Graphene as a substrate for tritium: hydrogenation and transmission

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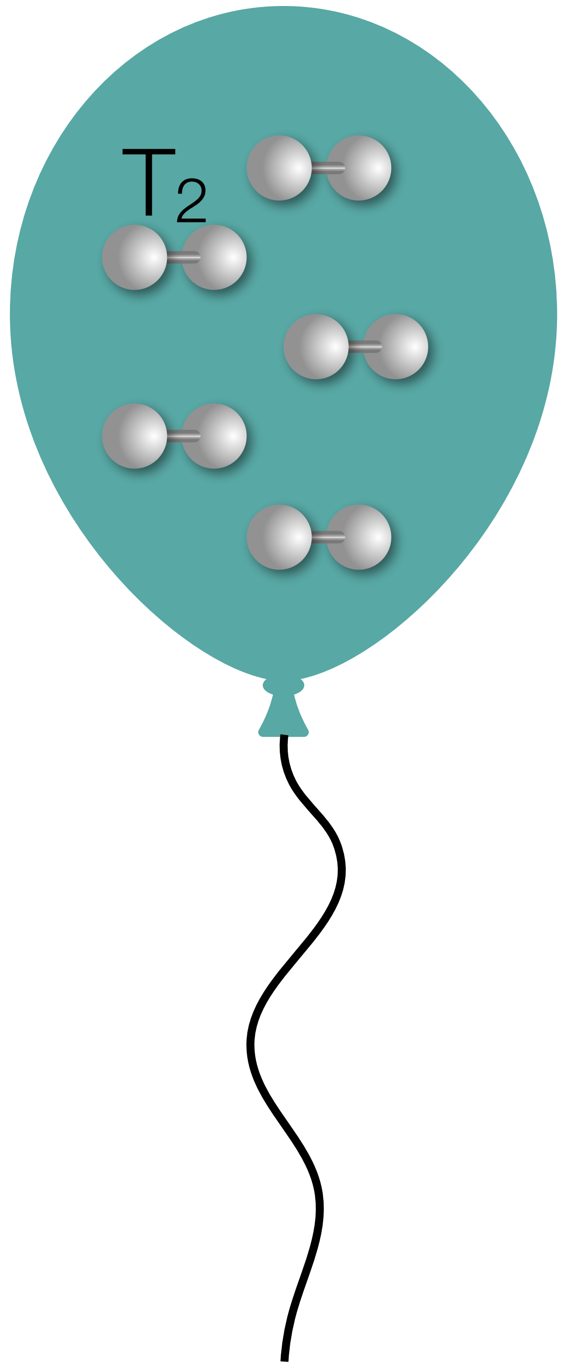
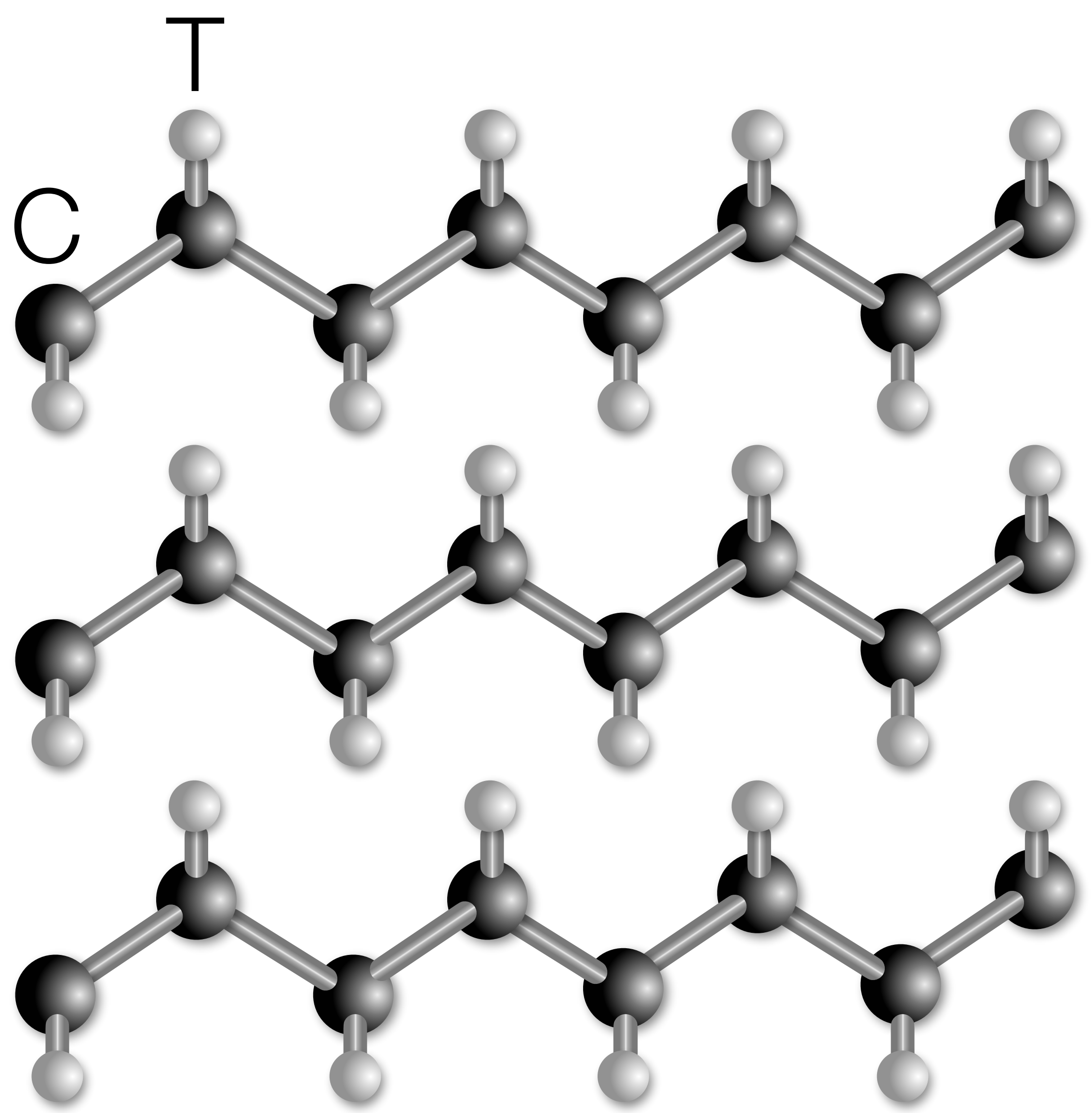
Tritiated C-nanostructures as PTOLEMY target

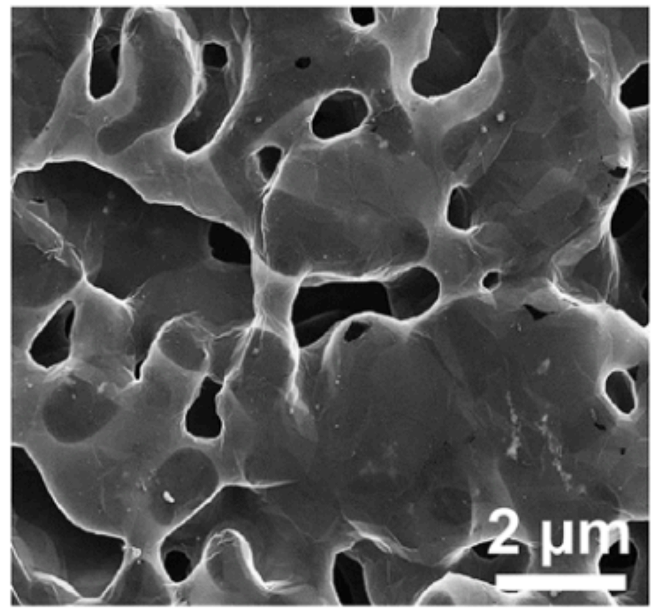
PTOLEMY experiment:

- ✤ Tritium in a solid-state target
- ✤ Tritium difficult to handle but same chemical properties of hydrogen
- ✤ Characterisation of hydrogenated graphene nanostructures
- ✤ Measure the transmission through graphene of electrons

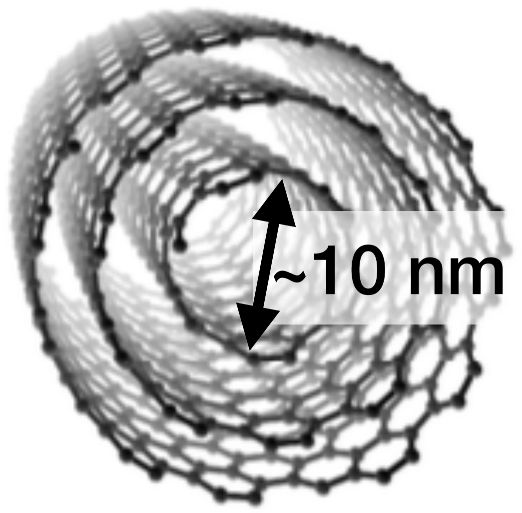
This talk!



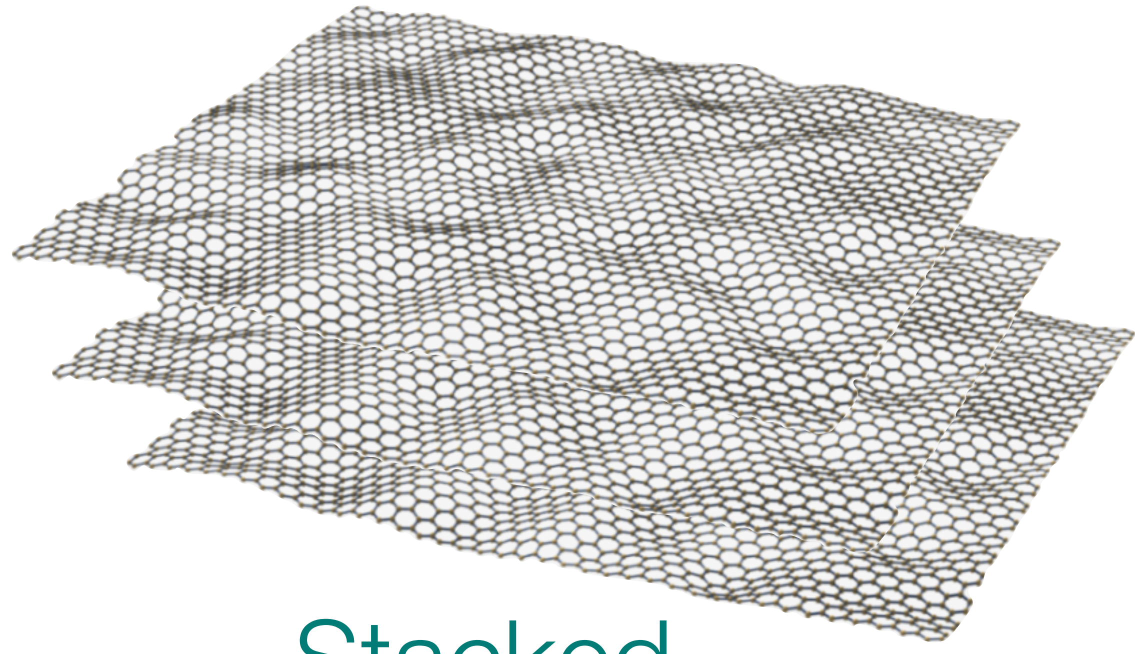




Nanoporous graphene

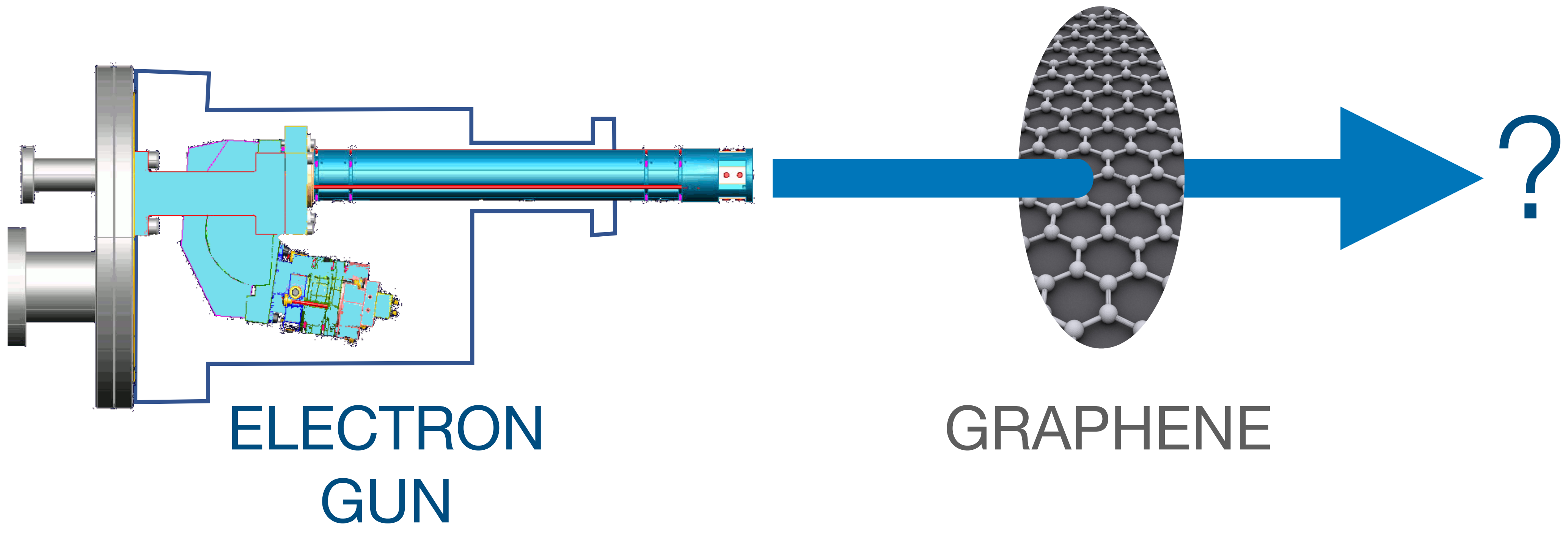


Carbon nanotubes



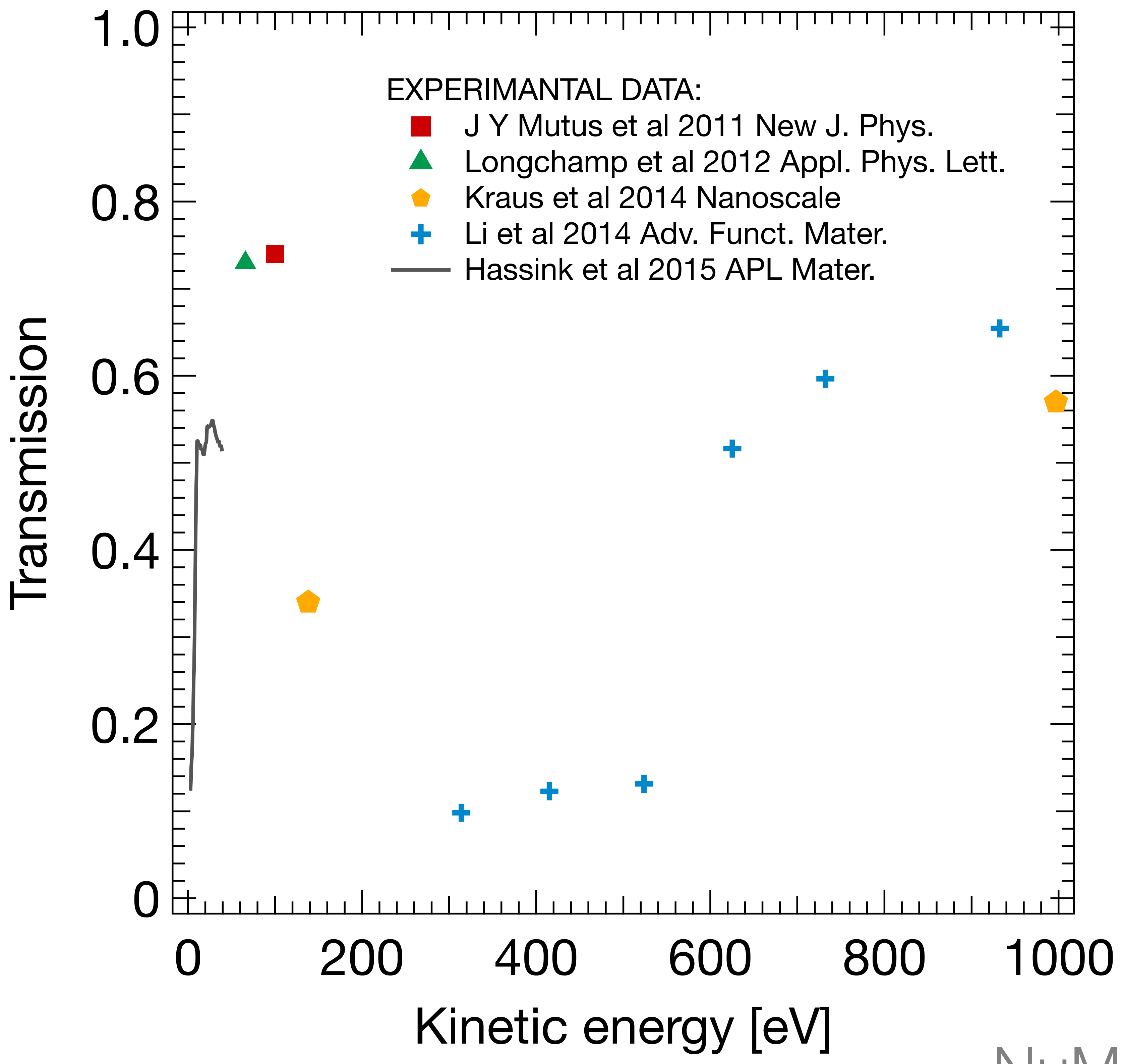
Stacked graphene

We can measure electron transmission < 1 keV



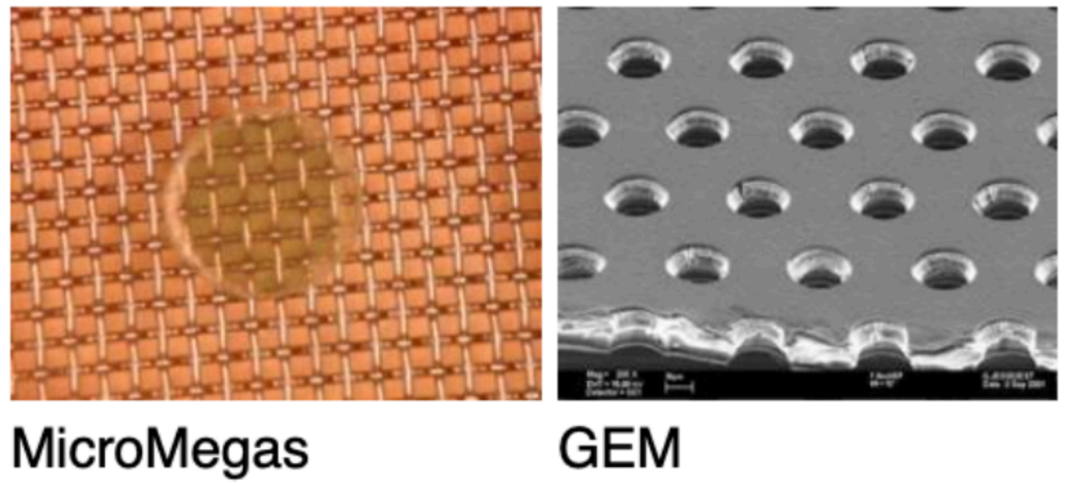
Electron Transmission measurement:

- Electron gun in our lab
- Electrons up to 900 eV
- Planning to extend energy up to 18 keV



A lot of physics to learn and of possible applications:

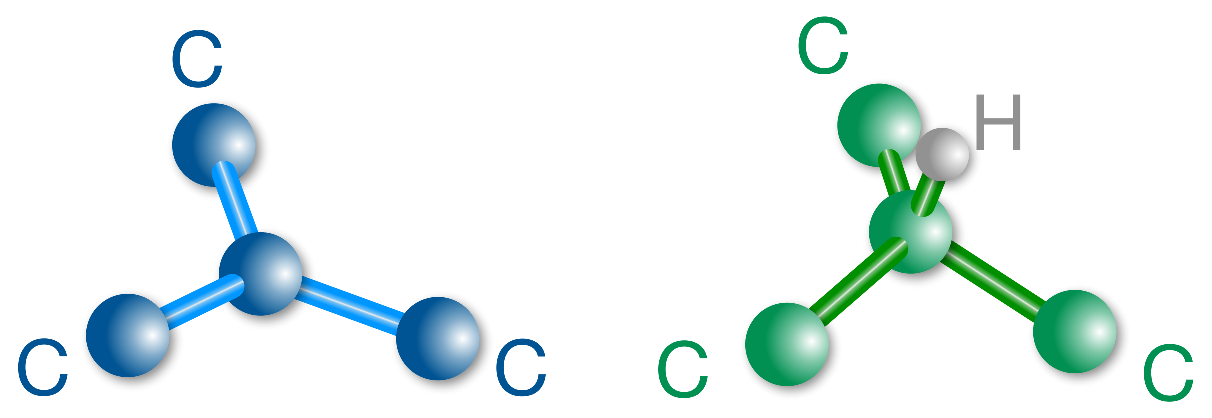
- Only a few experiments below 1 keV
- Discussion still open
- Integration of graphene in MPGD (transparency to electrons and impermeability to atoms)

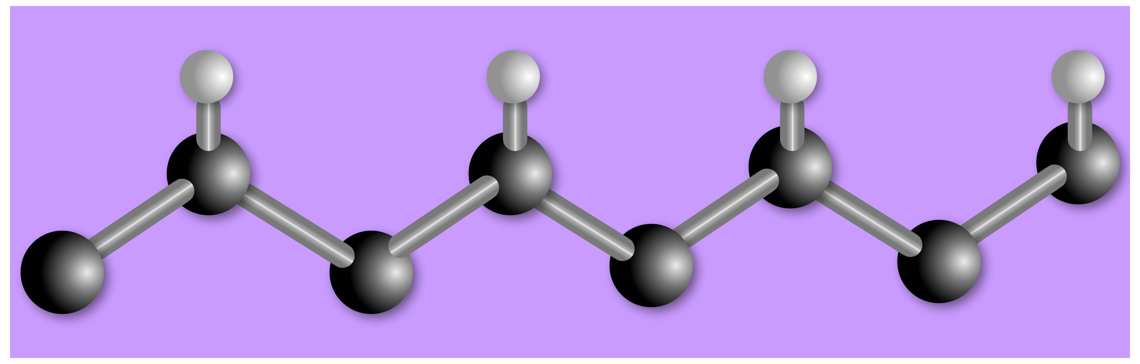


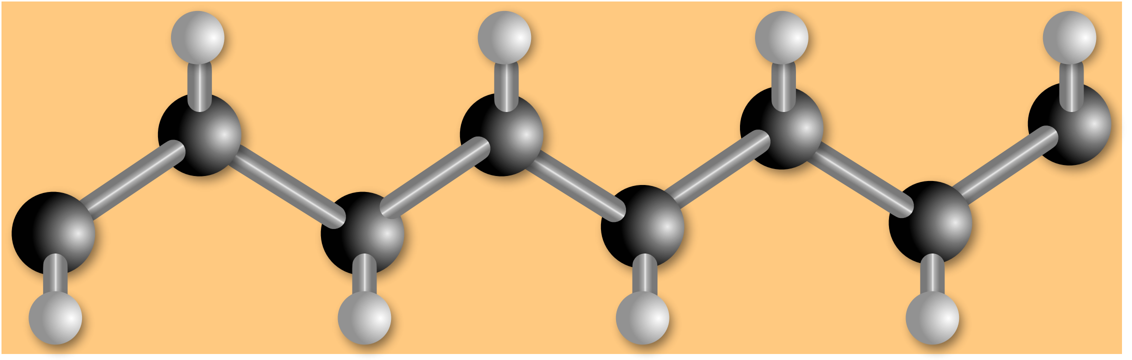
Graphene hydrogenation: experimental footprints

