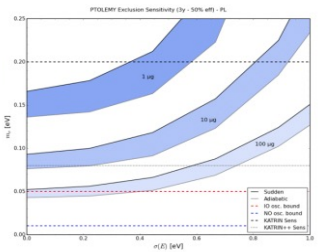
2. He Binding potential **changes in time**

- → The actual potential felt by He and the final charge state depend on the potential variation ΔV and the decay time τ
- → ΔV and τ depend on L and S and F



4. The sensitivity depends on the spectrum and directly on loading L

$$\sigma = \sigma(Sp, L) = \sigma(L, S, F)$$

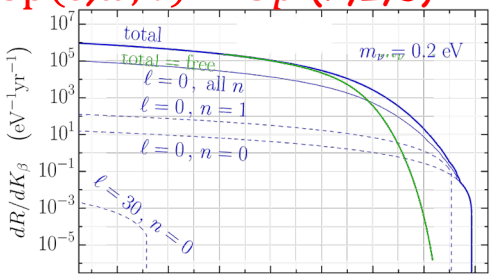


Material structure and its effects

Structure (S)
+
environment (F)
+
Loading (L)

β spectrum

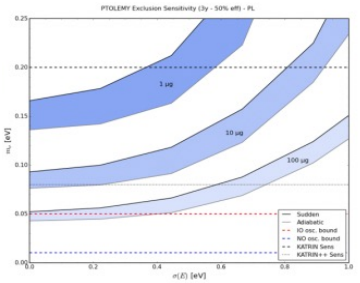
$Sp(\varepsilon,\omega,\tau) = Sp\,(F,L,S)$



+L

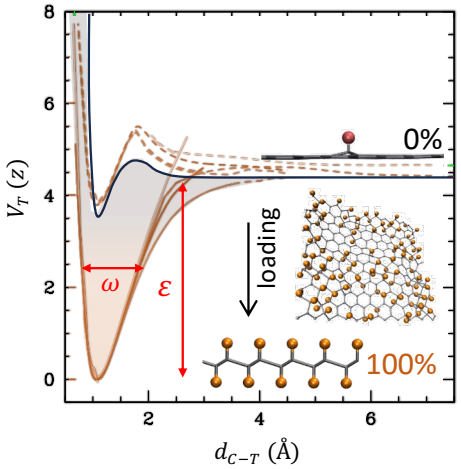
Sensitivity

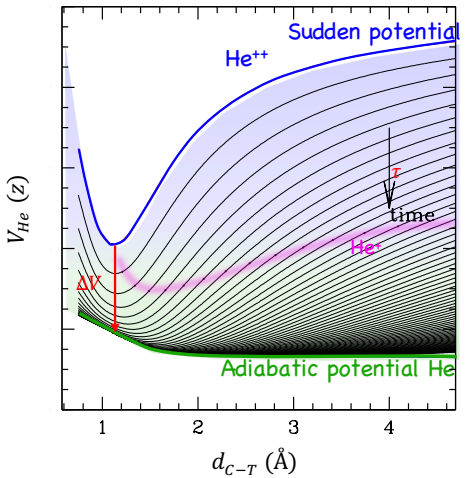
$\sigma = \sigma(Sp, L) = \sigma(L, S, F)$



Potentials

$\varepsilon(F,L,S)$, $\omega(F,L,S)$ $\tau\,(F,L,S)$





Take home messages

- ✓ The sensitivity depends **directly** on **T load** and on the **potentials**
- ✓ The **potentials** depend on **T load** and on **graphene structure**
- ✓ Other relevant quantities depend on **T load** and gr structure
  - The **relaxation** of the system after the decay
  - The **conductance** of the system and its **mechanical** props
  - The **adsorption of β**

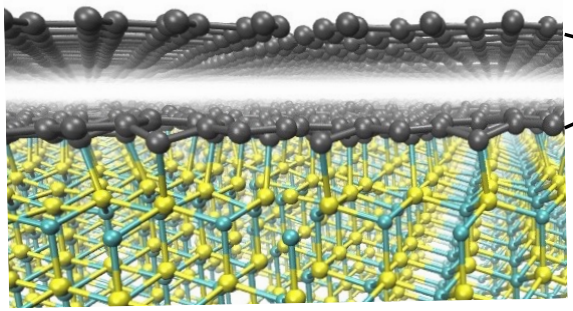
In the following:

- ✓ How does the **T load depend on graphene structure**?
- ✓ How does load influence the other relevant properties?
- ✓ What happens to the material after the decay/capture?
- ✓ What happens to the β electron?