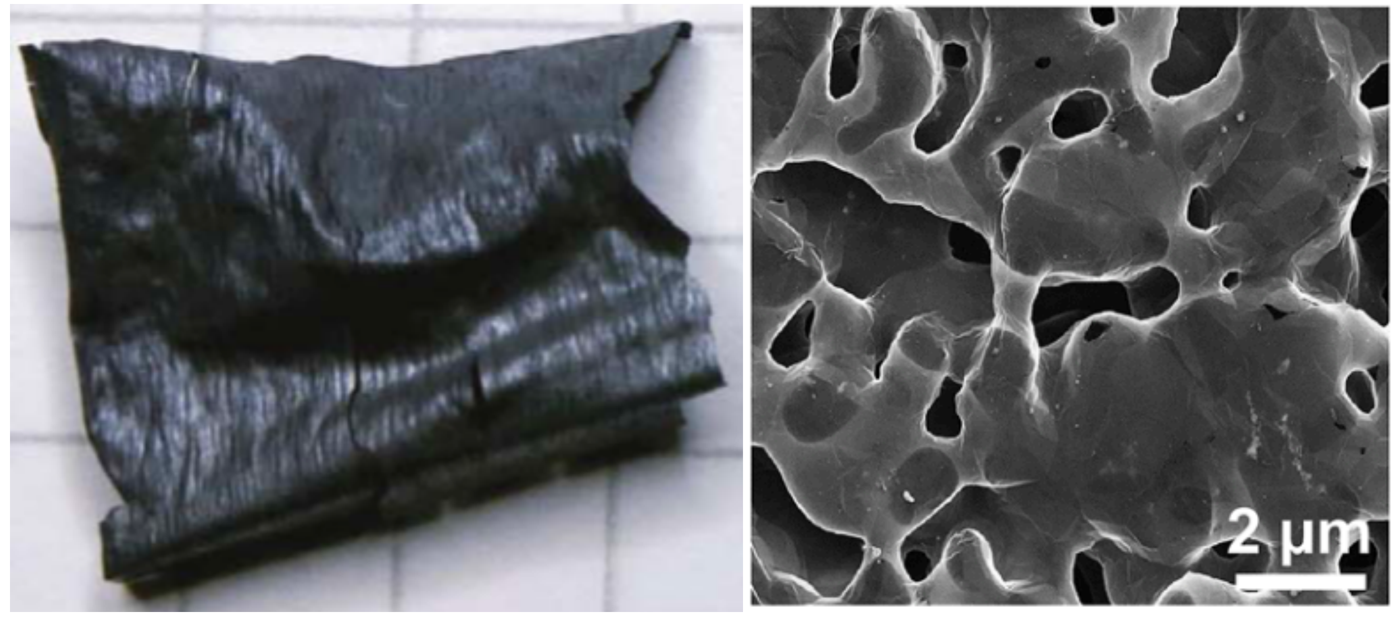
Hydrogen bonding to graphene:

- ✤ C bonds changes from sp^2 to sp^3
- ✤ Band gap opening
- ✤ Most stable CH morphologies 1-side and 2-side









Nanoporous graphene hydrogenation seems to realize in 2-side mono- and bi- layer structures

Betti, M.G. *et al.*, *Nano Letters* (2022), https://doi.org/10.1021/acs.nanolett.2c00162

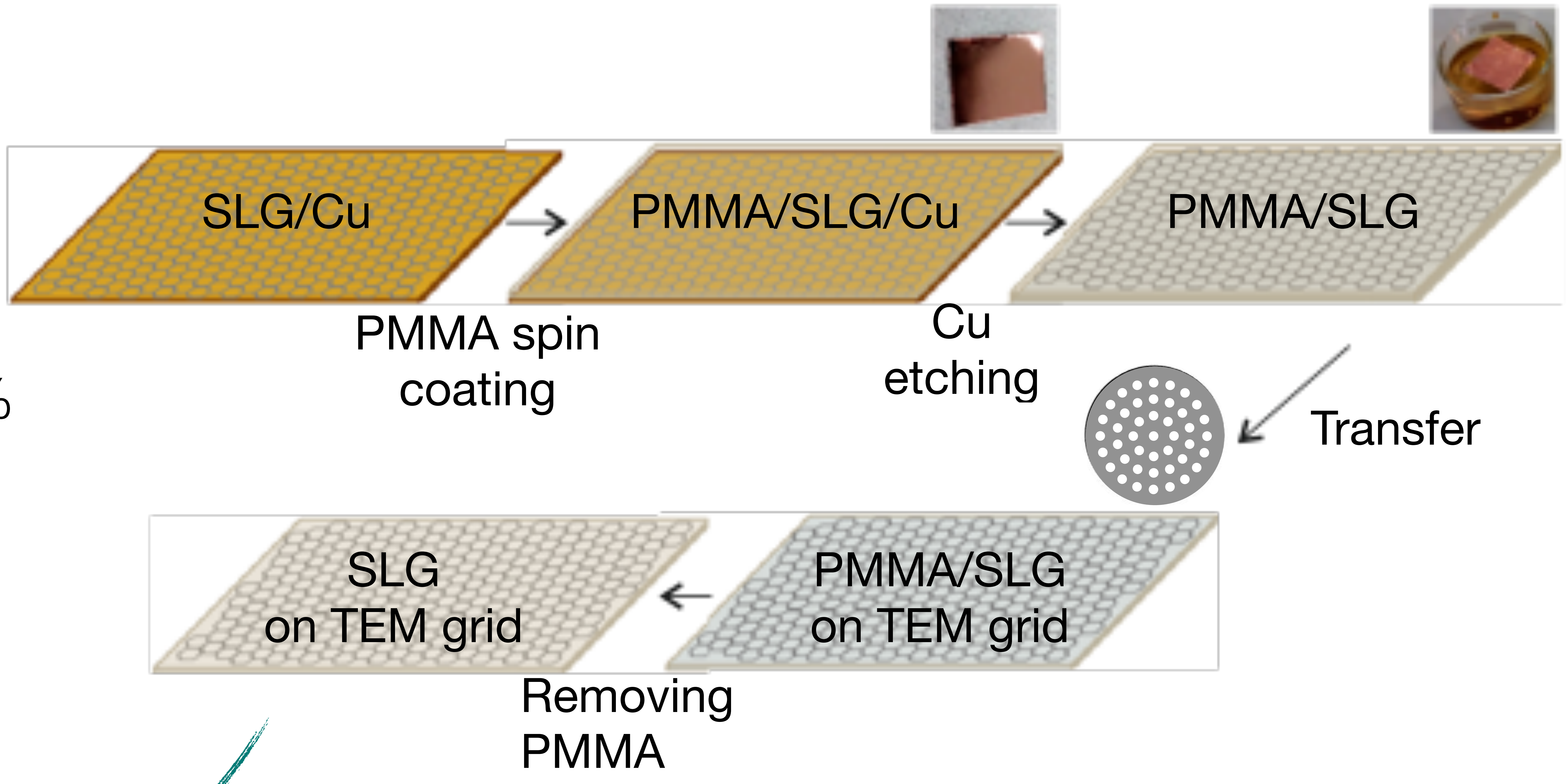
↓

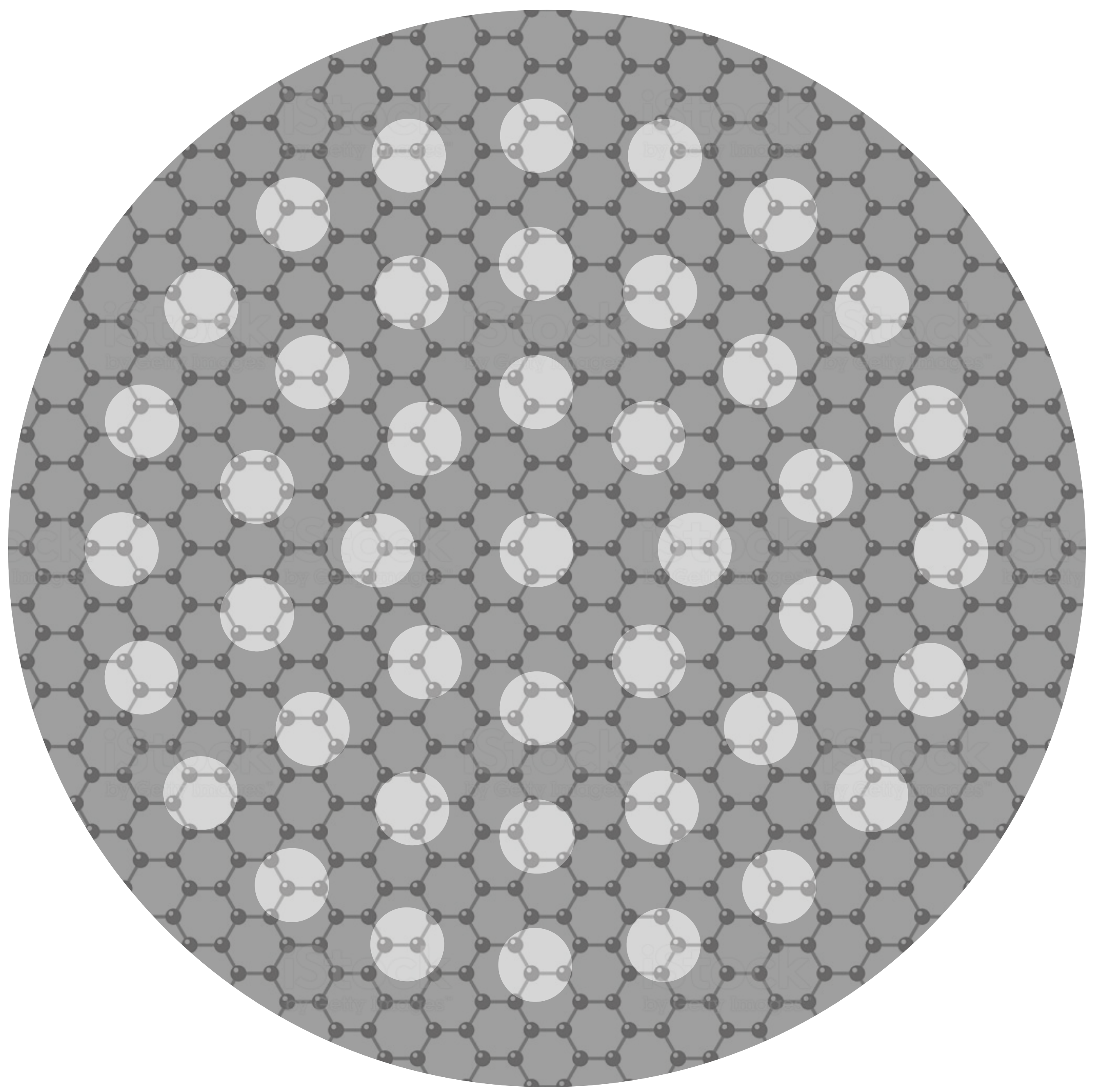
Hydrogenation of suspended graphene as a starting point to better understand

Graphene growth and transfer on metallic grid

Monolayer graphene on nickel grid:

- ✤ G2000HAN - Ted Pella Inc.
- ✤ Hole width 8 μm
- ✤ Nominal geometrical transmission 41%



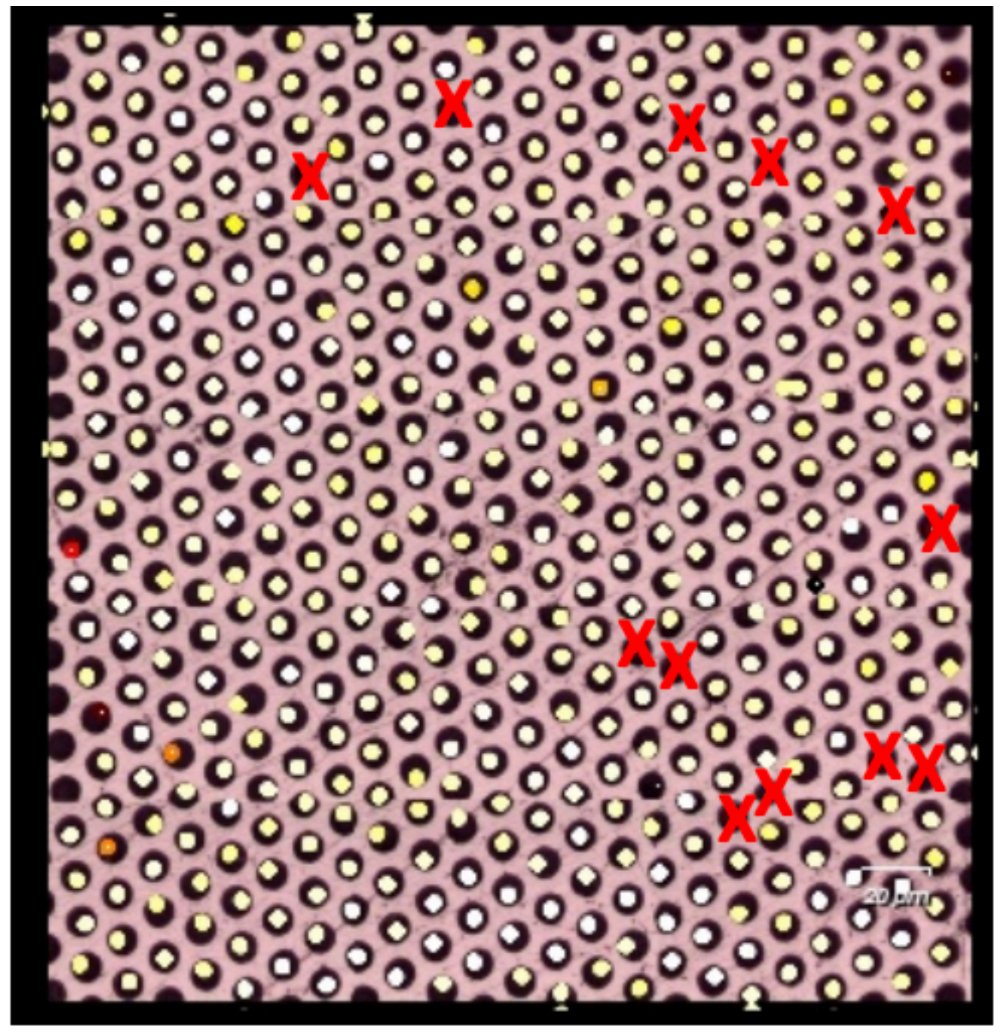


PMMA = Poly-methyl-methacrylate $(C_5O_2H_8)_n$

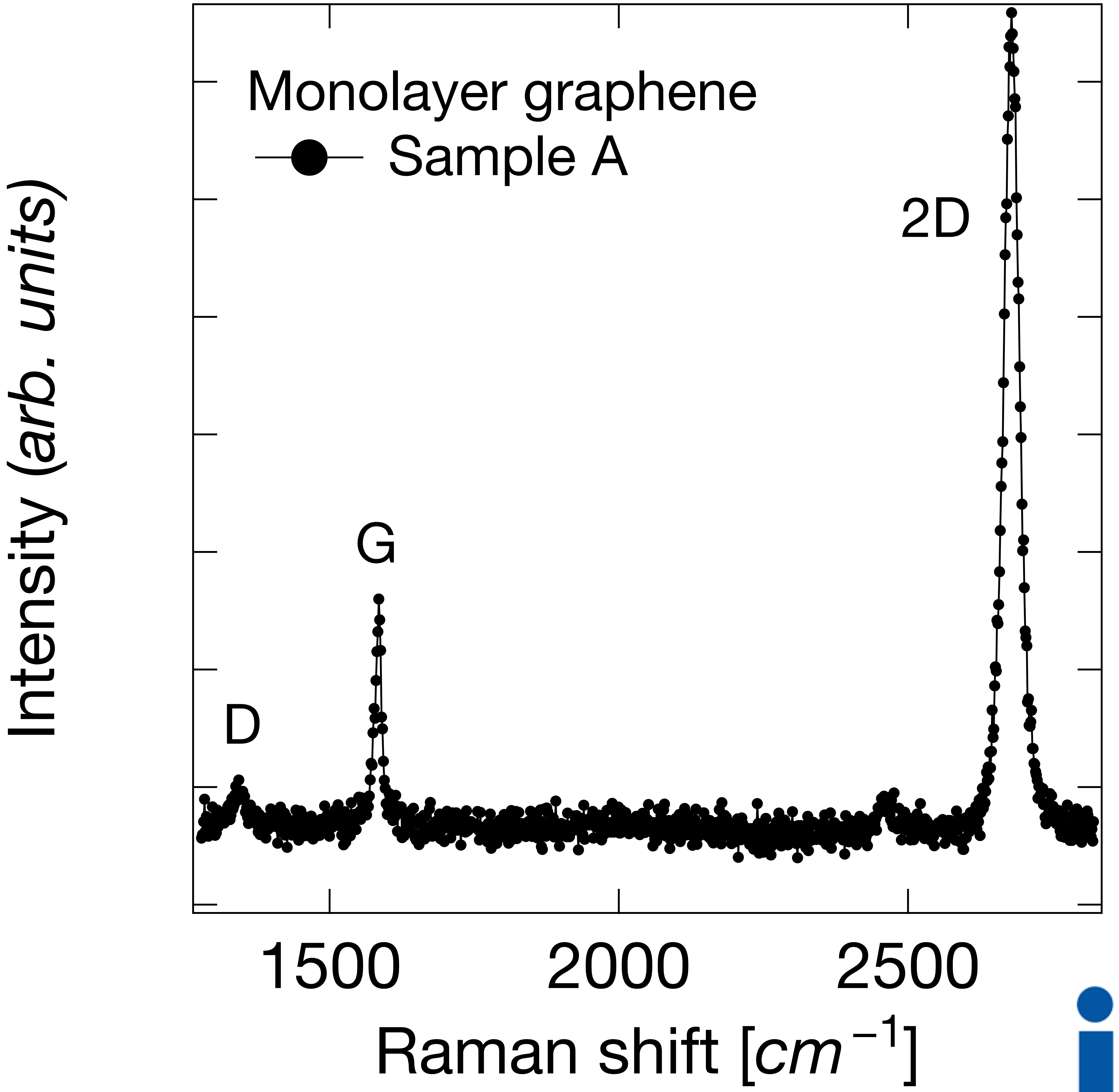
Full coverage good quality graphene

Micro-Raman maps:

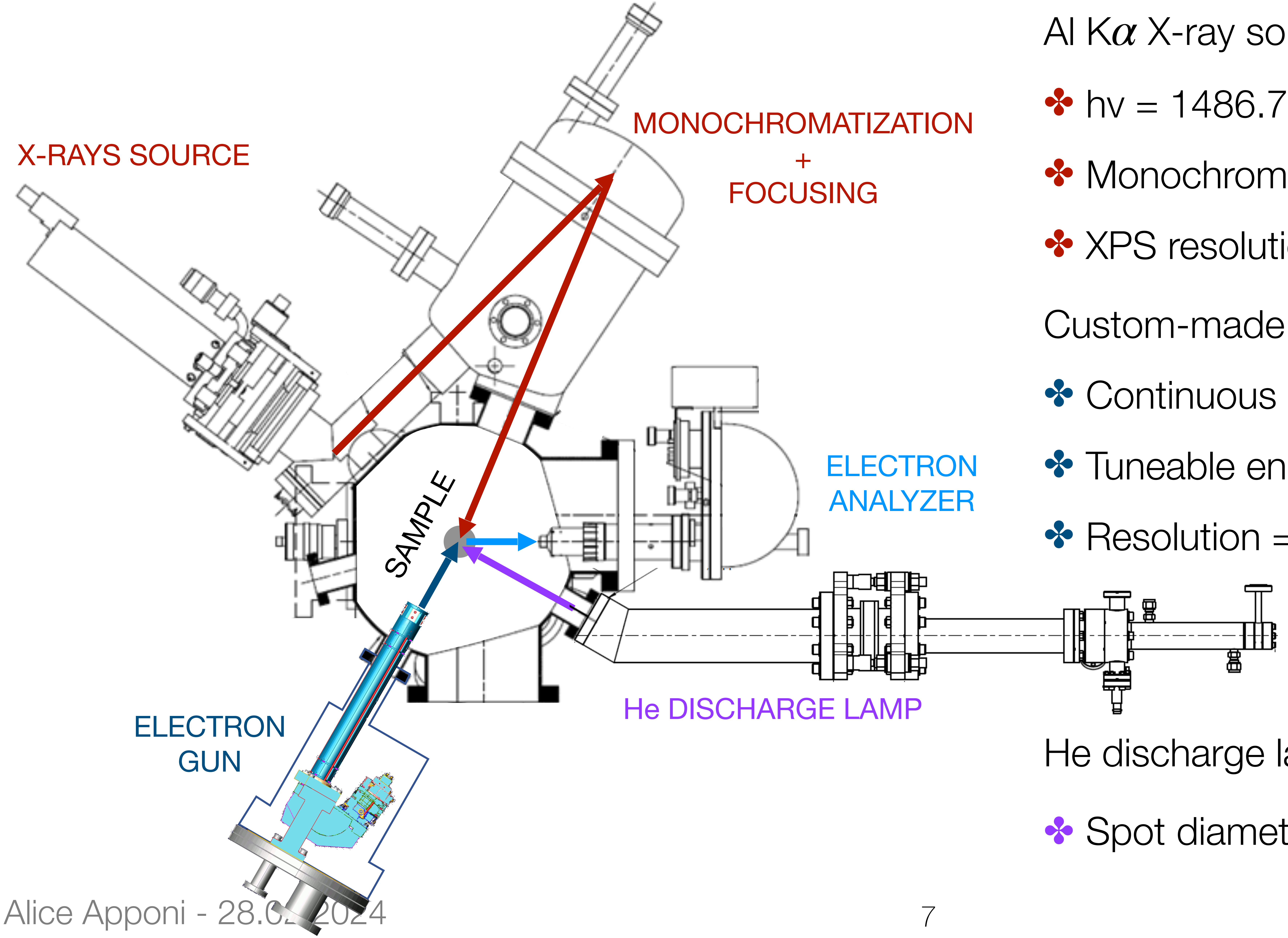
- Full coverage achieved
- Few spots without graphene X
- From typical spectrum low D peak, prominent G and 2D peaks



Good quality!



The LASEC experimental chamber



Al Kα X-ray source:

- hv = 1486.7 eV
- Monochromatized beam
- XPS resolution = 0.46 eV

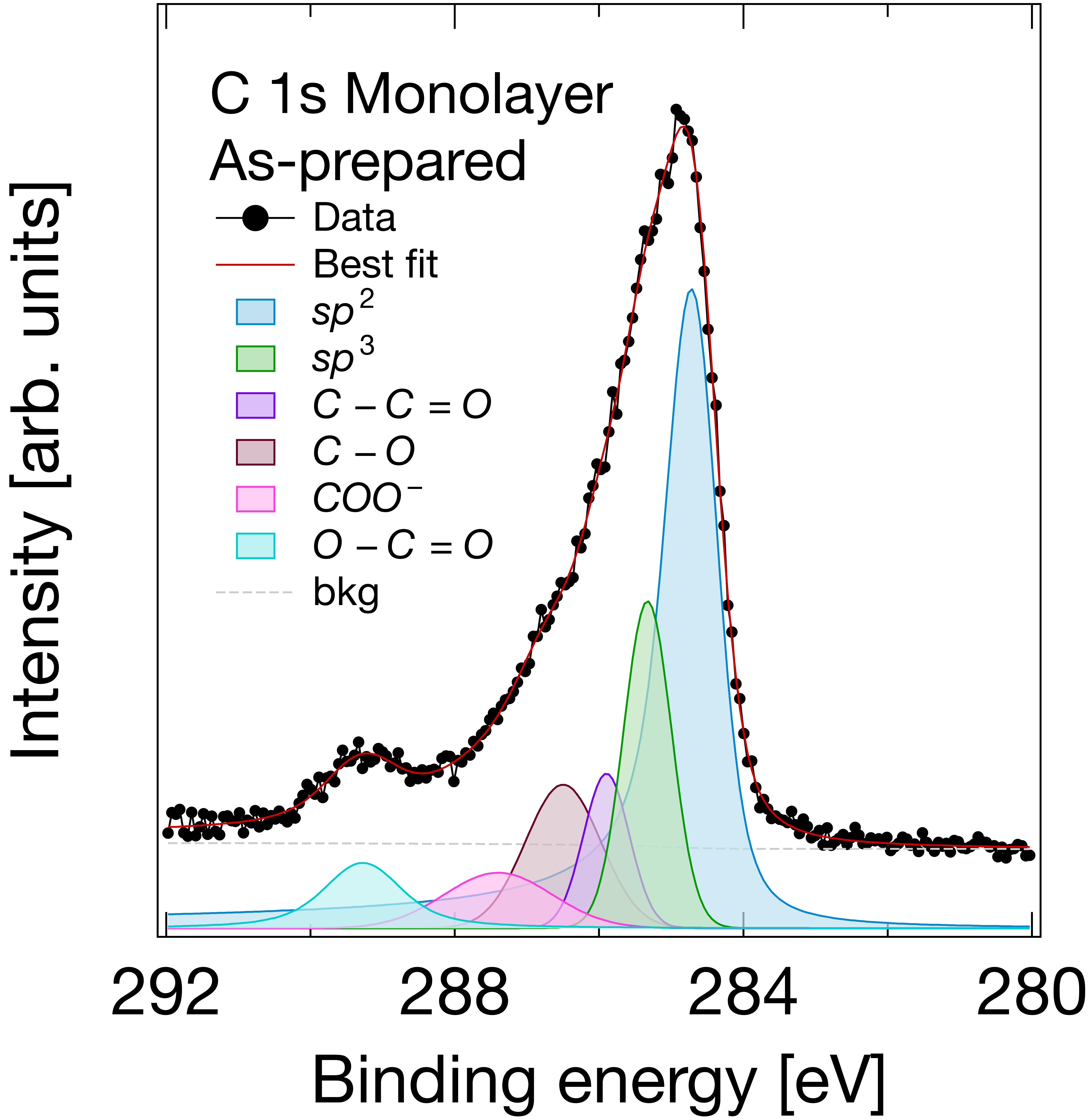
Custom-made monochromatic electron gun:

- Continuous electron beam
- Tuneable energy 30 - 900 eV
- Resolution = 45 meV

He discharge lamp:

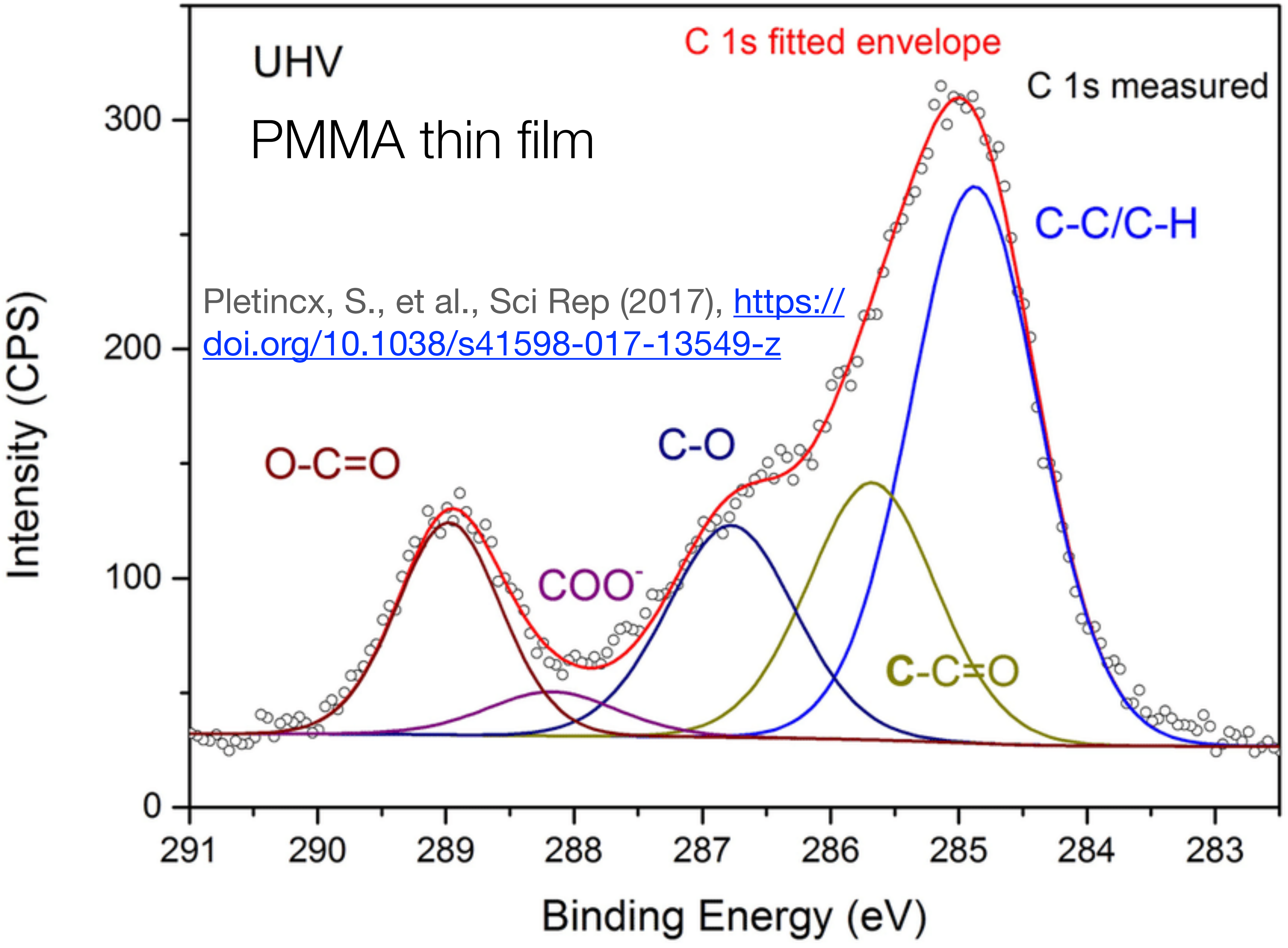
- Spot diameter 300 μm

XPS reveals high contamination



Monolayer sample measured as prepared:

- ✤ High contamination
- ✤ PMMA residues due to graphene transfer
- ✤ Cleaning treatment is necessary



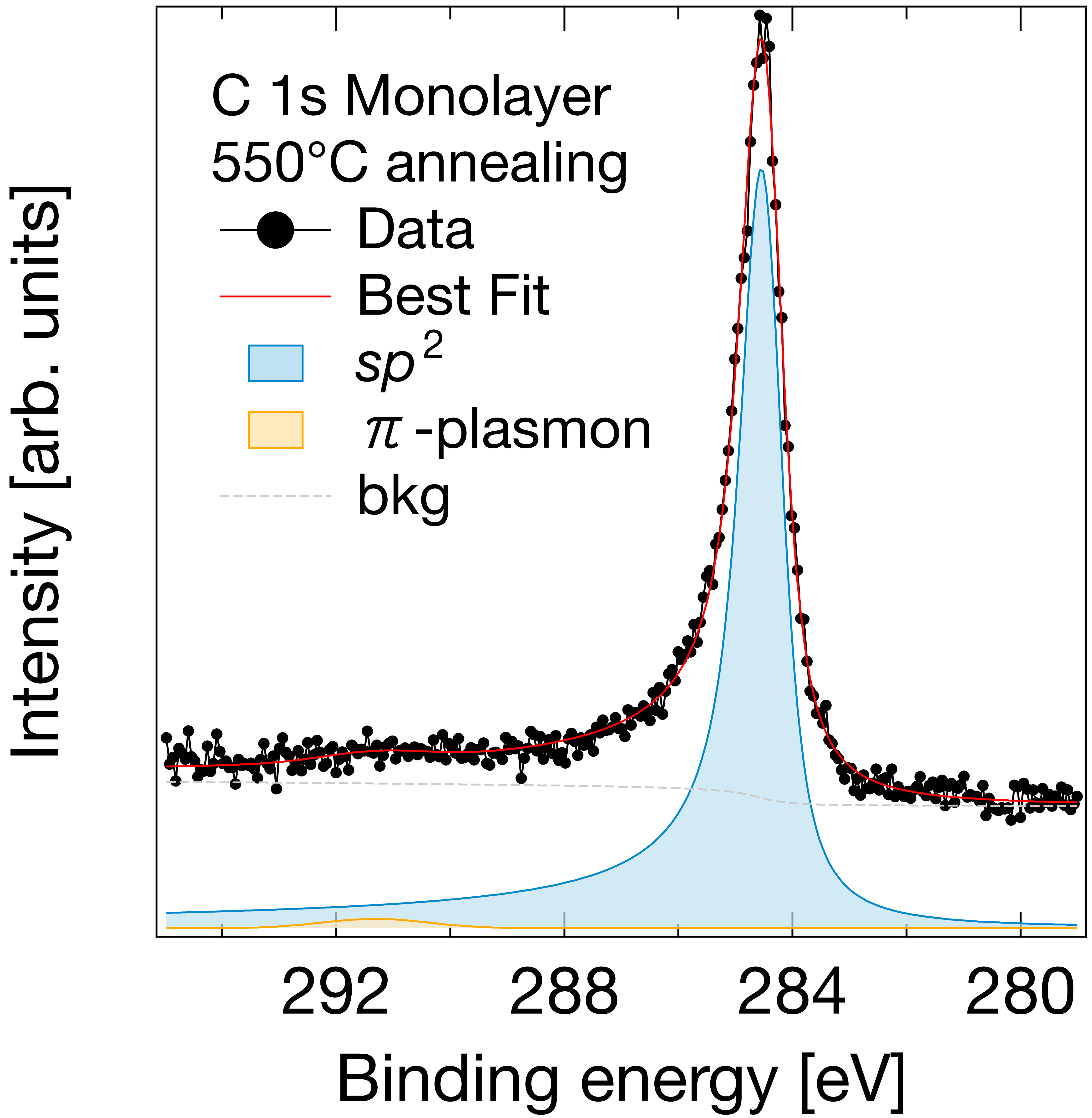
Pletincx, S., et al., Sci Rep (2017), https://doi.org/10.1038/s41598-017-13549-z

High temperature annealing: good quality graphene

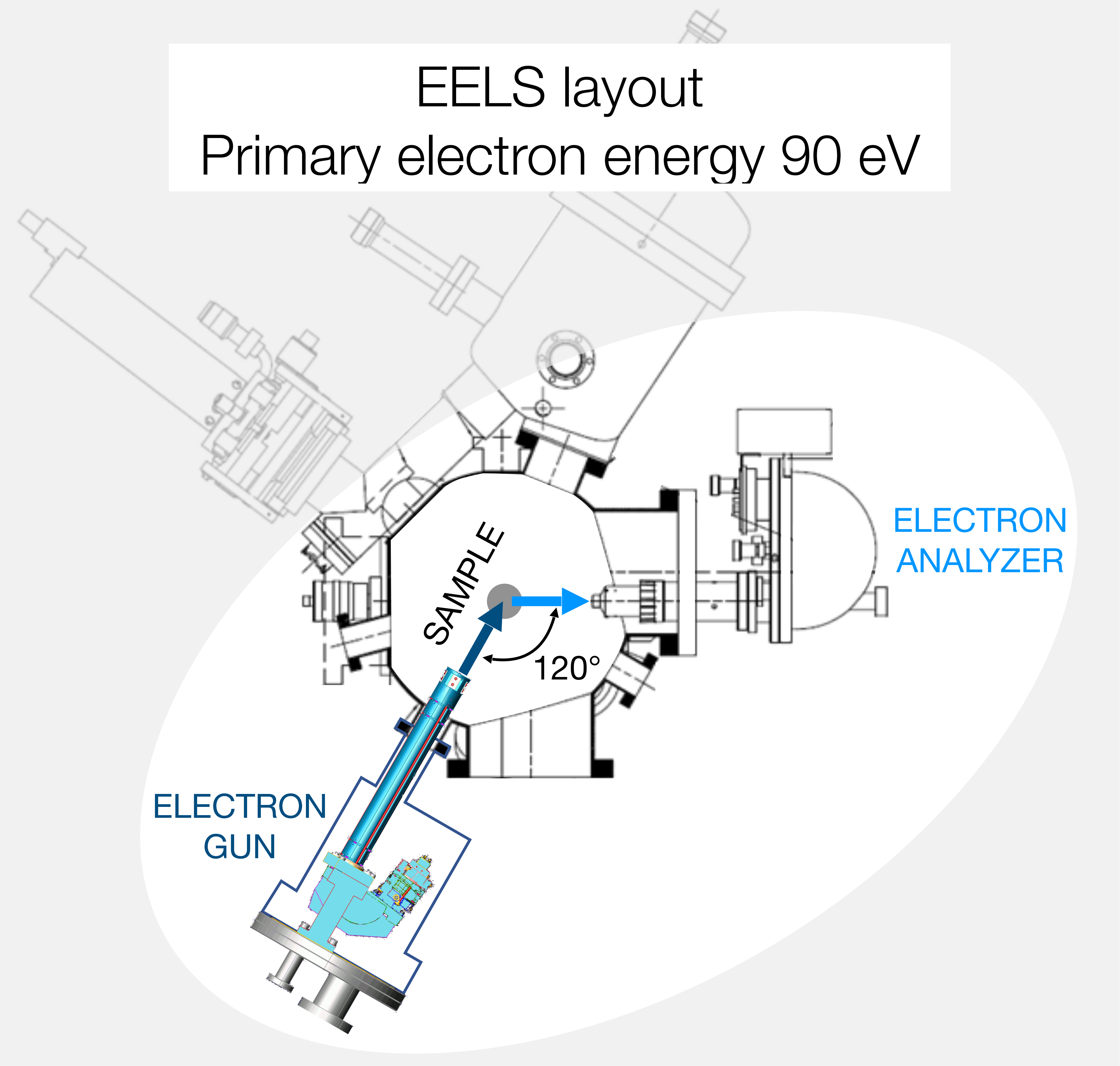
550°C annealing
in vacuum

C 1s spectrum reveals a good quality graphene:

✤ Purely sp² line-shape

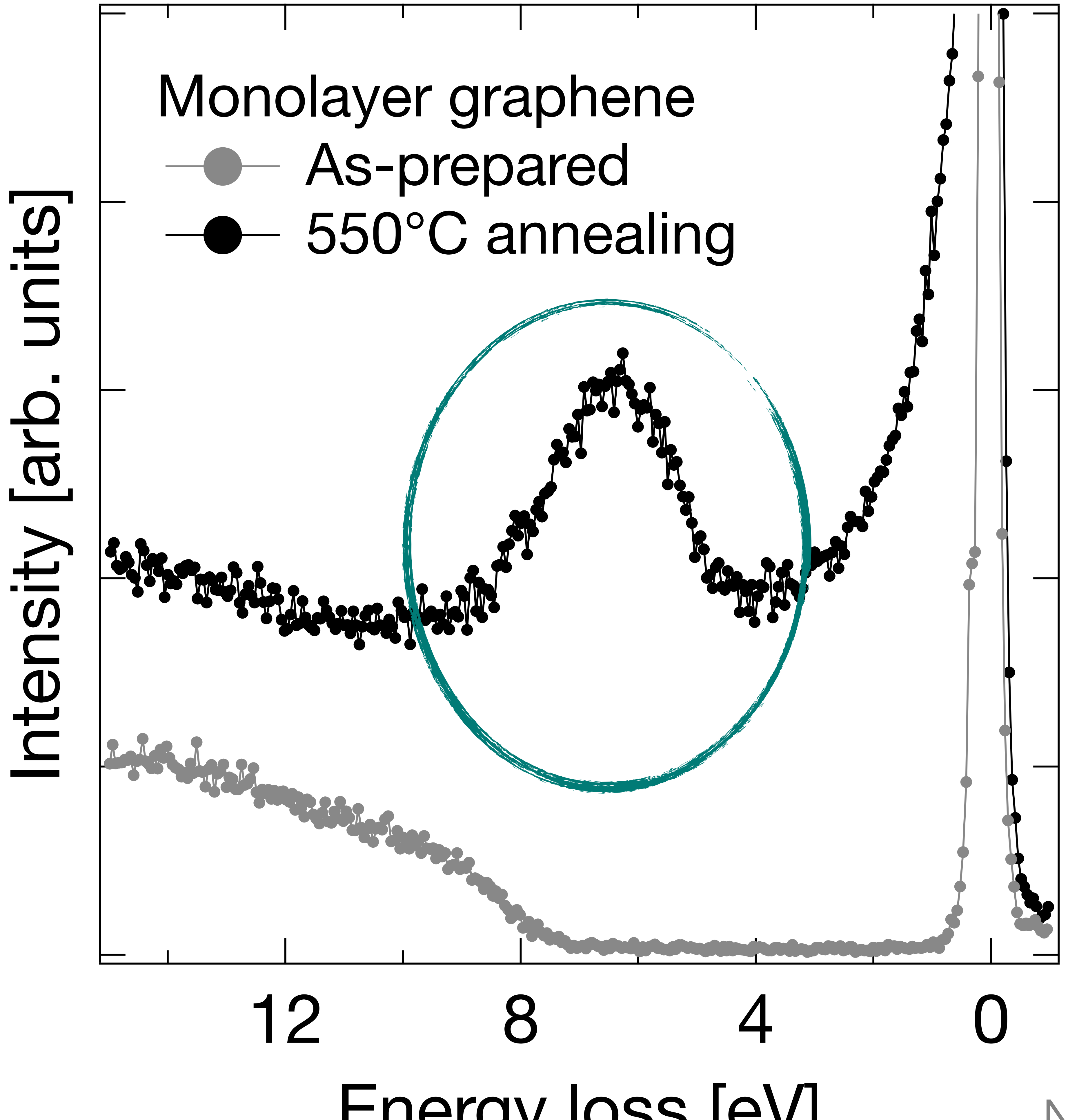


From insulator to π-plasmon excitation

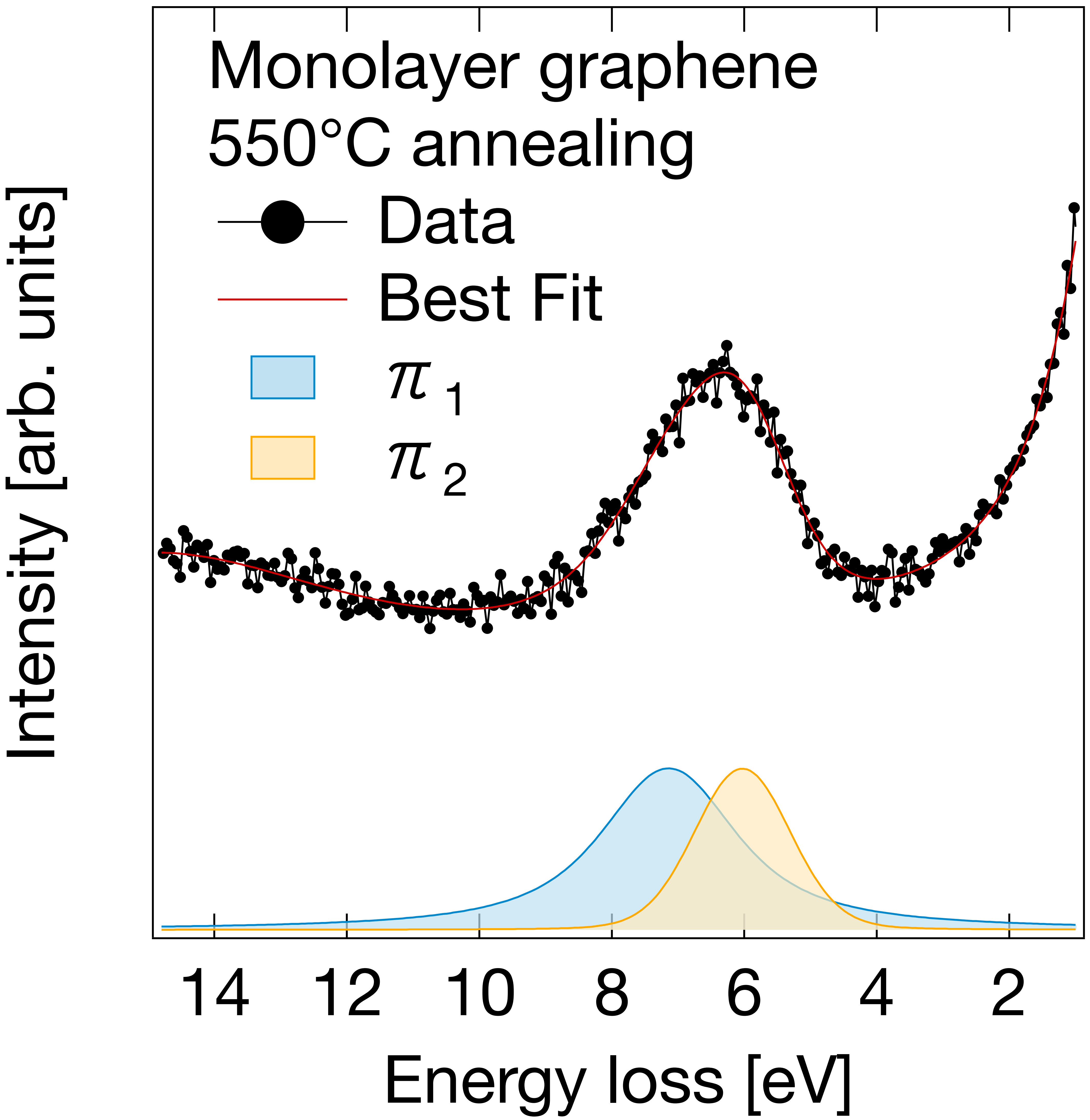


Focus on π-plasmon:

- Collective excitation associated sp^2 domains (> 5 nm)
- Footprint of good quality!