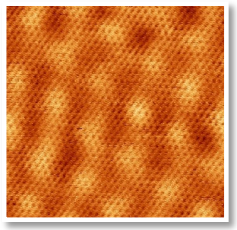
Different graphene materials and their characteristics

1. Epitaxial graphene

1.a **Si evaportion from SiC** surfaces and subsequent carbon layer reconstruction

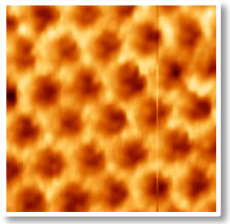


Heun et al

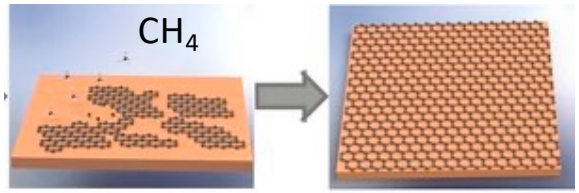


Monolayer

Buffer layer

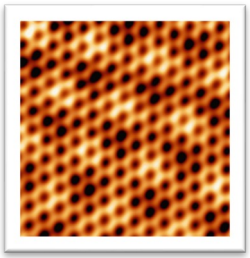


1.b **Chemical vapor deposition (CVD)** typically on metals (e.g. copper)



Coletti, Convention et al

Monolayer



Intrinsic characteristics

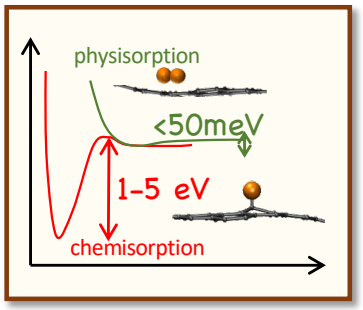
- ✓ **Structure**: **Monolayers** (or few layers), (poly)crystalline, almost flat, or rippled on the nanometer scale
- ✓ **Exposed surface:** very large (~2600 m^2/g)
- ✓ **Electronics**: very high carrier mobility 10^4-10^5 cm^2/V sec
  n or p doping depending on the substrate

➔ The regularity allows a more accurate evaluation of the theoretical systematics

T(H) loading capability

chemisorption by exposure to atomic H

- ✓ **Stoichiometry H(T):C** 50% to 100%
- ✓ **Gravimetric density** = $m_{H(T)} / (m_{H(T)} + m_C)$
  For H: 4.0% to 7.7% **For T:** **11.1% to 20%**
- ✓ **Surface density of T:** 0.01-0.02µg/cm^2
  On SiC: 10x10 cm^2 → **1-2 µg**
  On copper: 5x50 cm^2 → **5 µg**



Use, cost, scalability

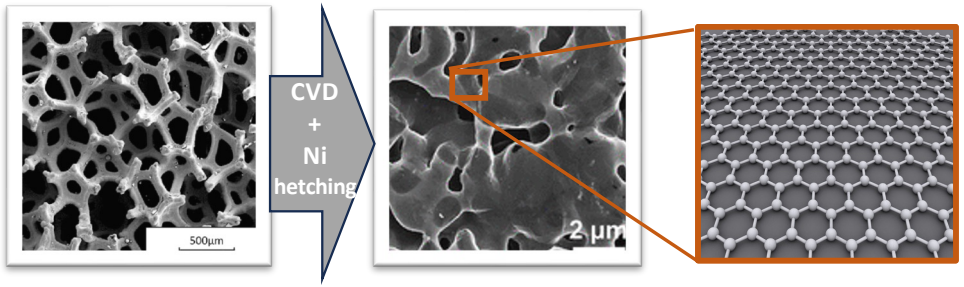
- ✓ High cost and low scalability **if high structural regularity is required** but… **hight regularity may not be essential for T loading**
  ➔Scalability can be improved
- ✓ **Monolayer must be transferred** to the support in the Ptolemy apparatus and this might be difficult with a single monolayer
  ➔ **Depositing directy on the support?**

Different graphene materials and their characteristics

2. nanoporous graphene

(still from epitaxy)

2.a Desposition on metallic foams (e.g. Ni)



Apponi, Ruocco, Coletti et al

Intrinsic characteristics

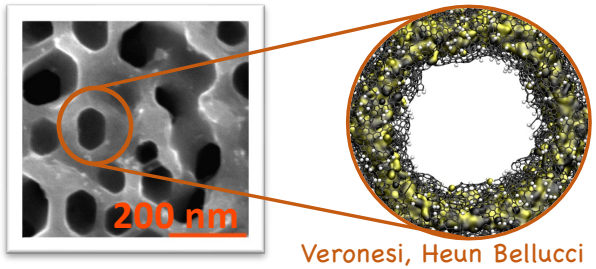
- ✓ Locally flat and regular as epitaxial, high el mobility
- ✓ Very large exposed surface, more robust than epitaxial

T(H) loading capability

As CVD: up to 90-100%, 20% GD or 0.02µg/cm²

Use, cost, scalability Better scalability, lower cost, easier use

2.b Evaporation from nanoporous SiC



Veronesi, Heun Bellucci et al

Intrinsic characteristics

- ✓ Very edgy and defective
- ✓ Lower exposed surface

  → Might not be a problem for loading, but the interaction potential is more variable and systematics calculations might be more difficult

T(H) loading capability Potentially op to 50-100%, but with very variable binding energy

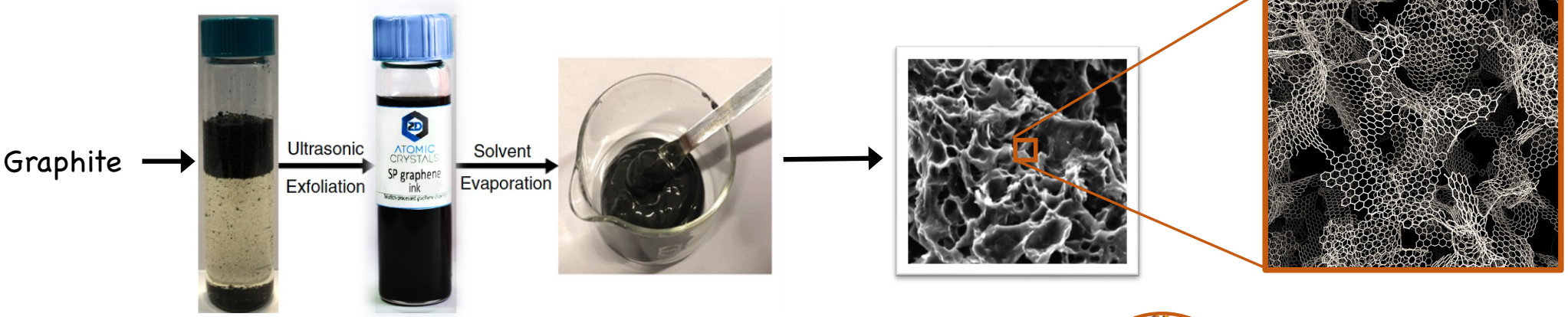
Use, cost, scalability Medium scalability, high cost, SiC substrate cannot be eliminated

Different graphene materials and their characteristics

2. nanoporous graphene

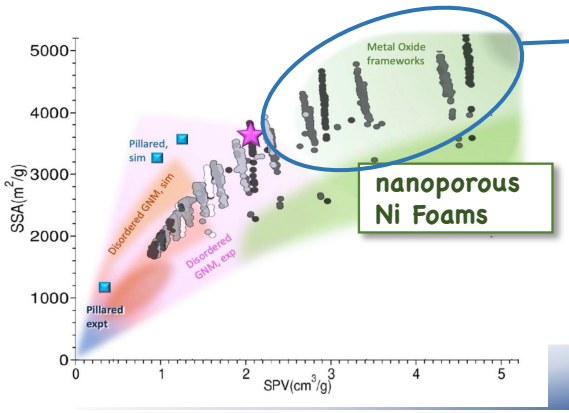
(from inks)

2.c From graphite(oxide) flakes inks "nanoporous scaffolds"



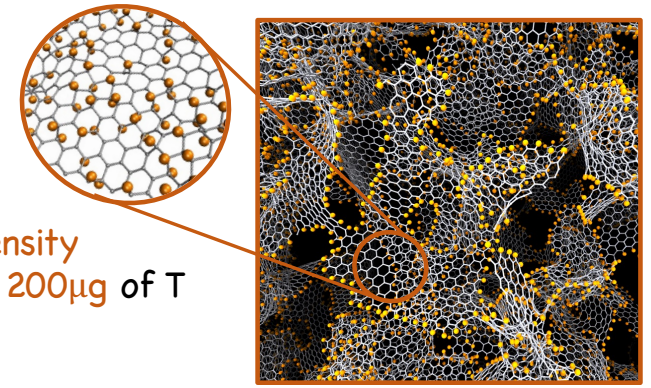
Intrinsic characteristics

- ✓ Very edgy and defective
- ✓ El mobility 5000-7500 $cm^2/V{\cdot}s$
- ✓ Exposed surface very variable, but potentially very high, due to edges



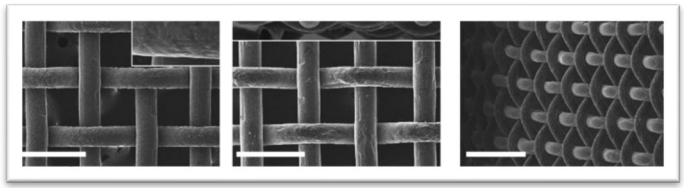
T(H) loading capability

- ✓ Chemisorption T:C 100% on edges
- ✓ ~10% on internal sites
  - ➔ Possible up to 50% loading
  - ➔ up to 10-15% gravimetric density
  - ➔ 2 mg of material could load 200µg of T