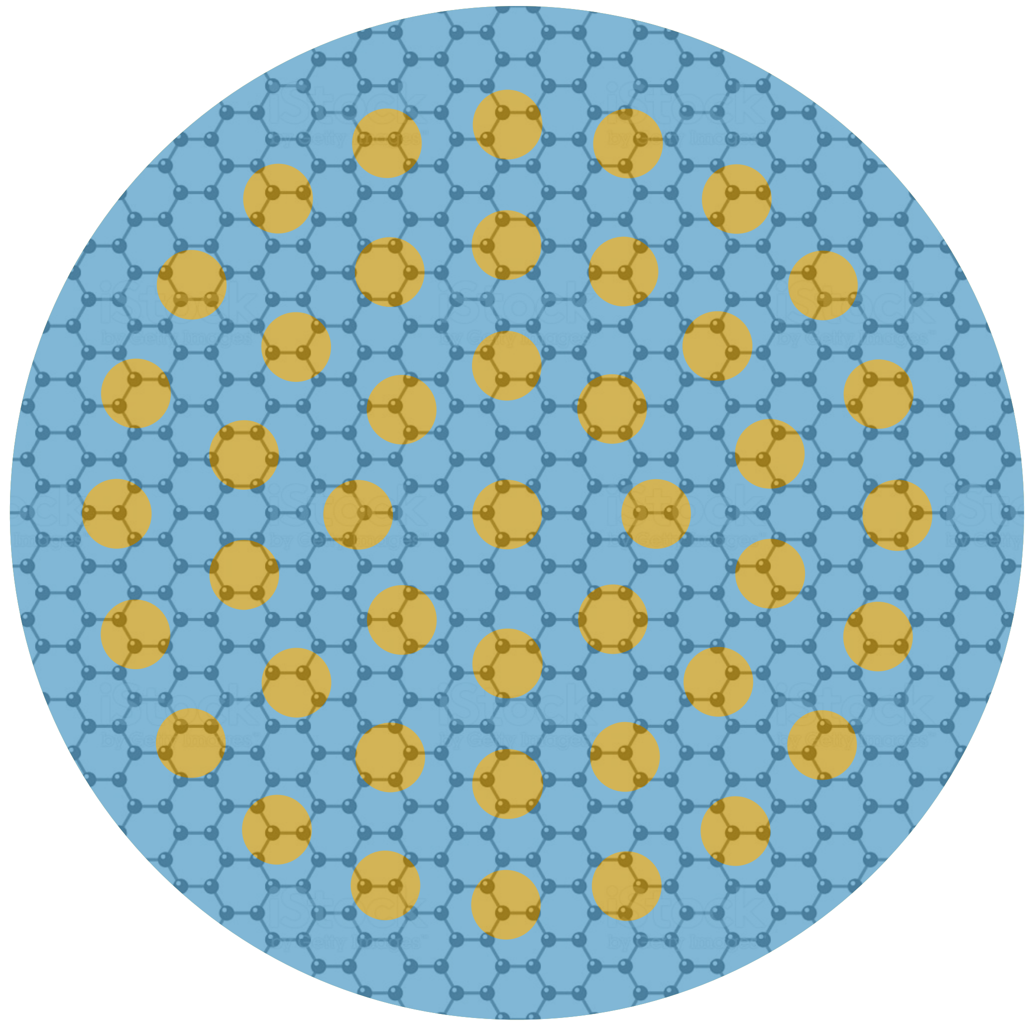


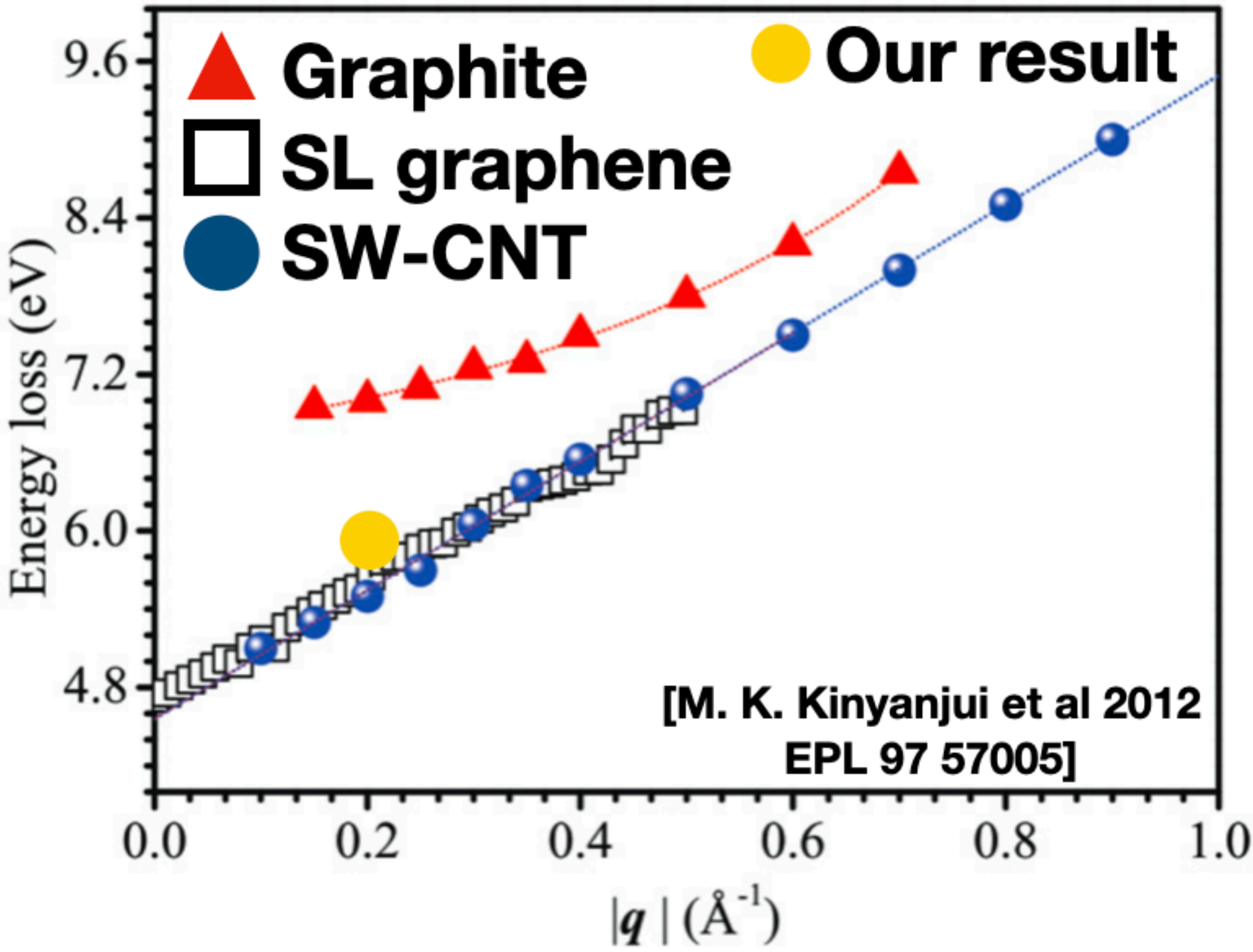
EELS on monolayer: suspended graphene footprint



Monolayer graphene

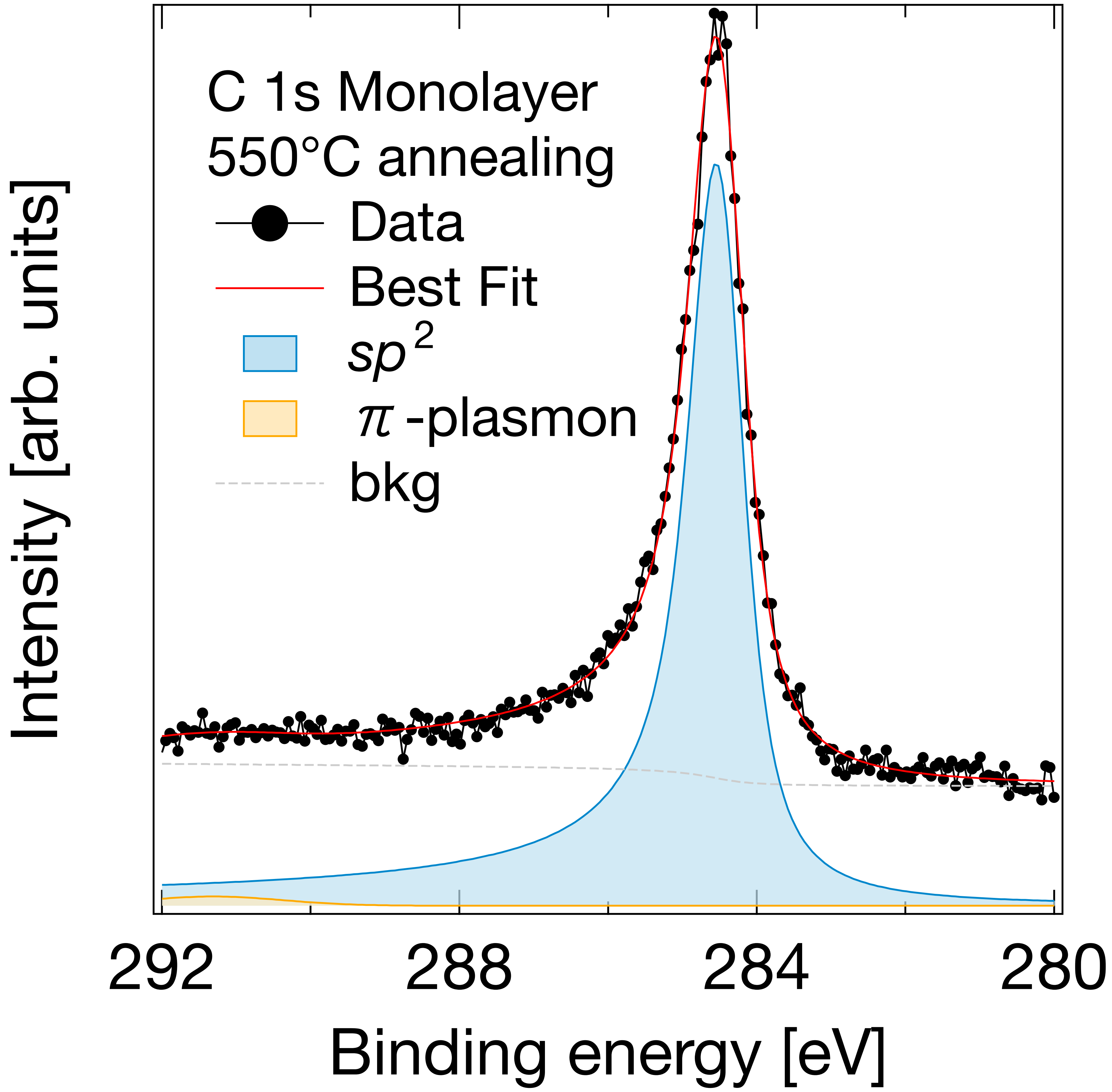
Component	Energy loss [eV]	Area	FWHM [eV]
π_1-plasmon	6.9	143	2.3
π_2-plasmon	5.9	87	1.7

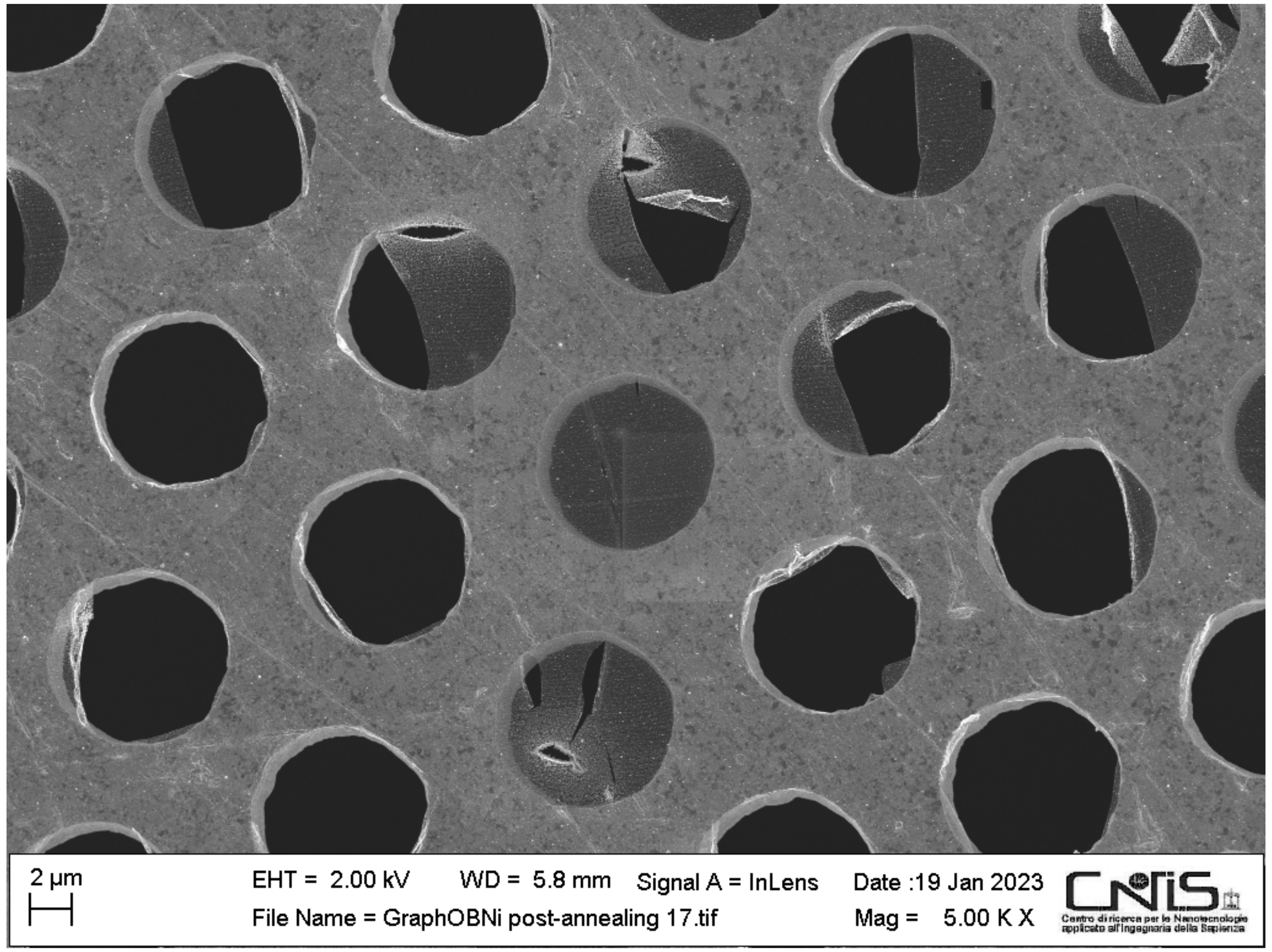




High temperature annealing cleans…but damages

550°C annaling removes PMMA → but damages graphene



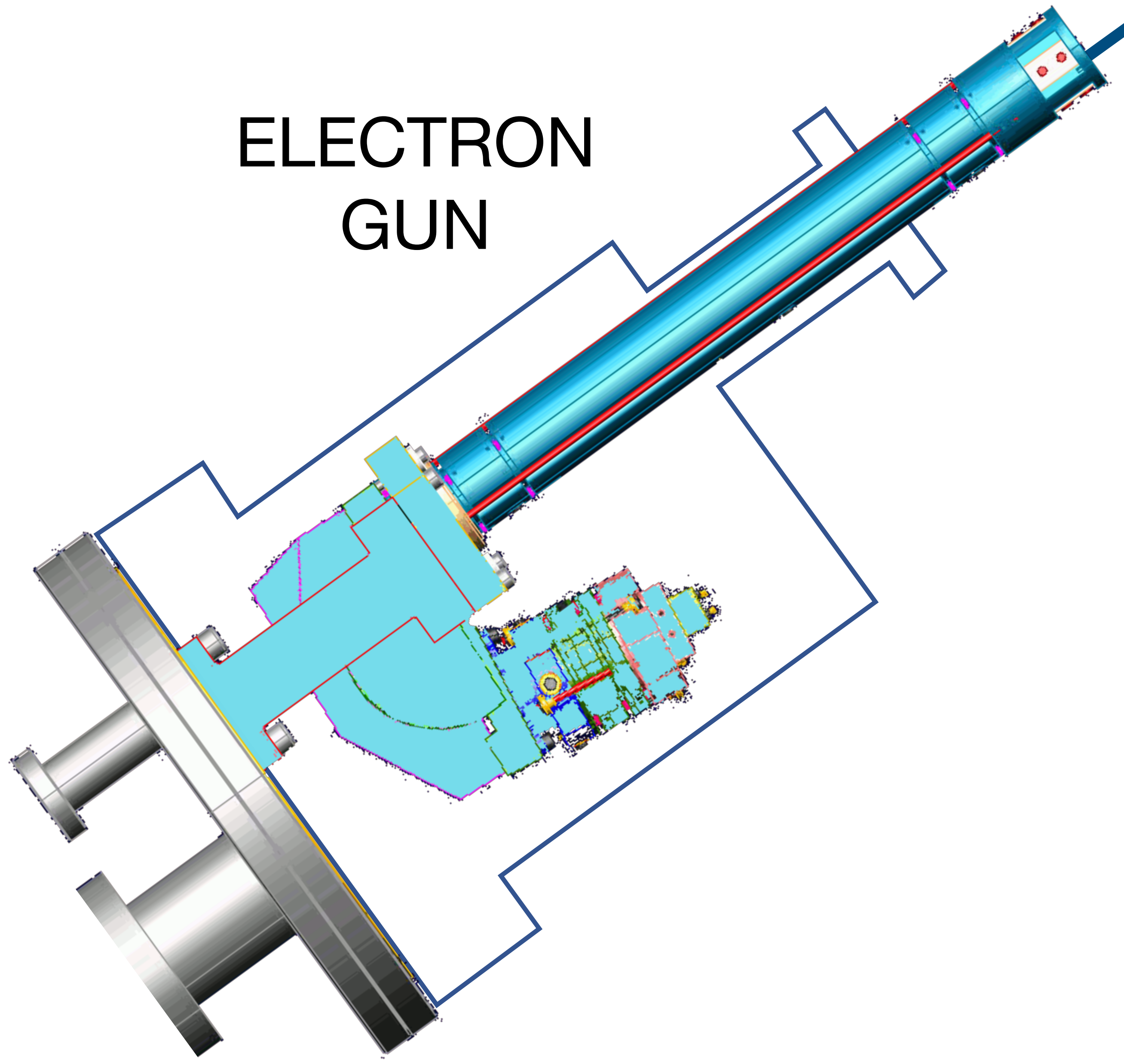


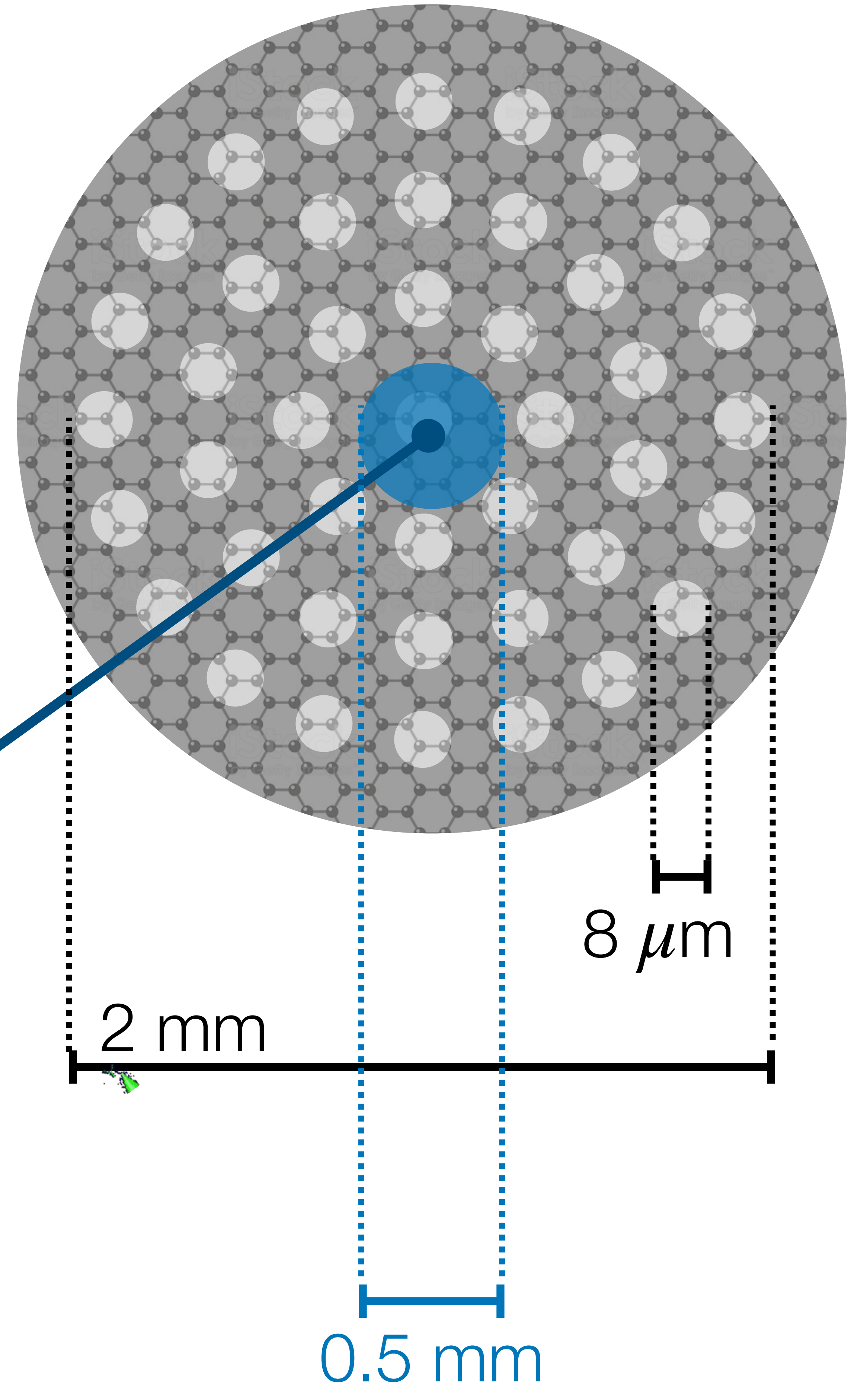
Damages probably caused by strain due to different thermal expansion coefficients of Ni and Graphene