Use, cost, scalability

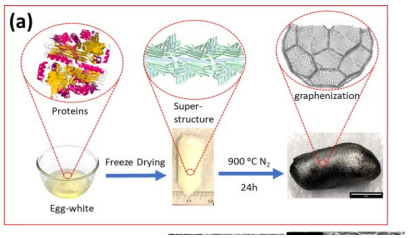
- ✓ Low cost, high scalability
- ✓ Very versatile: thin films (nm) can be transferred on grids/supports of different materials and types or directly sprayed on supports



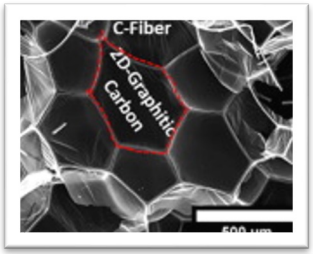
Different graphene materials and their characteristics

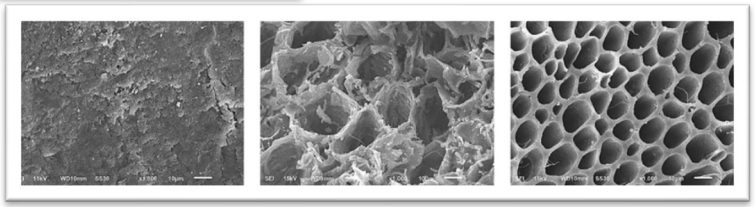
2.d Pyrolysis of biological materials

Pyrolysis of amyloid bio-material (egg white, meat collagen)

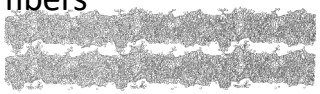


Treatment of vegetables (rice straw, palm fronds...

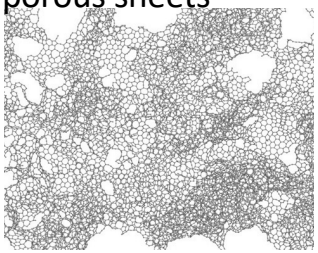




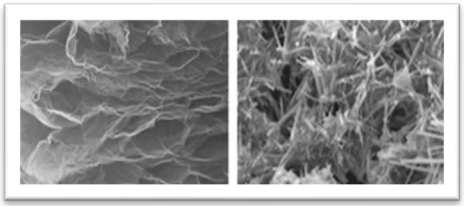
fibers

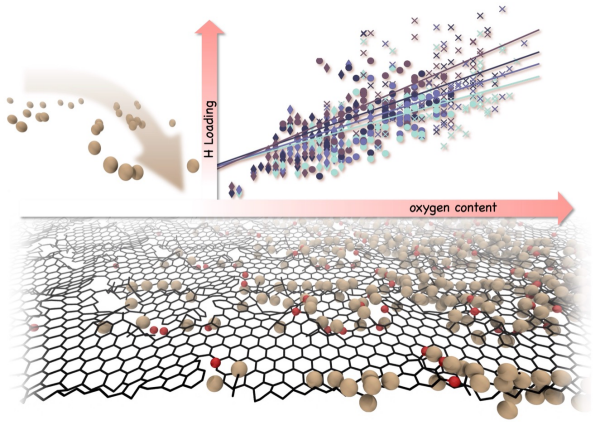


porous sheets



2.e (reduced) graphene oxide





2. nanoporous graphene

Intrinsic characteristics

- ✓ Locally disordered and defective
- ✓ Inclusion of O and N
- ✓ Fibers and few layers sheets
- ✓ Low conductance

T(H) loading capability

Loading similar to that of nanoporous scaffolds from graphite, enhanced by the presence of heteroatoms