Transmission measurement: average on several grid holes

Monochromatic electron gun:

- Continuous electron beam
- Tuneable energy 30 - 900 eV
- Resolution = 45 meV



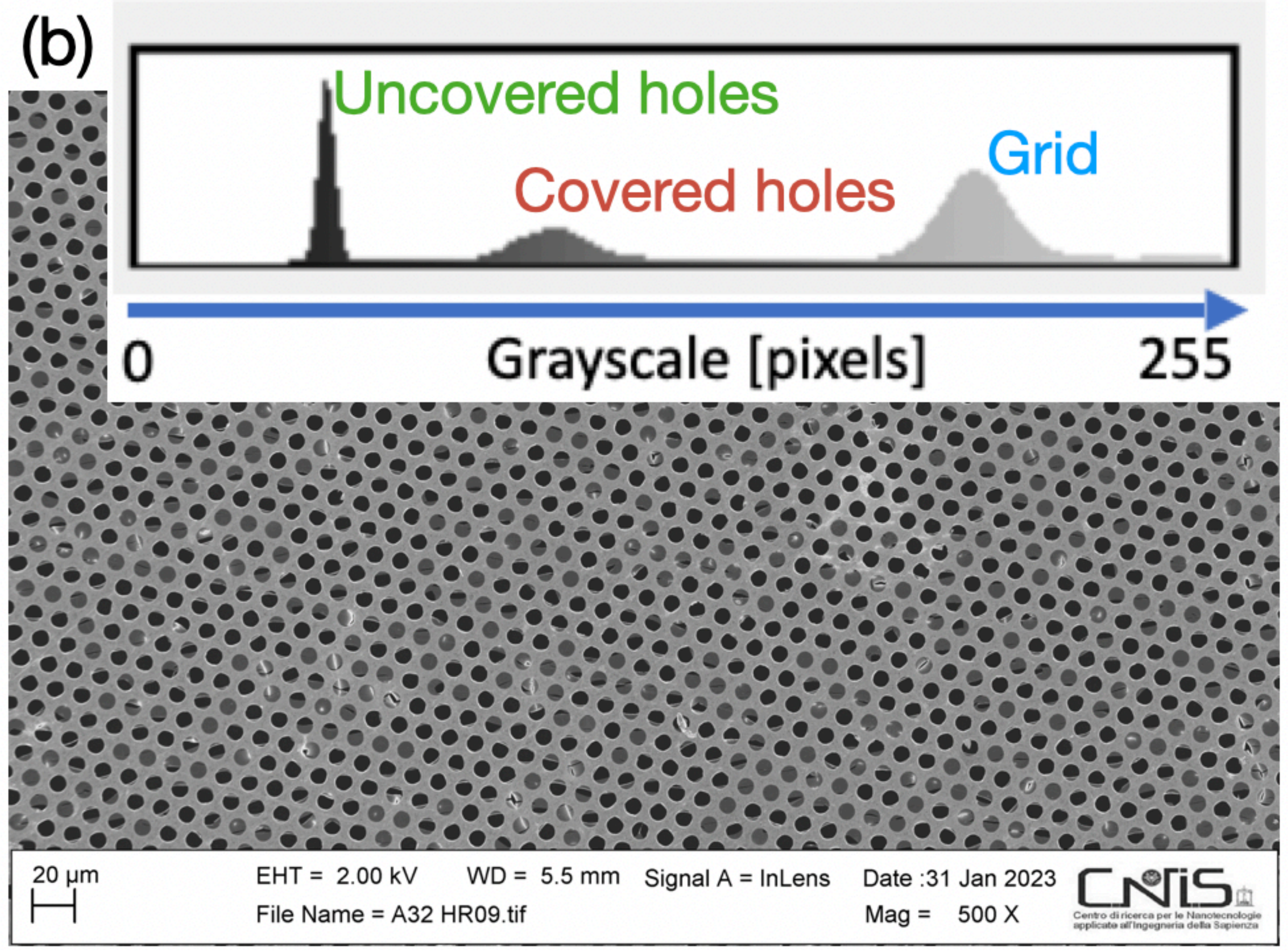


Dimension outline:

- Grid effective diameter 2 mm
- Grid hole width 8 μm
- Beam size ~ 0.5 mm

Evaluation of graphene coverage to correct transmission

- Software generates histogram based on pixels grey level
- Area of the covered holes, uncovered holes and grid regions
- Evaluate graphene coverage and geometrical transmission

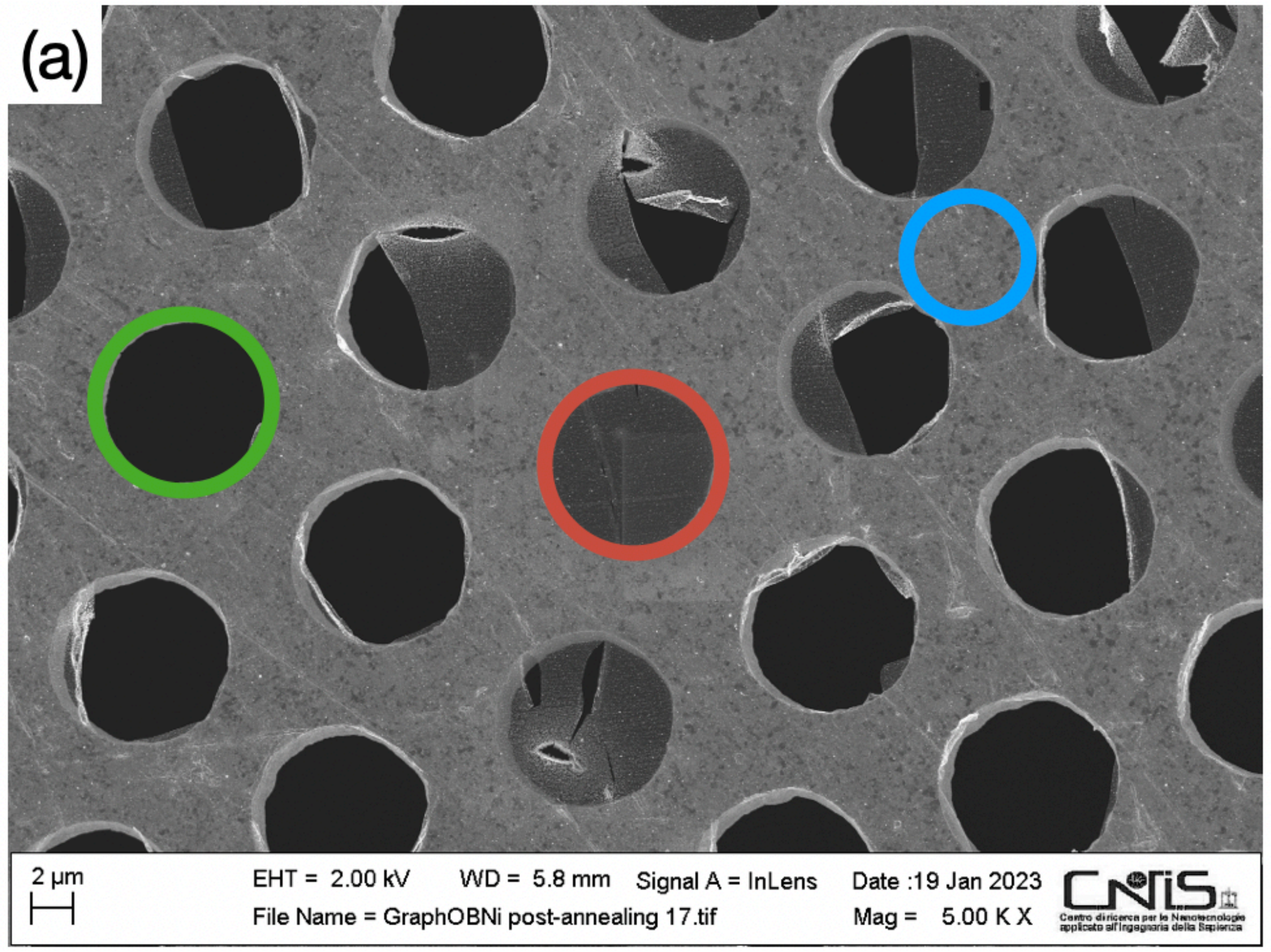


Grid geometrical transmission

- Sample A (37 ± 1)%
- Sample B (44 ± 1)%

Graphene coverage

- Sample A (38 ± 1)%
- Sample B (42 ± 1)%

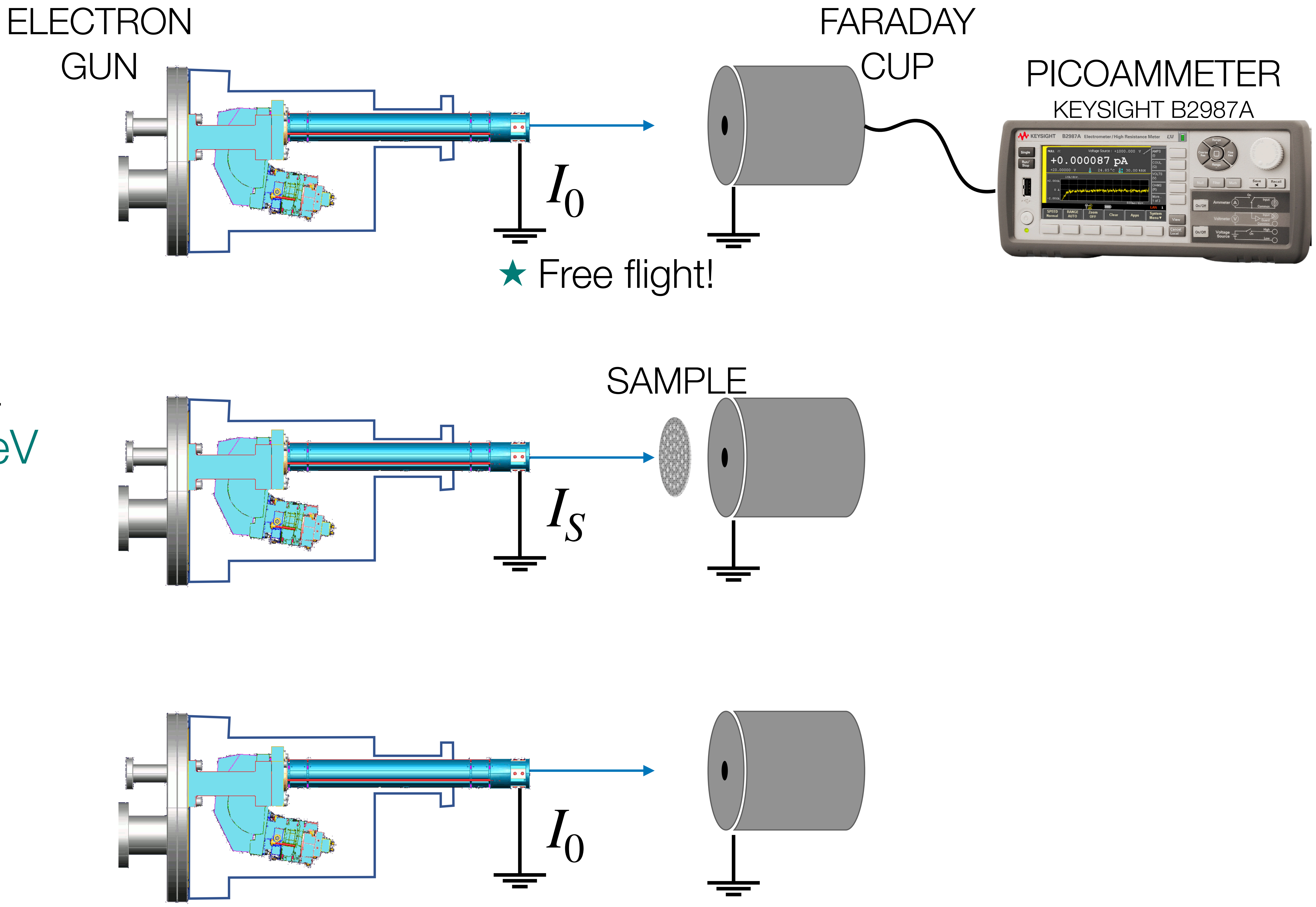


Electron current measured with a Faraday cup

Transmission defined as

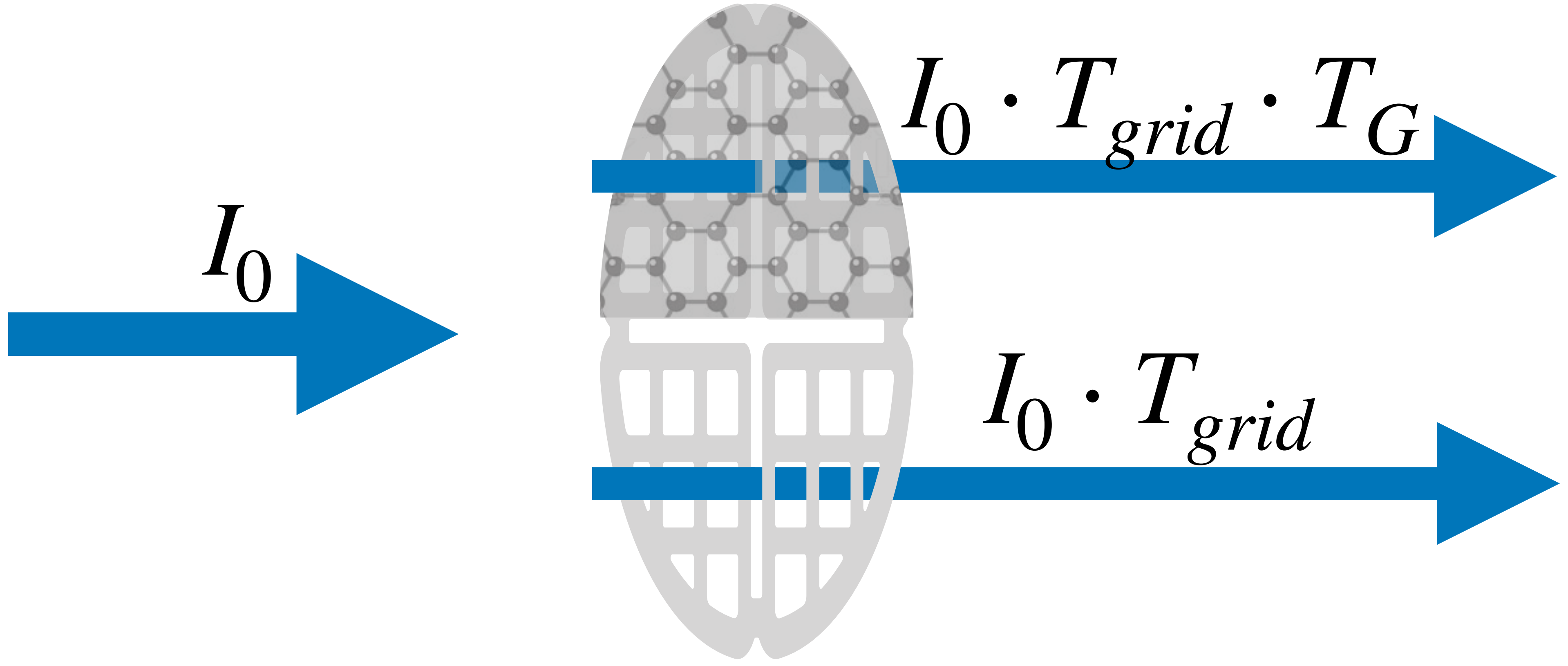
$$T_S = \frac{I_S}{I_0}$$

- For each step, current measured as a function of the energy within 30-900 eV
- Check stability with current measurement before and after



LAboratorio di Spettroscopie Elettroniche e di Correlazione

Graphene transmission: coverage correction



$$I_S(E) = a[I_0 T_{grid} T_G(E)] + b[I_0 T_{grid}]$$

$$a + b = 1$$

Coverage!

I_S = measured current

T_{grid} = grid geometrical transmission

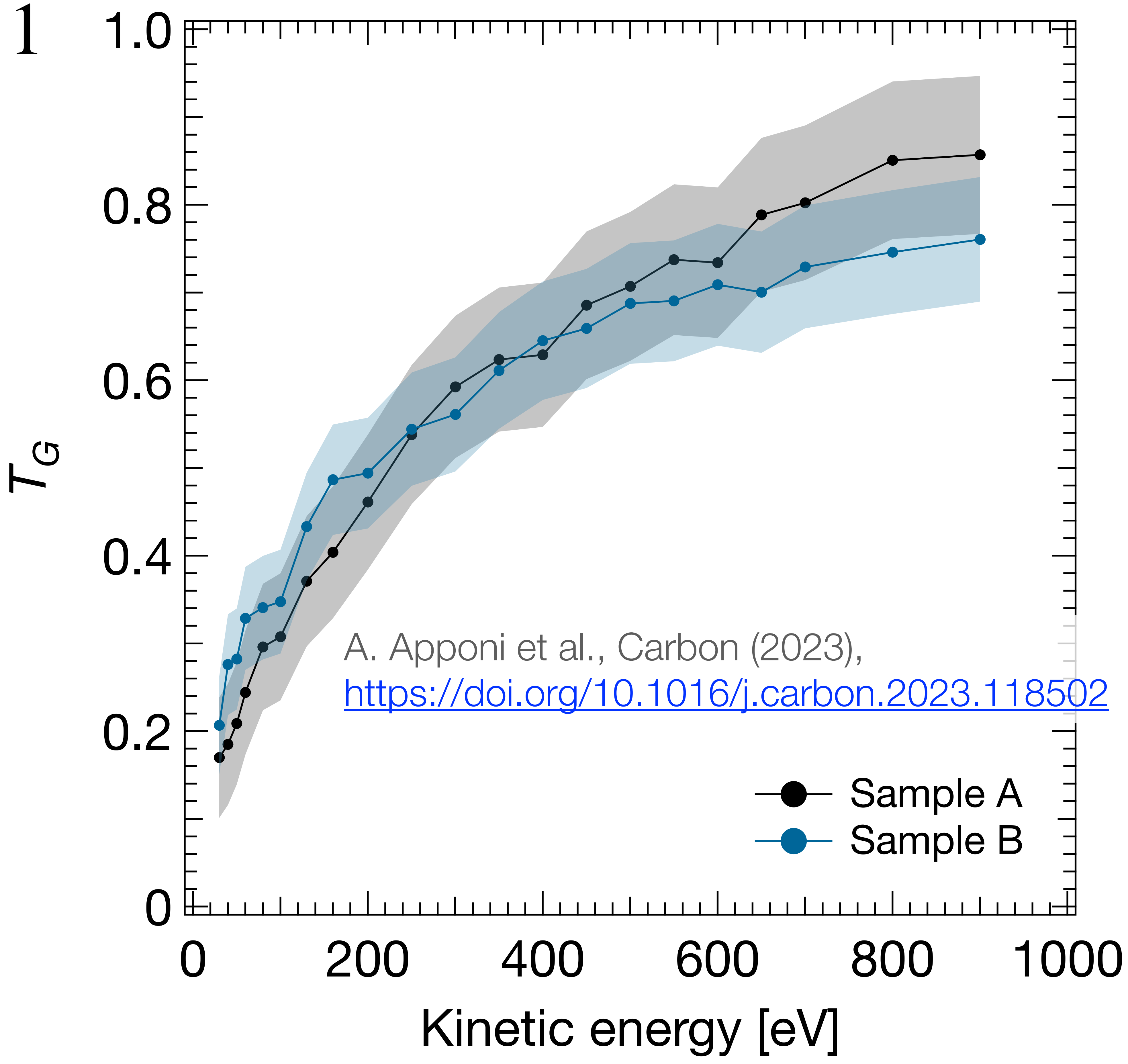
SEM analysis

T_G = graphene transmission

a = graphene coverage

SEM analysis

$$T_G = \frac{\frac{I_S}{I_0 T_{grid}} - b}{a}$$



A. Apponi et al., Carbon (2023), https://doi.org/10.1016/j.carbon.2023.118502

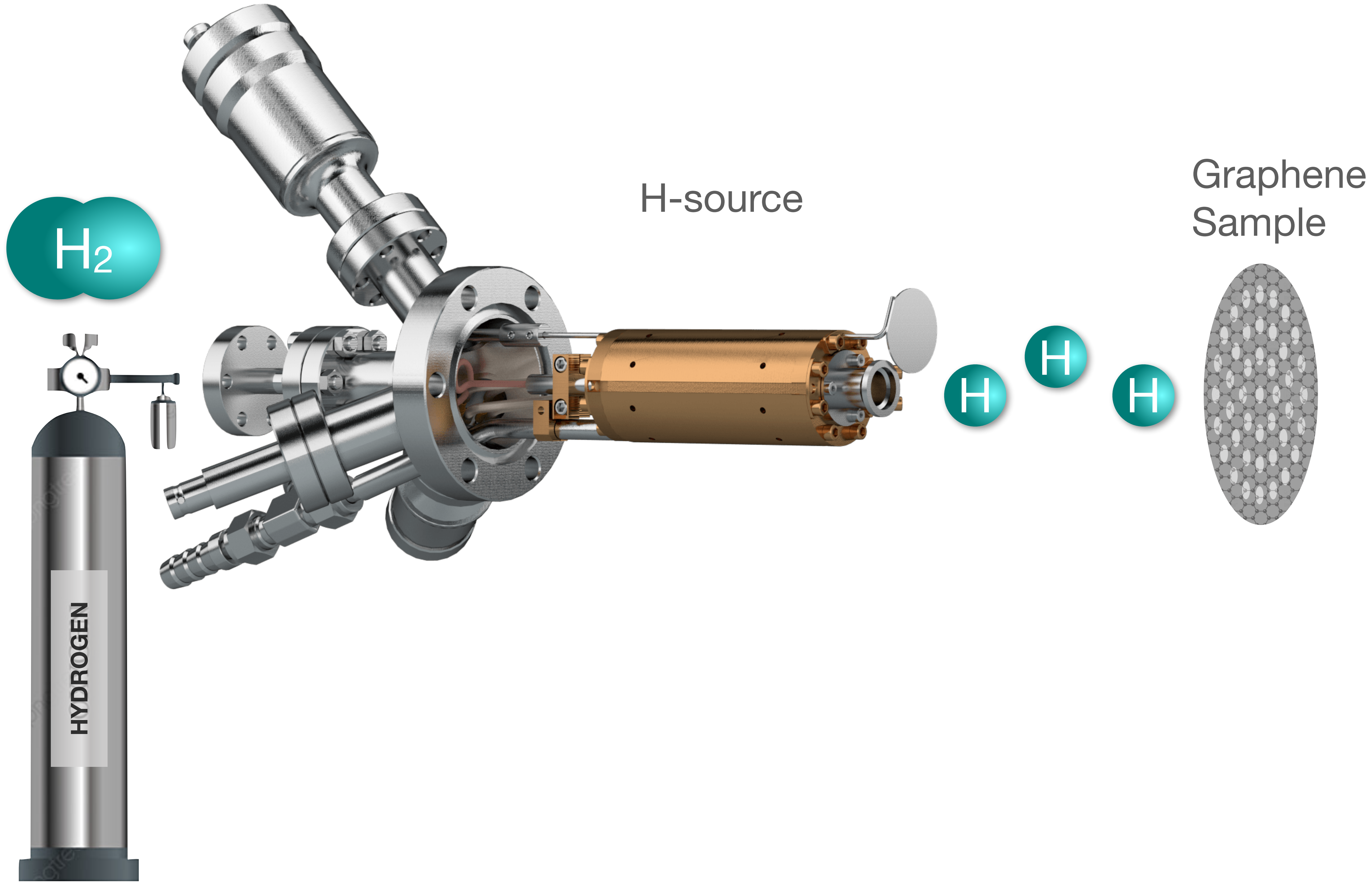
Let's try to hydrogenate graphene on grid