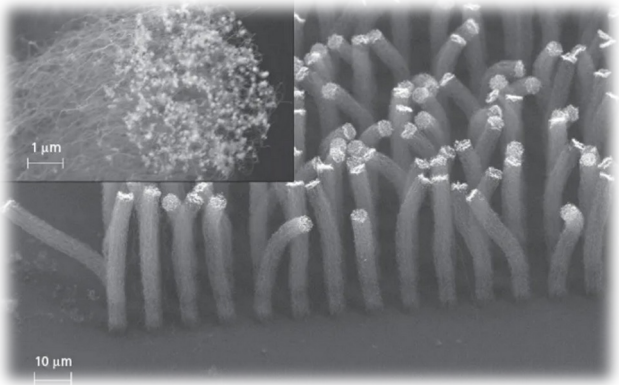
Use, cost, scalability

- ✓ Low cost
- ✓ High scalability
- ✓ Environmental sustaineability

Different graphene materials and their characteristics

3. Other graphene related materials

3.a nanotubes



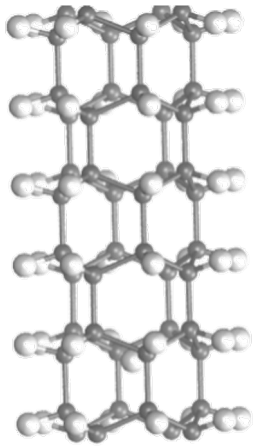
Intrinsic characteristics

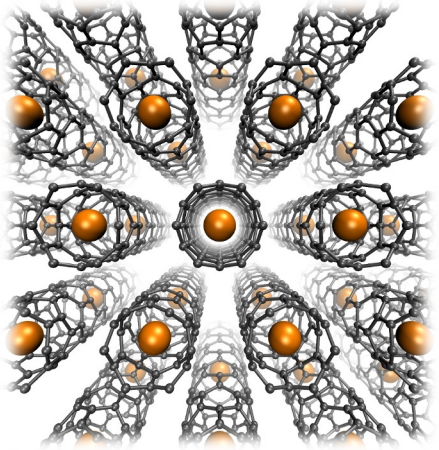
- ✓ Bundles of nanotubes vertically grown
- ✓ High mobility

T(H) loading capability

- ✓ Up to 12% GD (~60% T:C) by external chemisorption
- ✓ Theoretical possibility of encapsulation (~0.5% GD, 6% T:C)

Use, cost, scalability High cost, low scal





3.b fullerenes

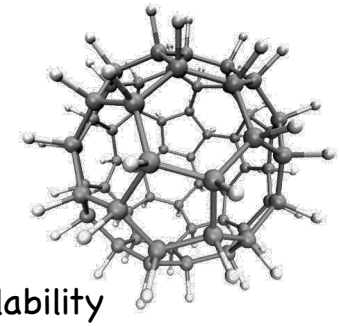
Intrinsic characteristics

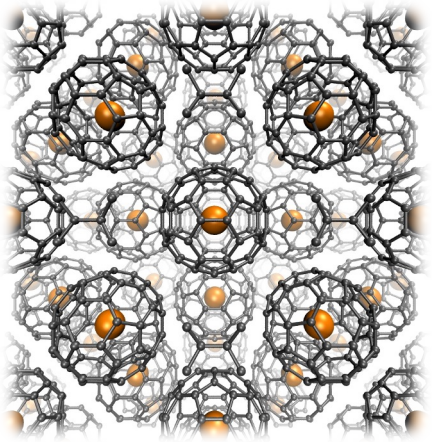
- ✓ Fullerite crystal
- ✓ semiconductor

T(H) loading capability

- ✓ Up to 15% GD (~80% T:C) by external chemisorption
- ✓ Theoretical possibility of encapsulation (~0.5% GD, 6% T:C)

Use, cost, scalability High cost, low scalability

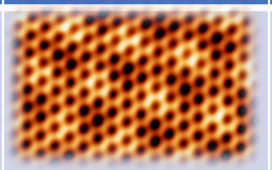
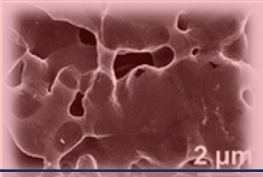
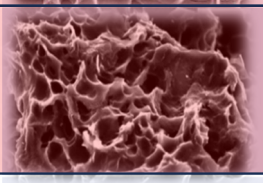
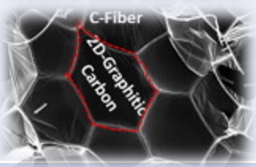
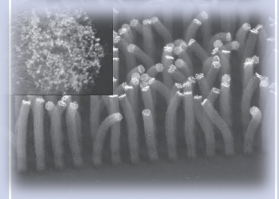




But… **encapsulation could be possible** and the almost free potential could be useful for CNB

Different graphene materials and their characteristics

Take home meassage: there is room for optimization of the material to the Ptolemy scopes

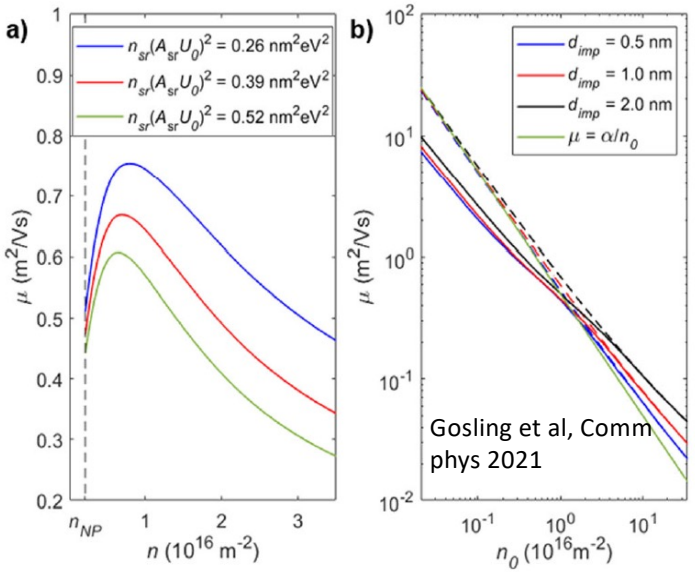
material	structure	image	Control of T binding potential	Hloading (T:C)	Gravimetric density	Scalability	Size for 200 µg	Adaptability different supports
Epitaxial	ideal		high	~100%	20%	low	100x100 cm^2 X 0.3nm thickness monolayer	Not easy
Nanoporous from foam	locally flat, seamless		high	~100%	20%	average	10x10 cm^2 X 100 nm thikness Porous layer	easier
Nanoporous from inks	Many edges		average	~50-60%	10-15%	high	100x100 cm^2 X 10 nm thickness Sprayed layers	easy
Nanoporous bio origin	Very defective, but seamless		low	~50-60%	10-15%	high	100x100 cm^2 X 10 nm thickness	easy
Nanotubes/ fullerenes	Controlled		high	~60%, 12%	15% , 0.5%	Quite low	10x10 cm^2 X 1 µm thickness 10x10 cm^2 X 30 µm thickness	Not easy