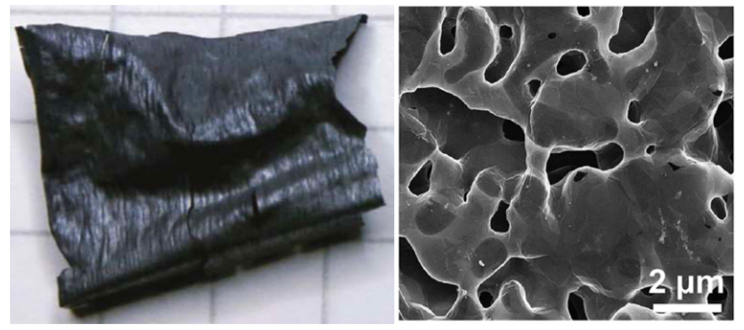
Atomic hydrogen source:

- Hot tungsten capillary
- H_2 thermal cracking into H

Graphene on grid hydrogenation:

- Flat suspended graphene regions
- Controlled number of layers (possibly 1)
- 2D material! No "in-depth" hydrogenation issues





Nanoporous graphene hydrogenation
M.G. *et al.*, *Nano Letters* (2022), https://doi.org/10.1021/acs.nanolett.2c00162

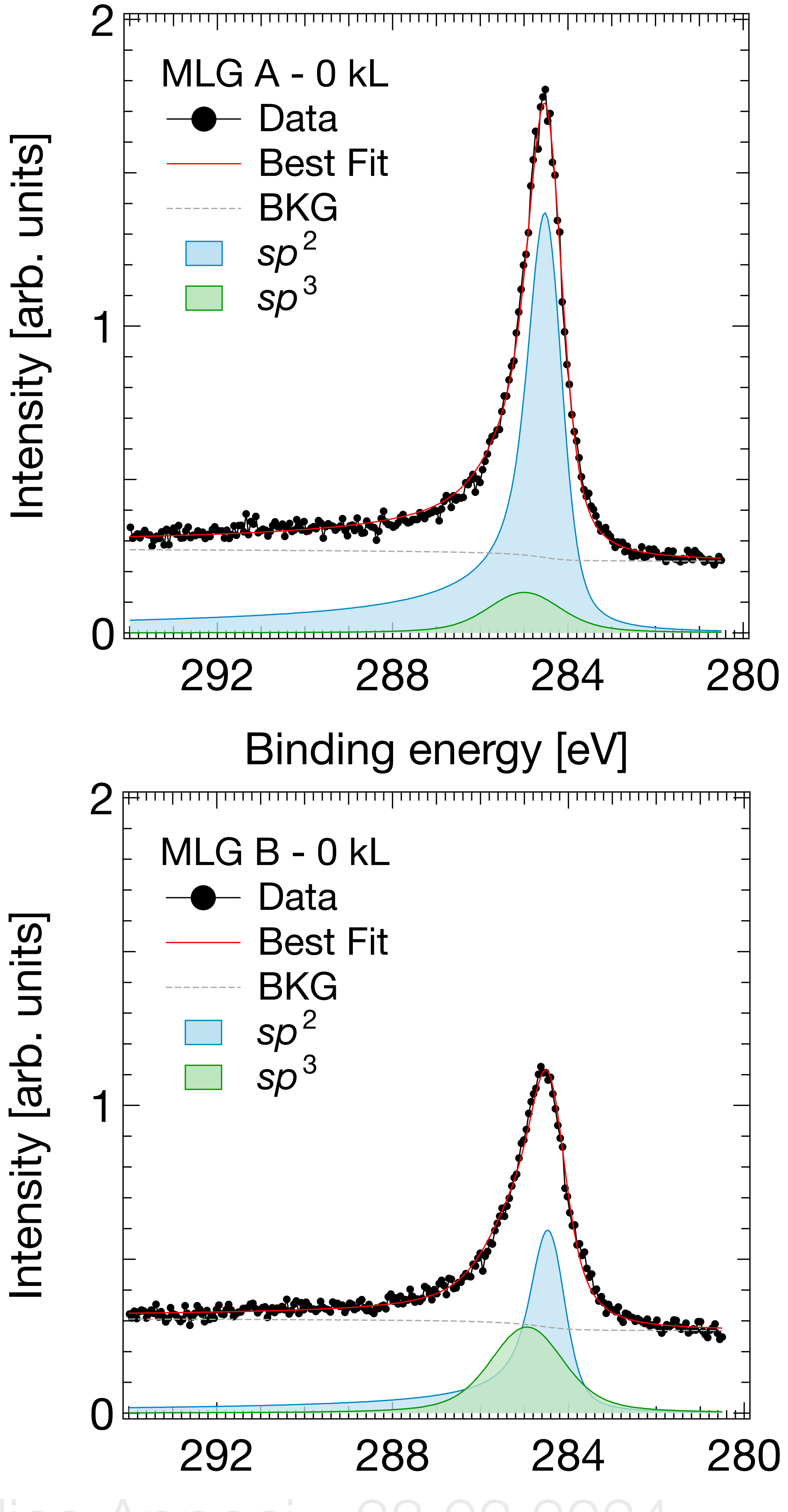
Two graphene on TEM samples from same growth

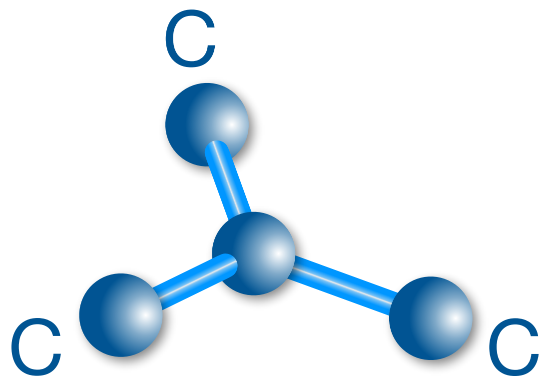
PRELIMINARY

0

Dose [kL]

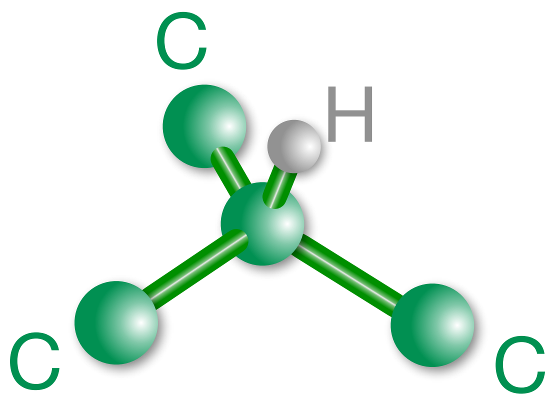
10 kL = $3.6 \cdot 10^{-6}$ mbar · hour





Carbon hybridization

changing from sp^2 to sp^3

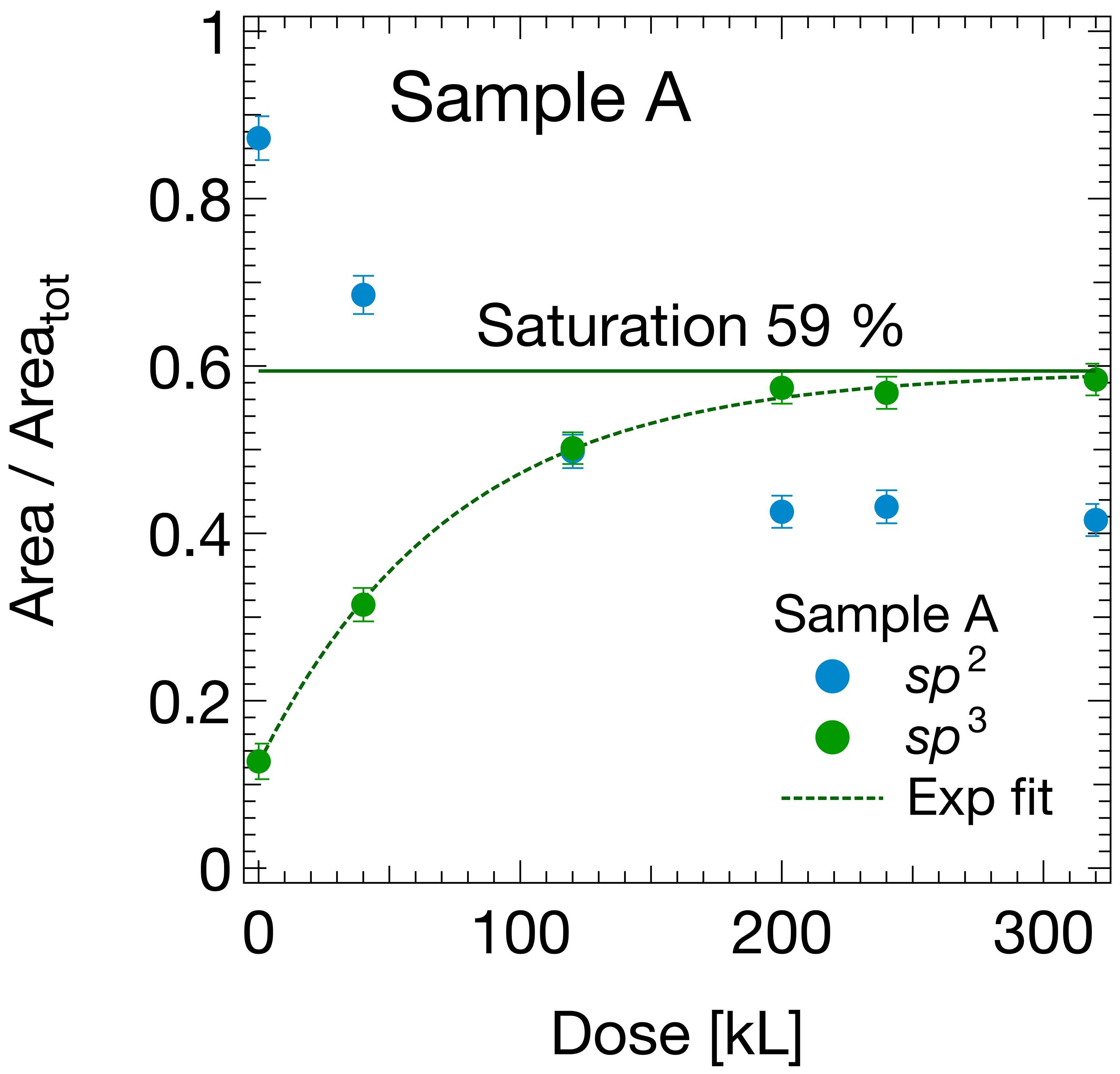


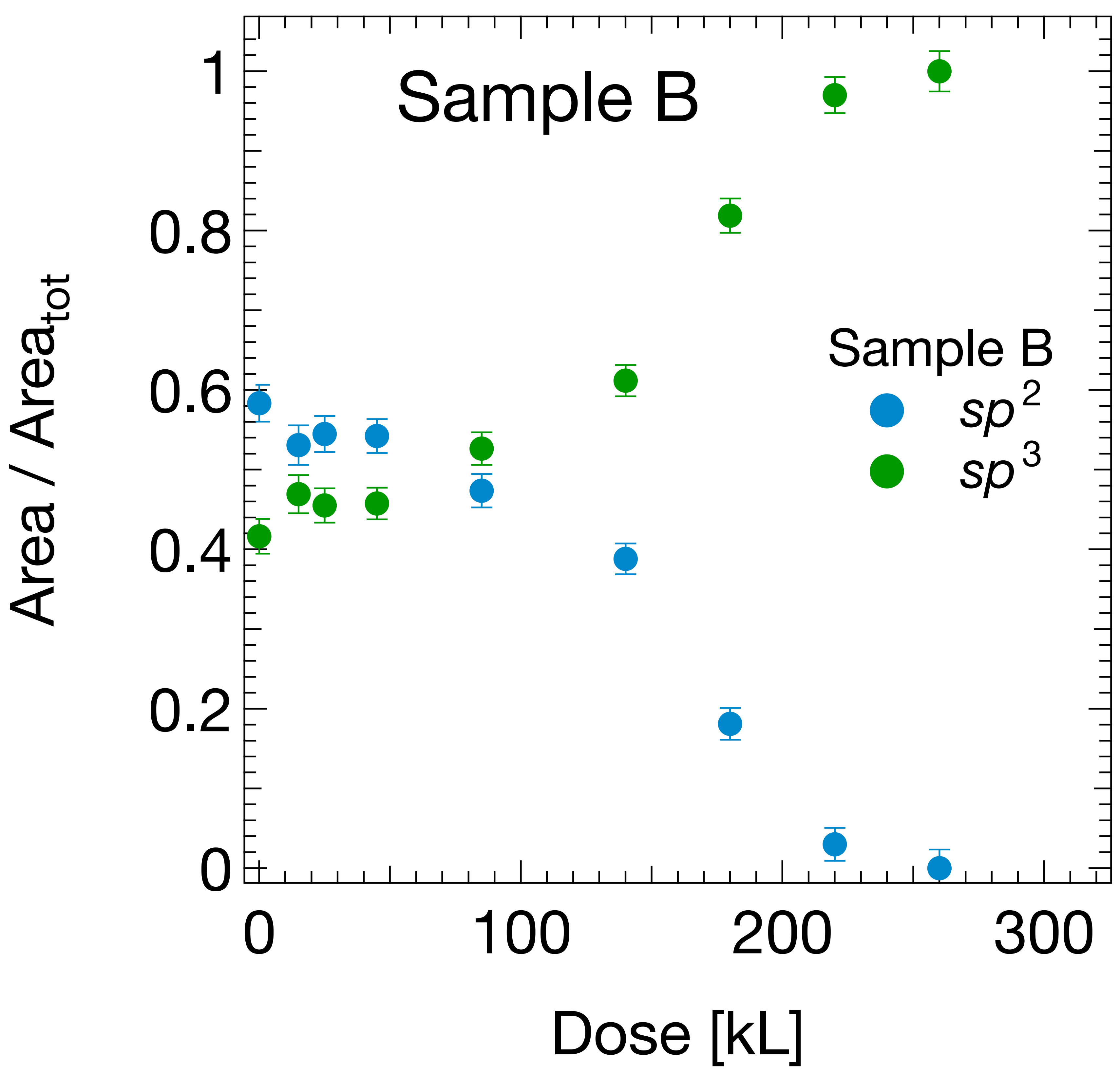
Different starting point, different saturation point

PRELIMINARY

The more is sp³, the higher will be H-uptake

PRELIMINARY





Sample A result:

- Start with ~13% sp^3
- 59% sp^3 saturation after 320 kL dose

Sample B result:

- Start with ~42% sp^3
- 100% sp^3 saturation after 260 kL dose

~6.2 eV band gap measured with EELS

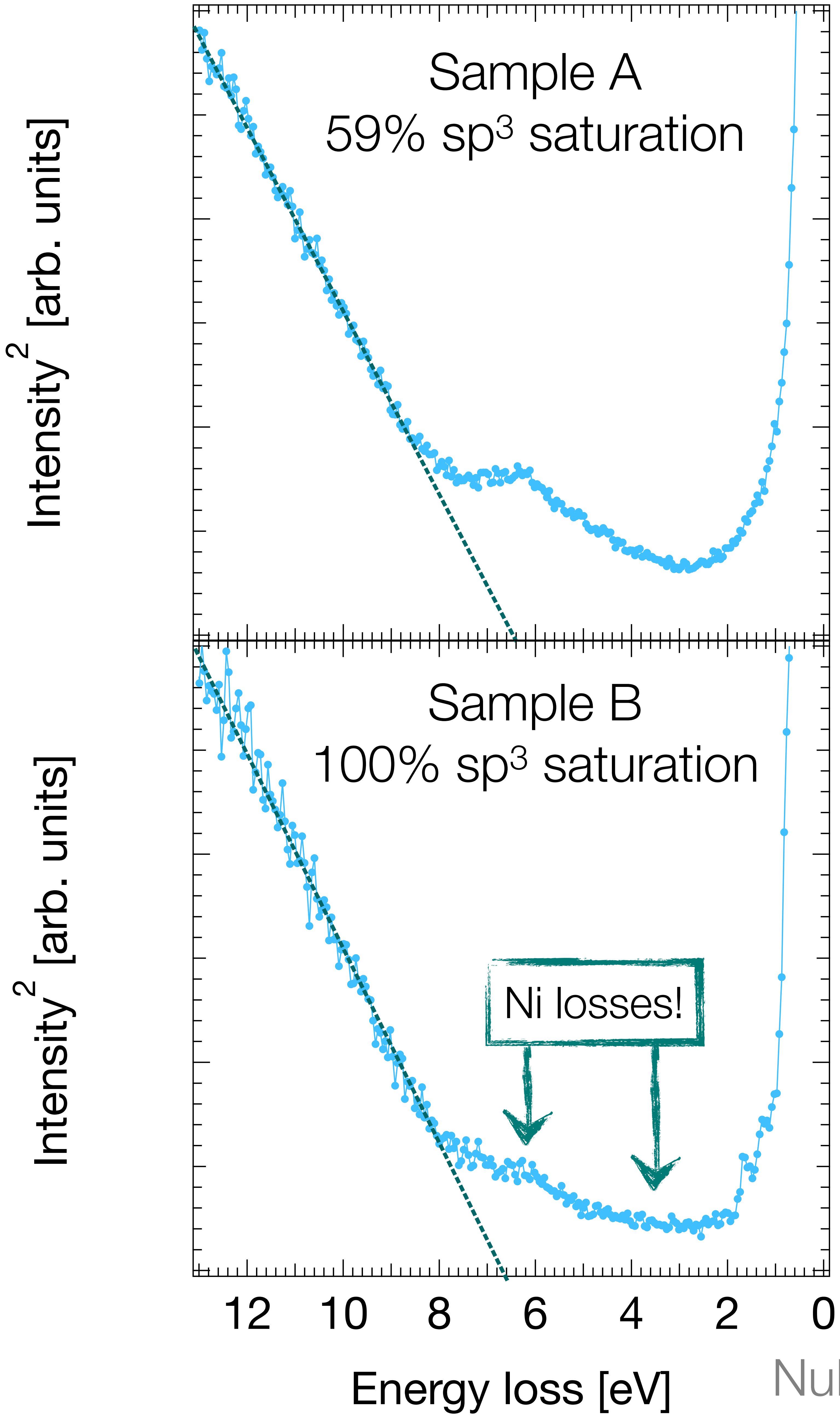
PRELIMINARY

Hydrogenated graphene:

- sp^2 to sp^3 distortion
- Band gap opening
- Electronic transition onset $\propto (E - E_g)^{1/2}$ for direct gap semicondutors
- EELS measurement ^{2} and fit with a straight line
- With this analysis E_g ~ 6.2 eV for both samples

HANDLE WITH CARE:

- Background
- Excitons

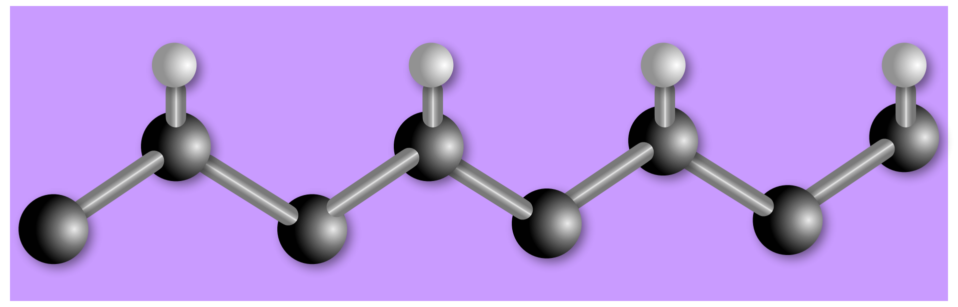


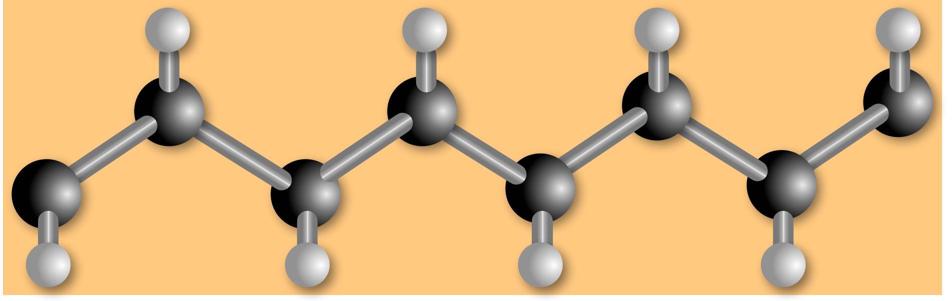
Valence band to understand CH bonding

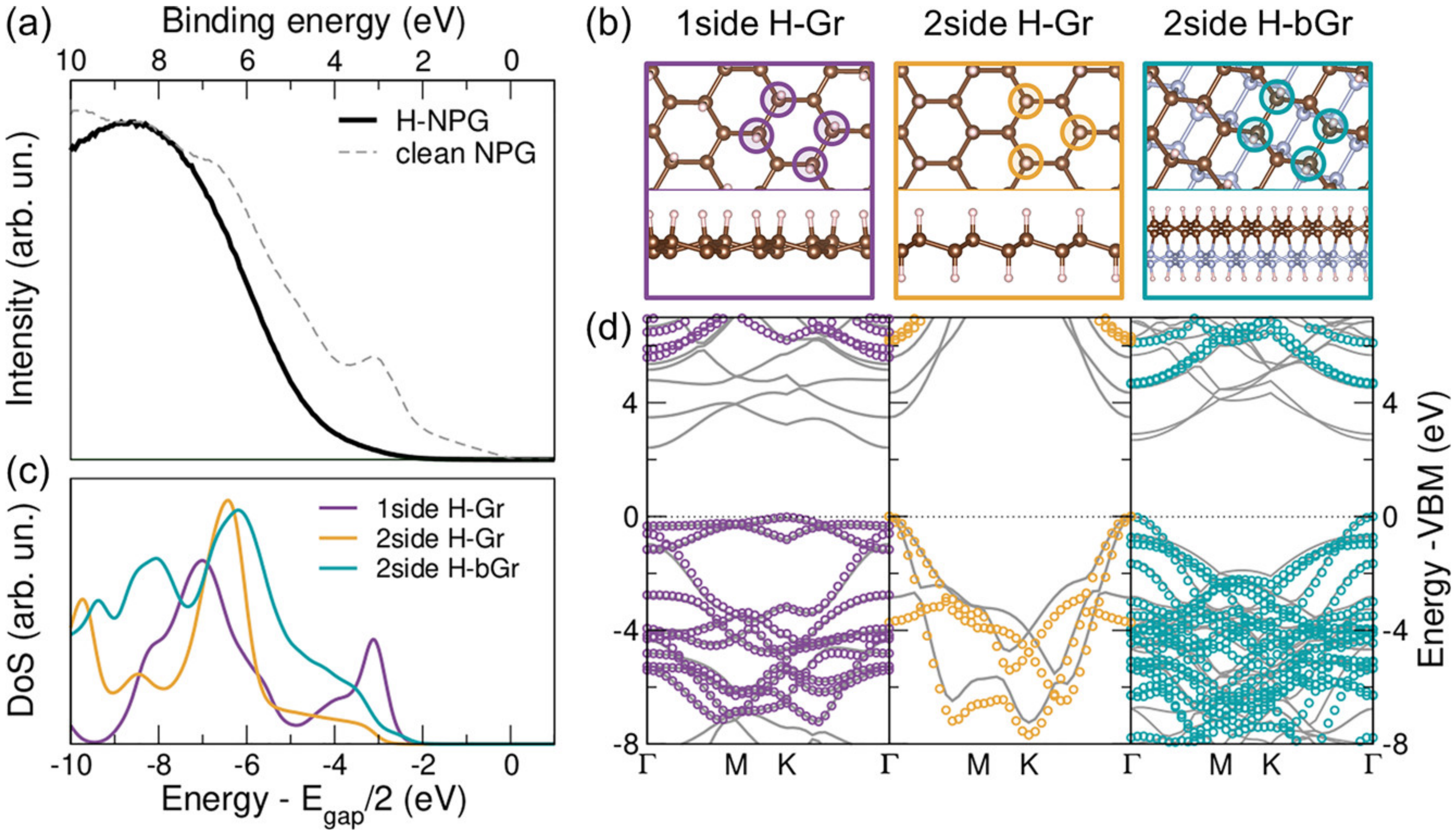
PRELIMINARY

How many sides?

- ✤ C 1s not an unambiguous marker
- ✤ UPS: valence band *features* and bands dispersion



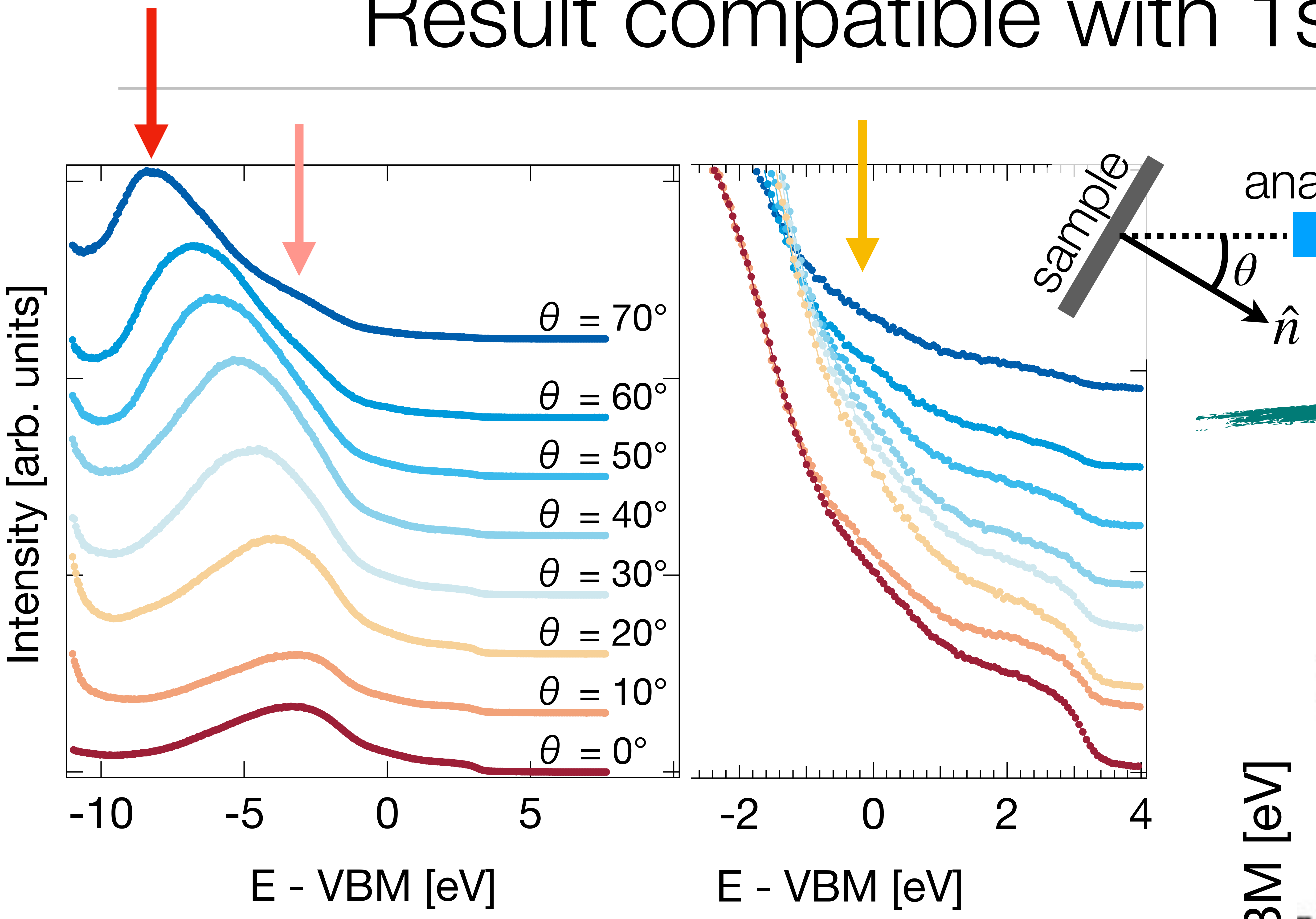




Betti, M.G. *et al.*, *Nano Letters* (2022), https://doi.org/10.1021/acs.nanolett.2c00162

Result compatible with 1side hydrogenation

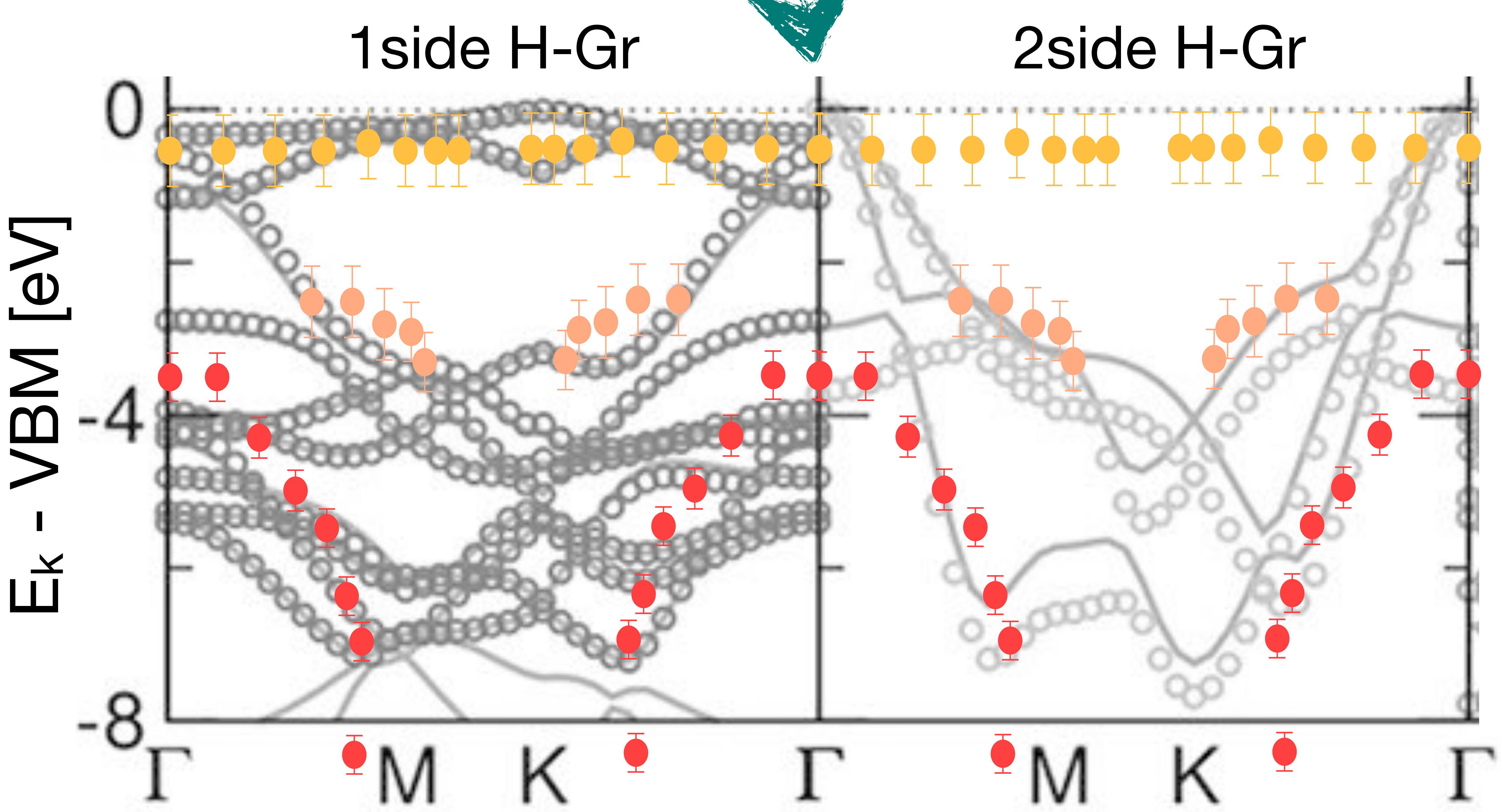
PRELIMINARY



He discharge lamp:

✤ Spot diameter 300 μm

$$k_{//} = \sqrt{\frac{2m}{\hbar^2} E_k} \sin\theta$$



✤ VBM = $E_F - E_g/2$, with $E_g = 6.2$ eV

✤ Clue of 1side hydrogenation

To Conclude

Spectrosopy on graphene

550 °C annealing breaks graphene

C 1s and π-plasmon: evidence of purely sp^2 suspended graphene

Non-damaging cleaning

Transmission through graphene

Transmission of electrons measured in an extended energy range (30 - 900 eV)

Extend energy range up to 18 keV

Hydrogenation of graphene

Monolayer graphene: saturation depends on initial sp^2/sp^3 ratio

Deeper understanding (H-uptake, band gap, CH bonding)

The PTOLEMY Collaboration

and

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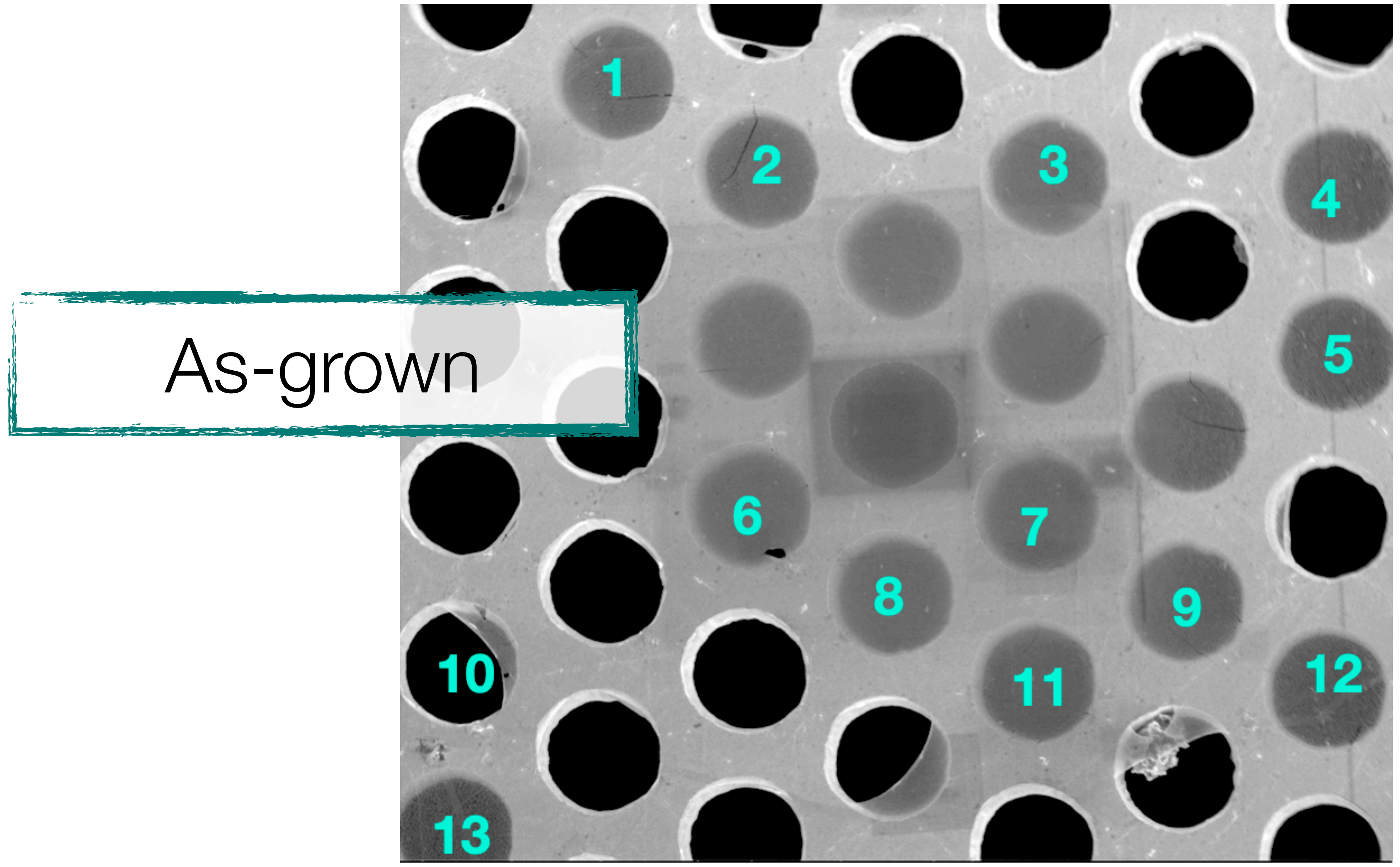
Carlo Mariani, Sapienza Università

Giovanni De Bellis, Sapienza Università and CNIS

BACK-UP

Looking for the Critical Temperature



Which is the critical temperature?

- ✤ Test sample (a *bad* one)
- ✤ Steps increasing annealing temperature
- ✤ SEM at each step

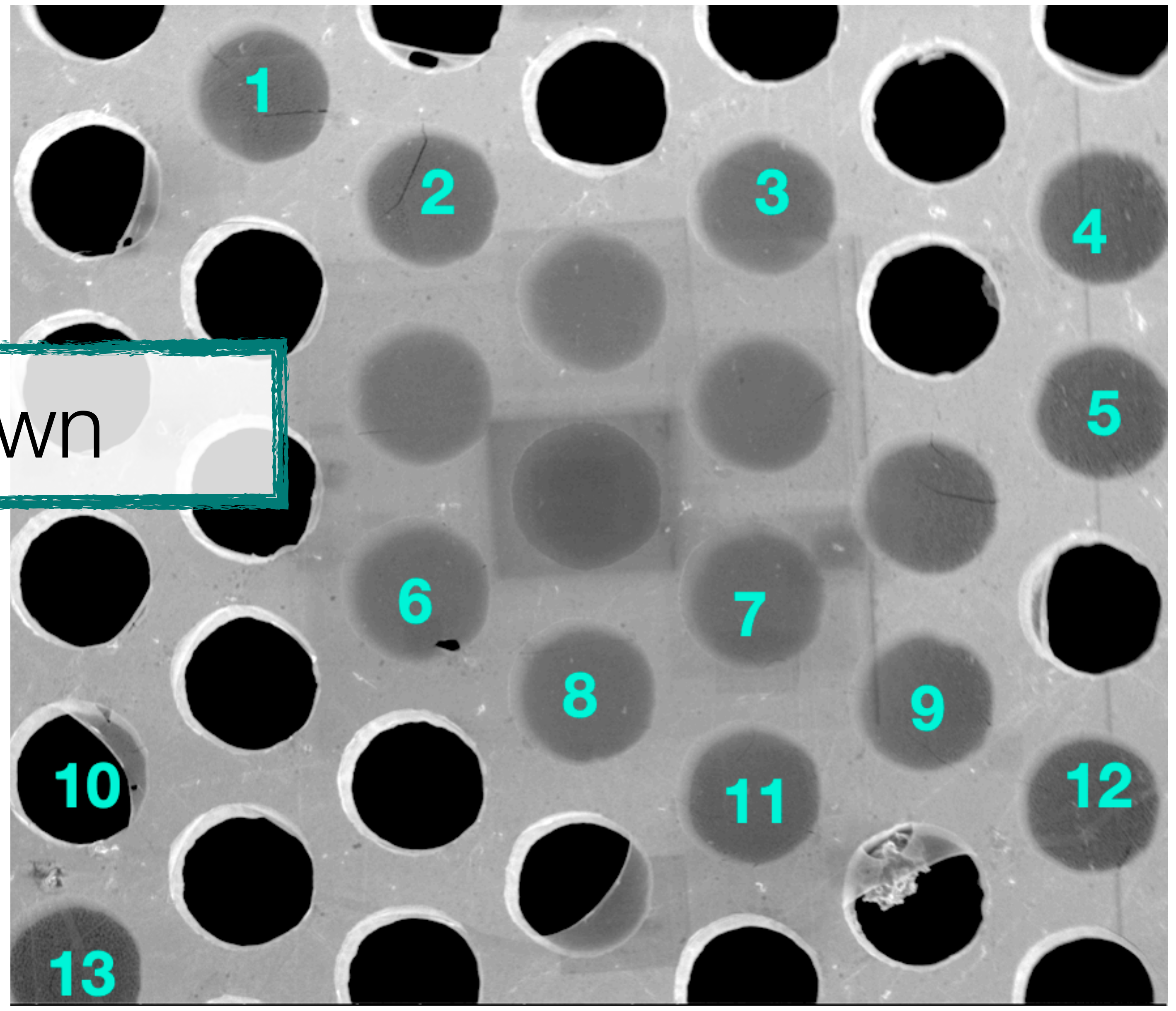
Looking for the Critical Temperature

Which is the critical temperature?

- Test sample (a *bad* one)
- Steps increasing annealing temperature
- SEM at each step
- Nothing happens

As-grown

300 °C annealing



Looking for the Critical Temperature

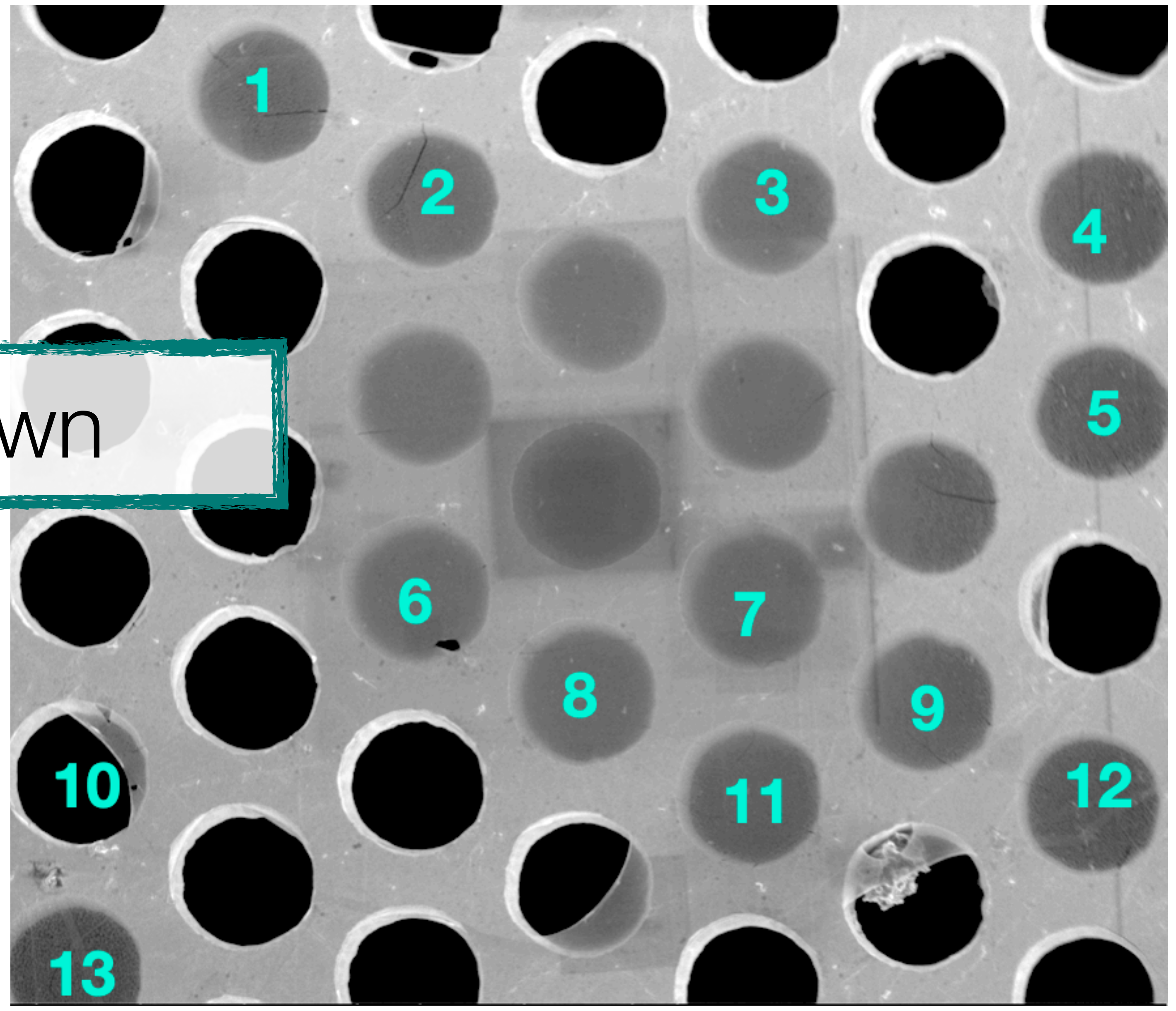
Which is the critical temperature?