Electronic properties of tritiated materials

conductance $\sigma = e\,\mu(n, n_d)\,n\left(E_g(n_d)\right) = e\,\mu(\mathrm{S,L})\,\mathrm{n(S,L)}$

- electronic mobility
- carriers density (**doping**)
- electronic band gap
- defects density (included adatoms, T)

Tritiation modifies mobility and doping

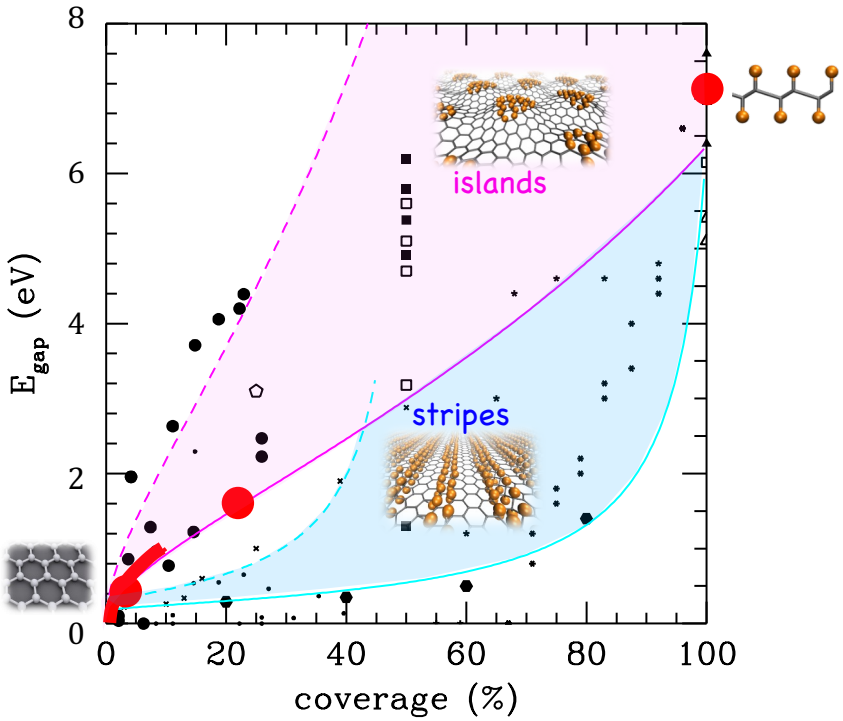


Take home messages

- ✓ Ultimately, everything again depends on S and L
- ✓ **Tritiation reduces the metallic character** of the material, but **patterning** could control this effect
- ✓ In general, tritiation and other disturbances of the graphene delocalization influence the **relaxation times of the system**

Tritiation opens an electronic band gap

- ✓ Confirmed both **experimentally** and **theoretically**
- ✓ Theoretical data are scattered
  → **gap opening** depends on distribution of T
- ✓ **Patterning** can be a way to **combine high load** with **small gap**



Relaxation of the system after T→He transformation

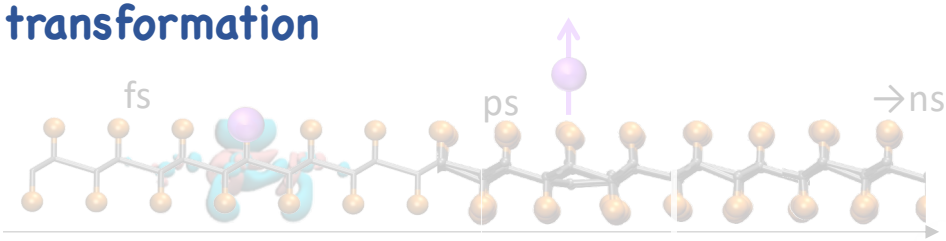
On the fs time scale:

- ✓ Immediately after decay "sudden" pot → He^{++}
- ✓ In the time τ the electronic system relaxes to the ground state → He
- ✓ As He moves, it feels intermediate potential → He^{+}
- ✓ The **final charge state** depends on the interplay between the recoil energy of He and the relaxation time τ

→ distribution of different final charge states

- ✓ But τ=τ(S,L) (1-100 fs)

→ dependence on load and structure

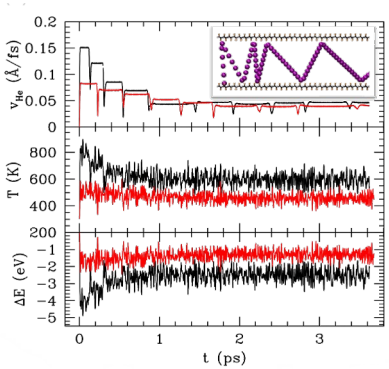


On the ps time scale:

- ✓ He is released and can hit other part of the substrate
- ✓ The recoil of the substrate excites vibrational modes

→ possible corrections to the β spectrum

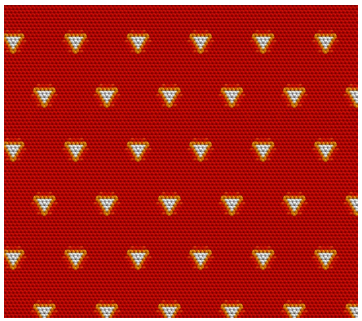
→ Heating/damage of the substrate

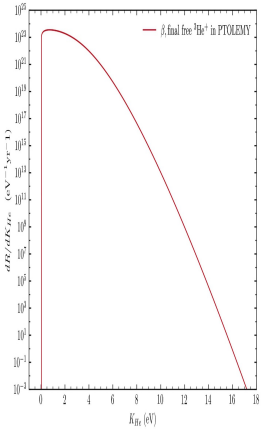


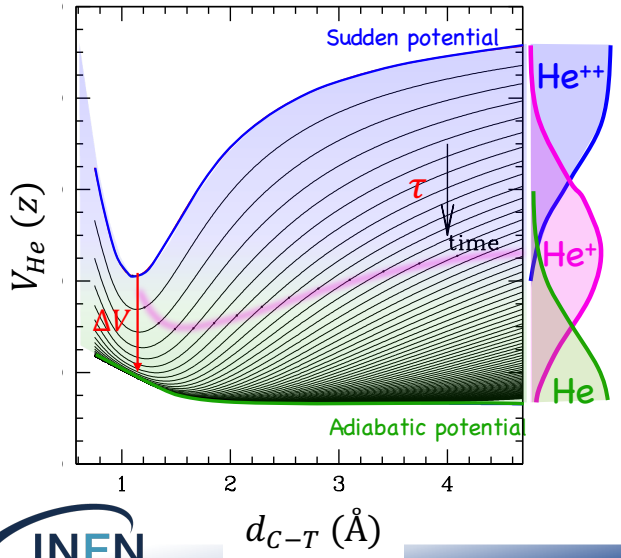
On the >ns timescale:

- ✓ Vibrational modes propagate and can generate specific signals related to the nuclear event

→ Vibrational excitation depends on Load (L) and structure (S)!! (again)



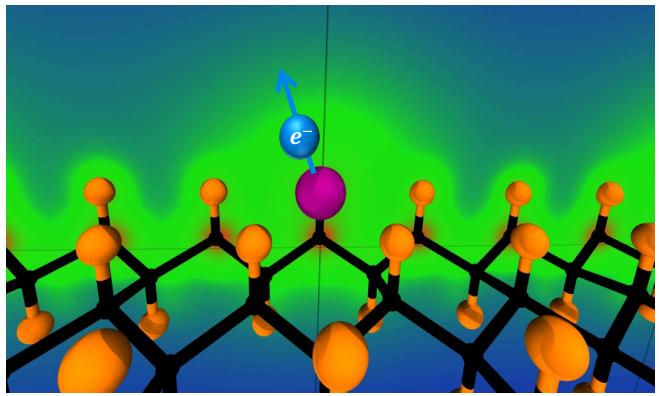




WORK IN PROGRESS

Interactions of β with the substrate

1. **Coulomb corrections** on β due to the strong electrostatic potential of the He and substrate can be calculated as a side result of DFT calculations. These depend on the loading and on the structure

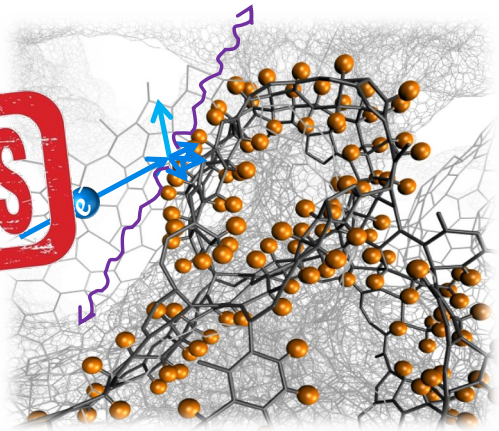


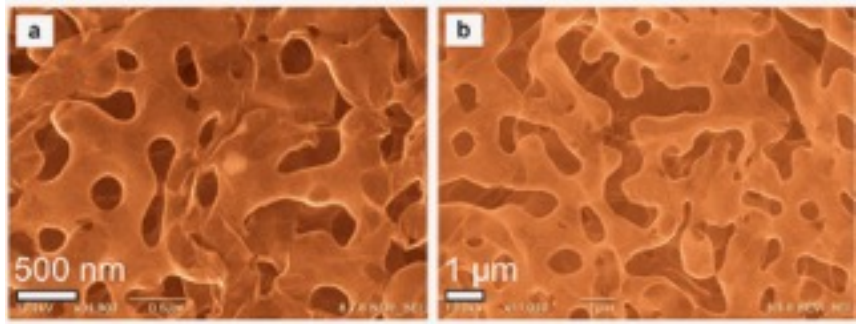
2. β also **releases energy** with other interactions with the substrate by
   - ✓ Primary scattering
   - ✓ Production of secondaries and scattering
   - ✓ Dissipation by interactions with electrons of the material
   - ✓ Dissipation by interaction with phonons of the material

These tasks are addressed by **F Pofi** with Monte Carlo simulations, but especially the last two are **strongly material dependent:**

- ✓ Loading (L) modifies the loss function and the phonons dispersion
- ✓ The global structure determines the average density and the number of interactions of the electron with the substrate

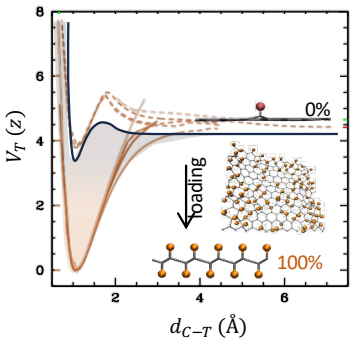
WORK IN PROGRESS

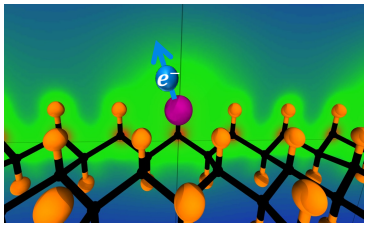




Summary

The **tritiated graphene material** is characterized by the structure of **pristine graphene** before loading (**S**) and **load and distribution** (L). These two (composite) parameters enters basically all properties relevant for the Ptolemy scopes:





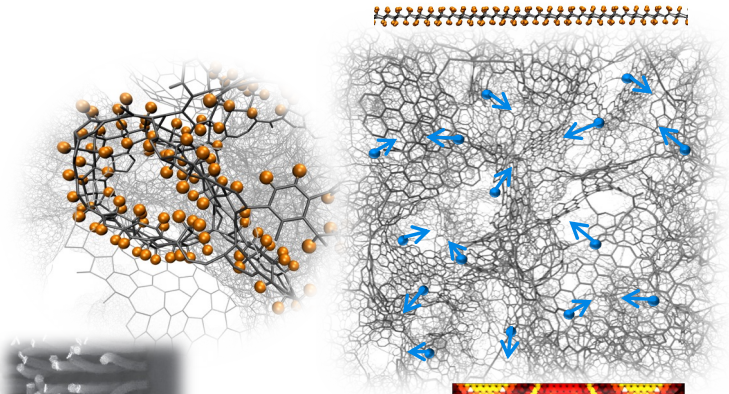
- ✓ Maximum amount of loadable tritium → sensitivity
- ✓ Potential of T and He → systematics
- ✓ Interactions of β → systematics
- ✓ Electronic properties → accuracy
- ✓ Mechanical and thermal properties → feasibility and durability

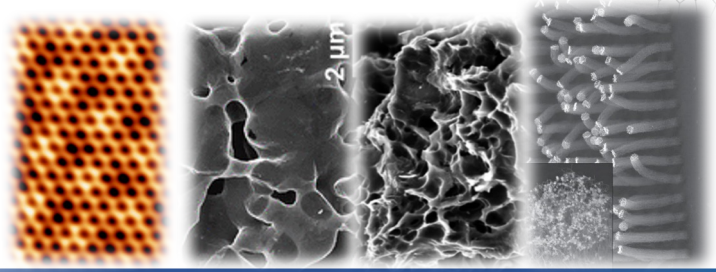
…

These could be called "materials effect" rather than solid state effects

The good new is that graphene materials are very different and versatile and there is room to tune them to the specific scope

The theoretical calculations can help in this





Thank you for your attention

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