- ✤ Test sample (a *bad* one)
- ✤ Steps increasing annealing temperature
- ✤ SEM at each step
- ✤ Nothing happens

As-grown

300 °C annealing

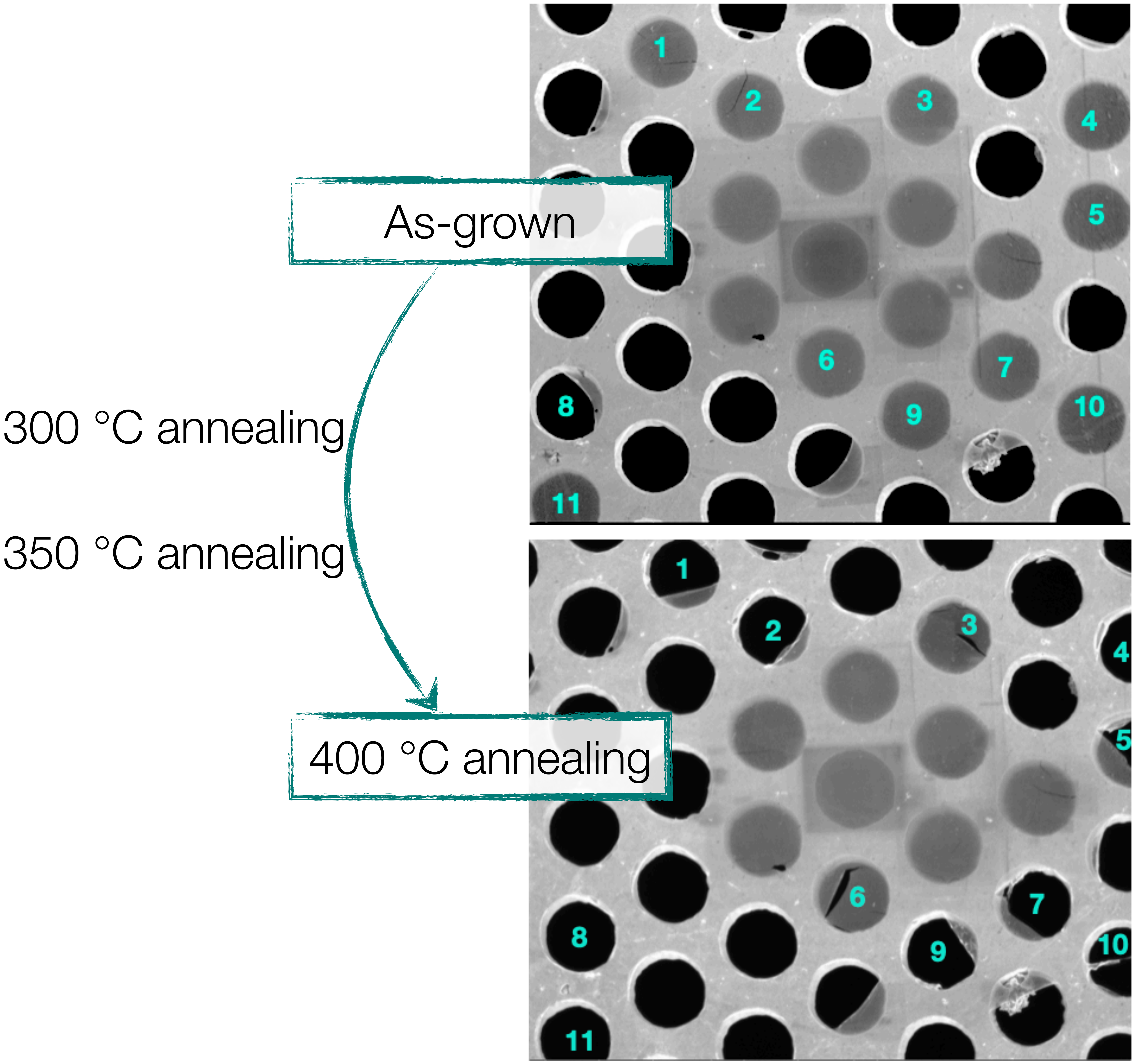
350 °C annealing



400 °C Is The Critical Temperature

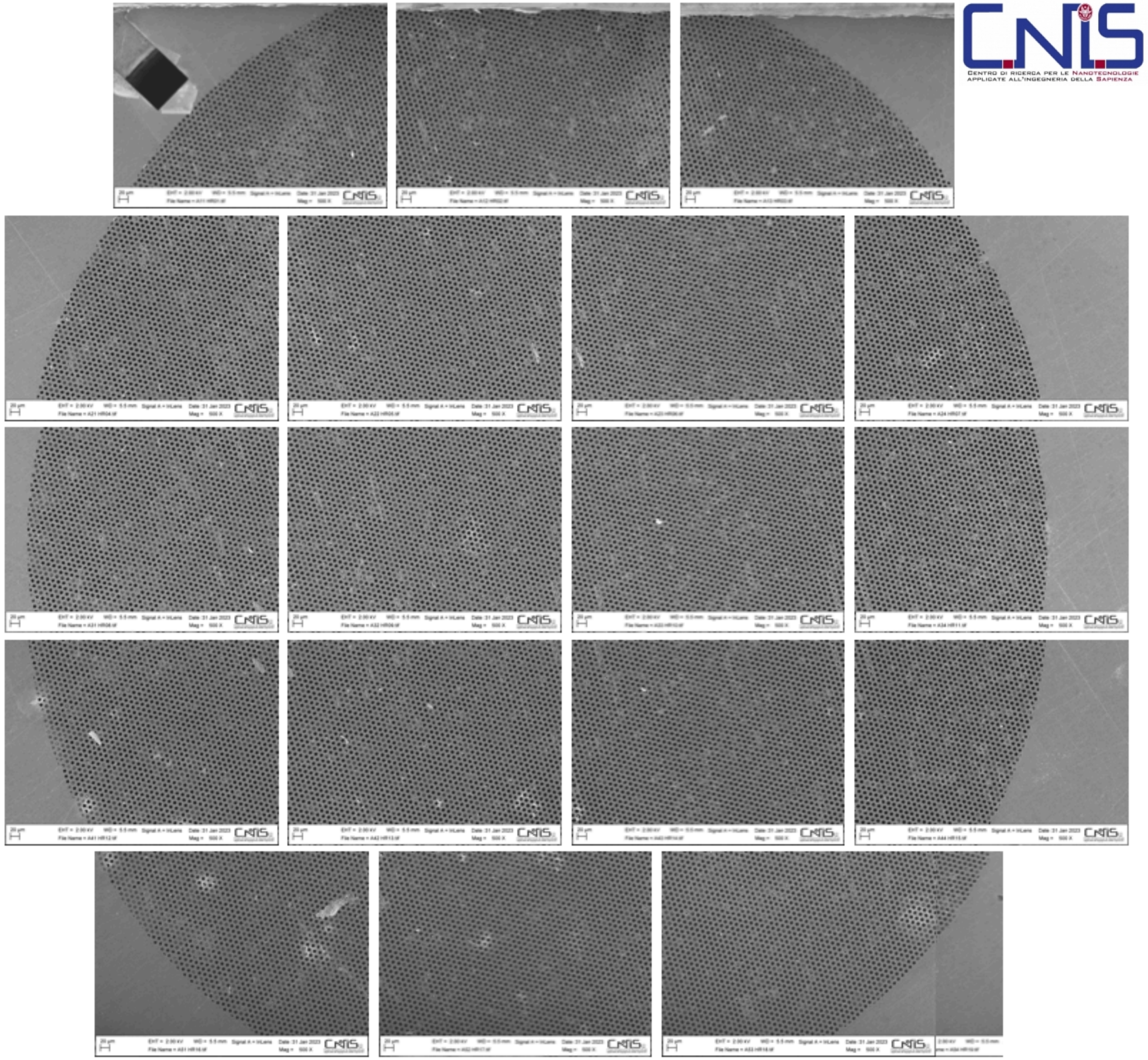
Which is the critical temperature?

- ✤ Test sample (a *bad* one)
- ✤ Steps increasing annealing temperature
- ✤ SEM at each step
- ✤ Nothing happens up to 400 °C

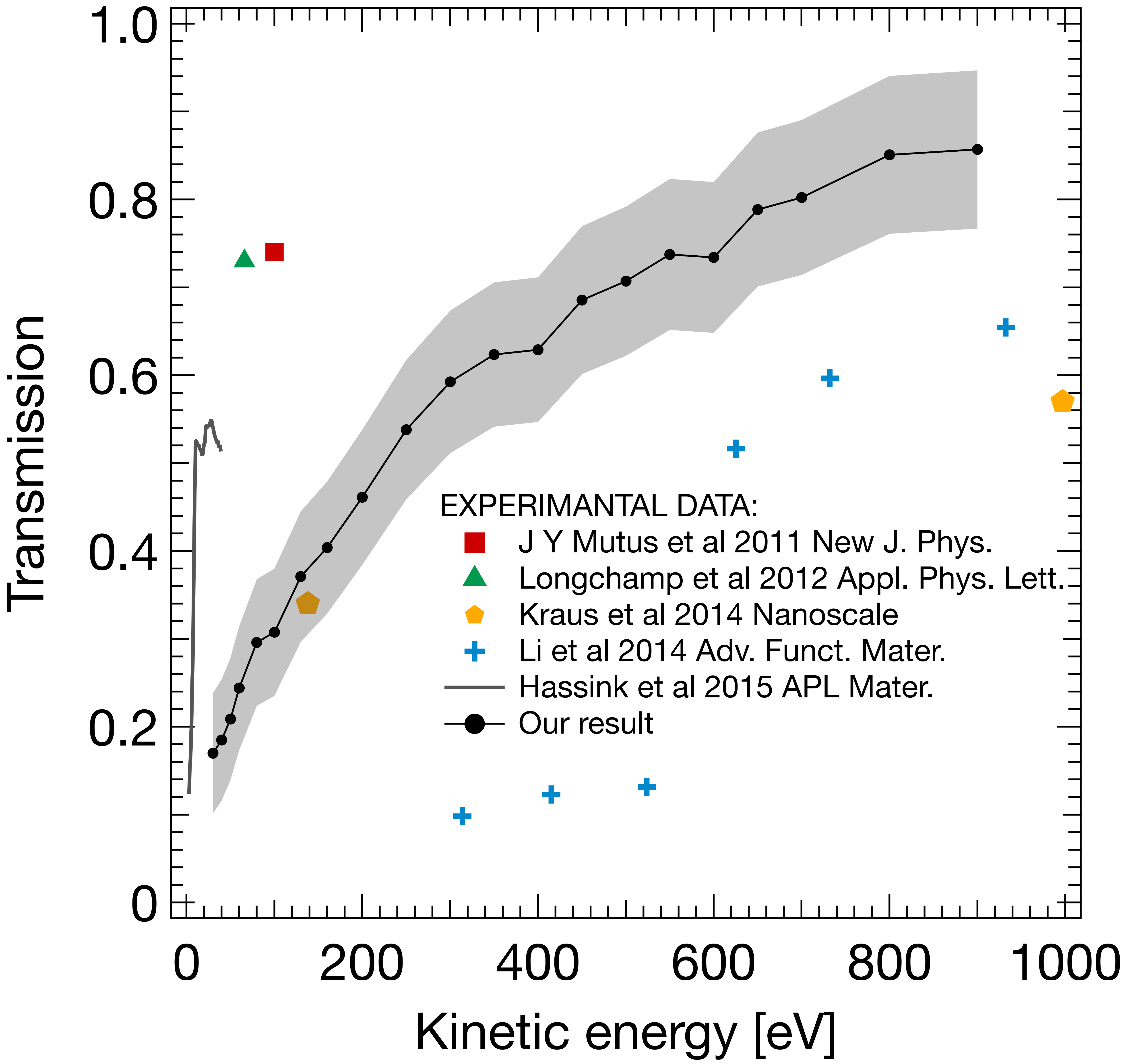


Evaluate Coverage and Correct Transmission Measurements

- Map the sample with fixed SEM parameters
- Evaluate actual coverage and geometrical transmission
- Correct the transmission

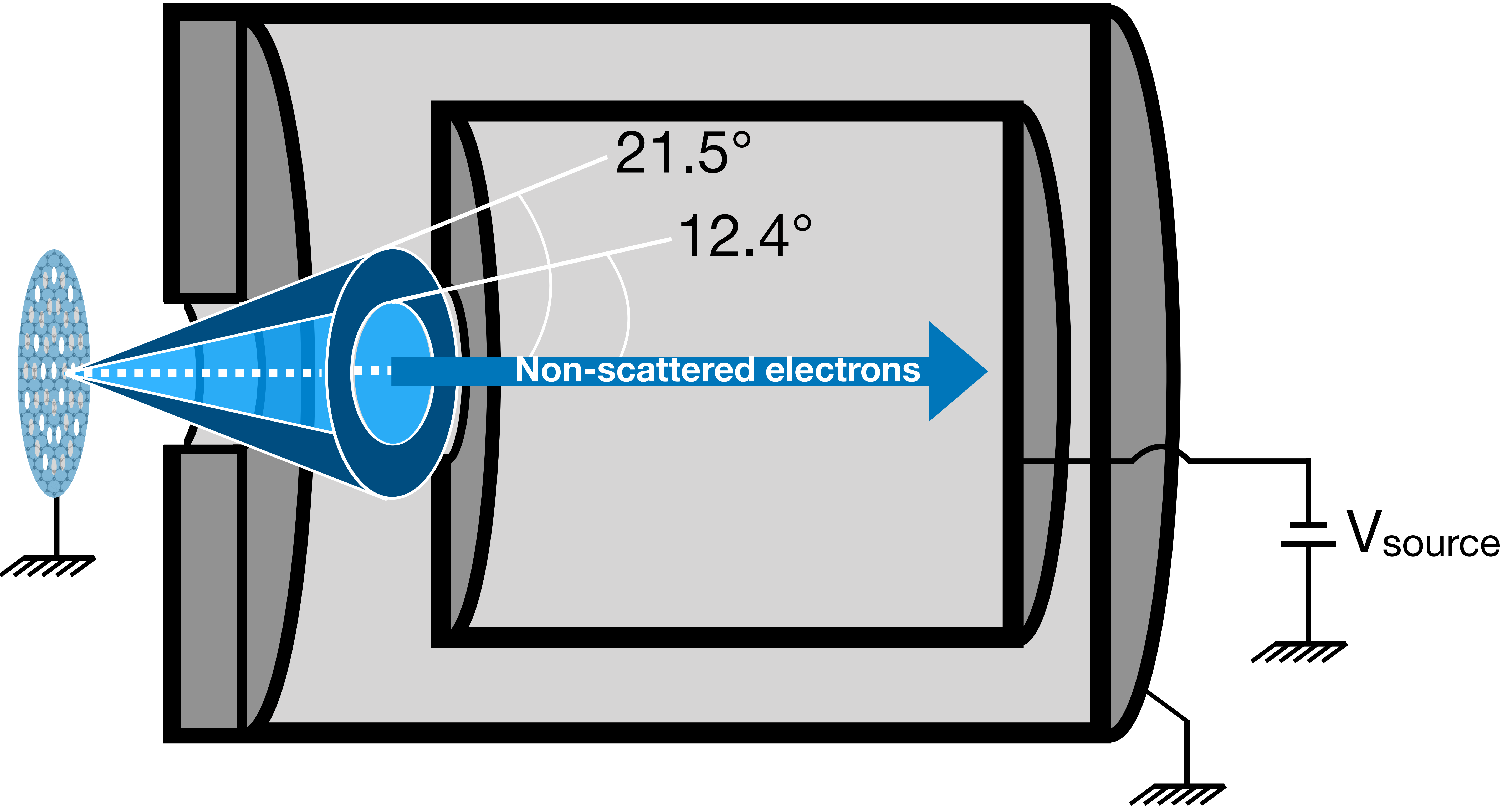


Careful Comparison: Experiments May Not Be Compatible



Which Is the Nature of Transmitted Electrons?

Scattered Electrons Contribution in the Order of 10%



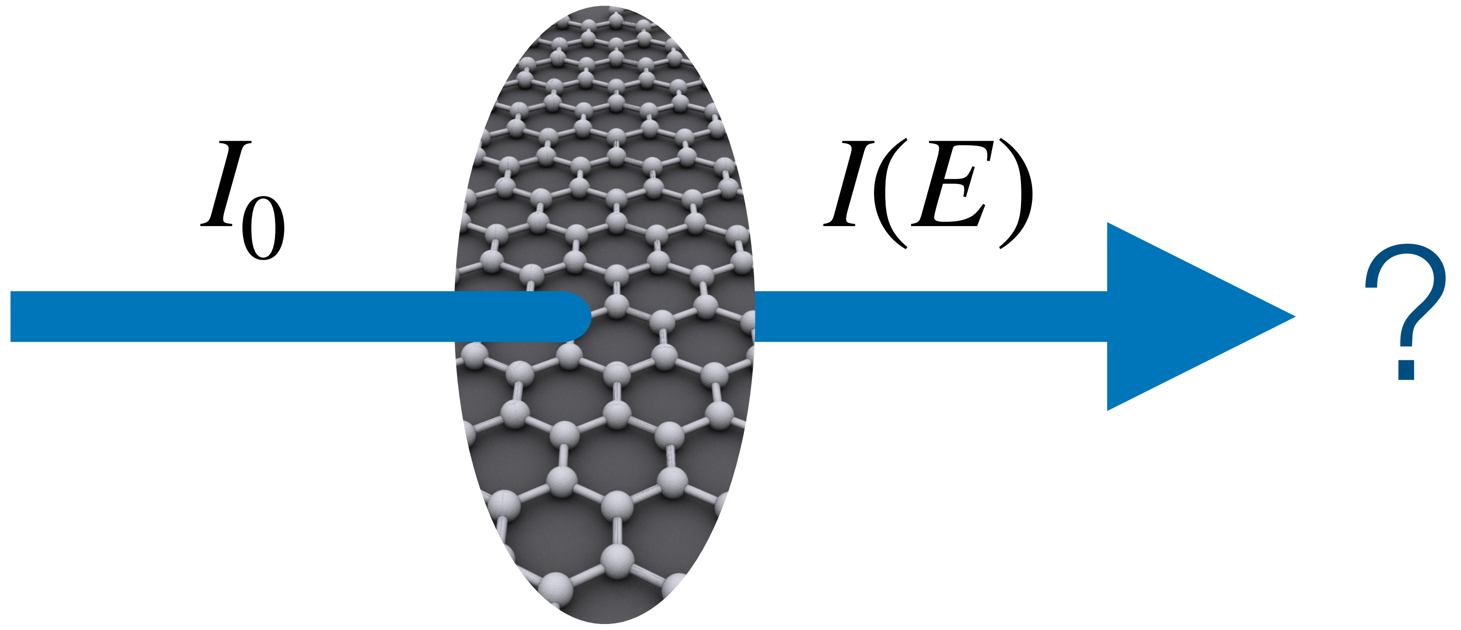
Contribution of scattered electrons:

- Measure current polarising (or not) internal cup
- Current variation due to scattered electrons refocusing
- Take into account accepted solid angle
- Scattered electrons contribution of 11% for E_k = 30 eV

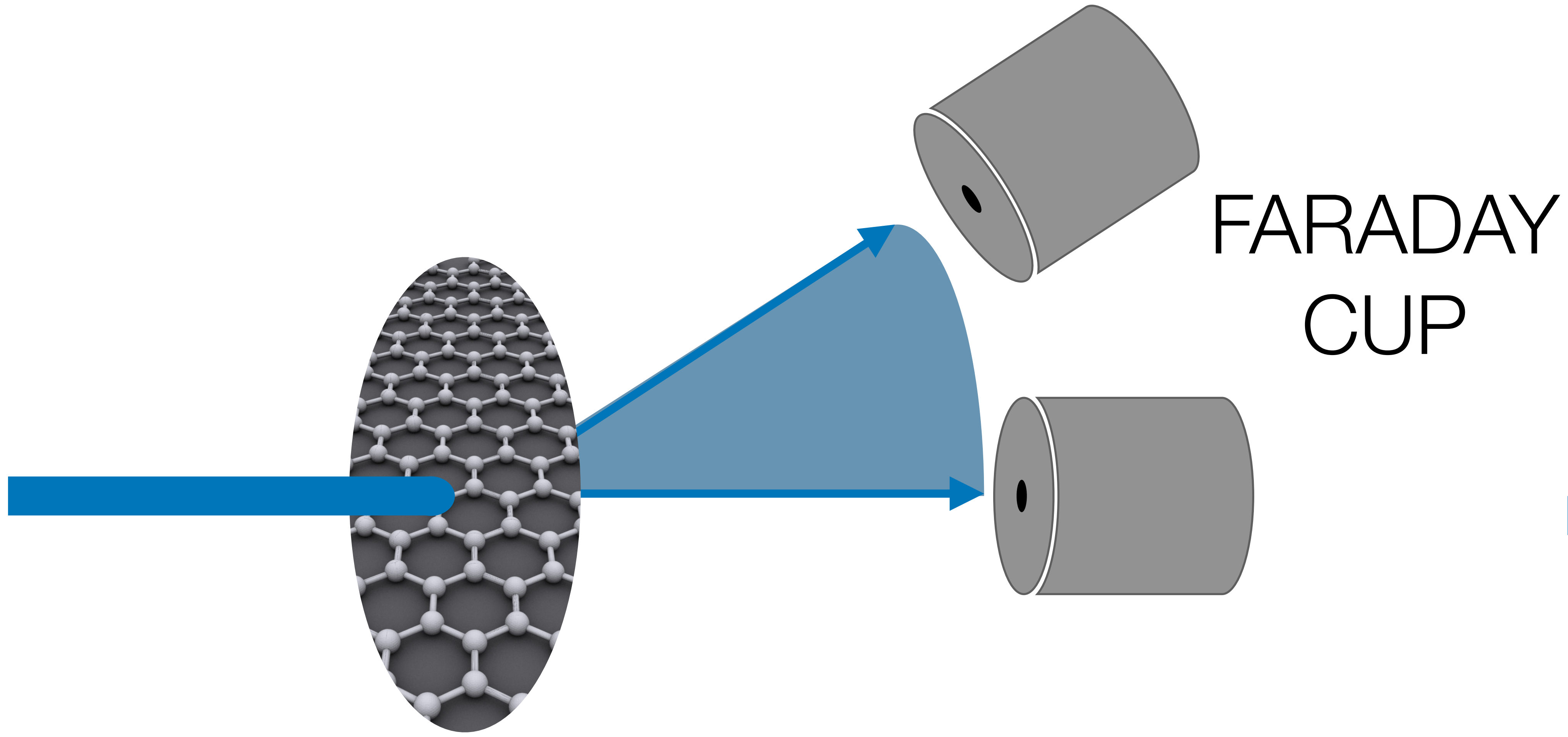
Transmission Outlook: Total Cross-Section Measurement

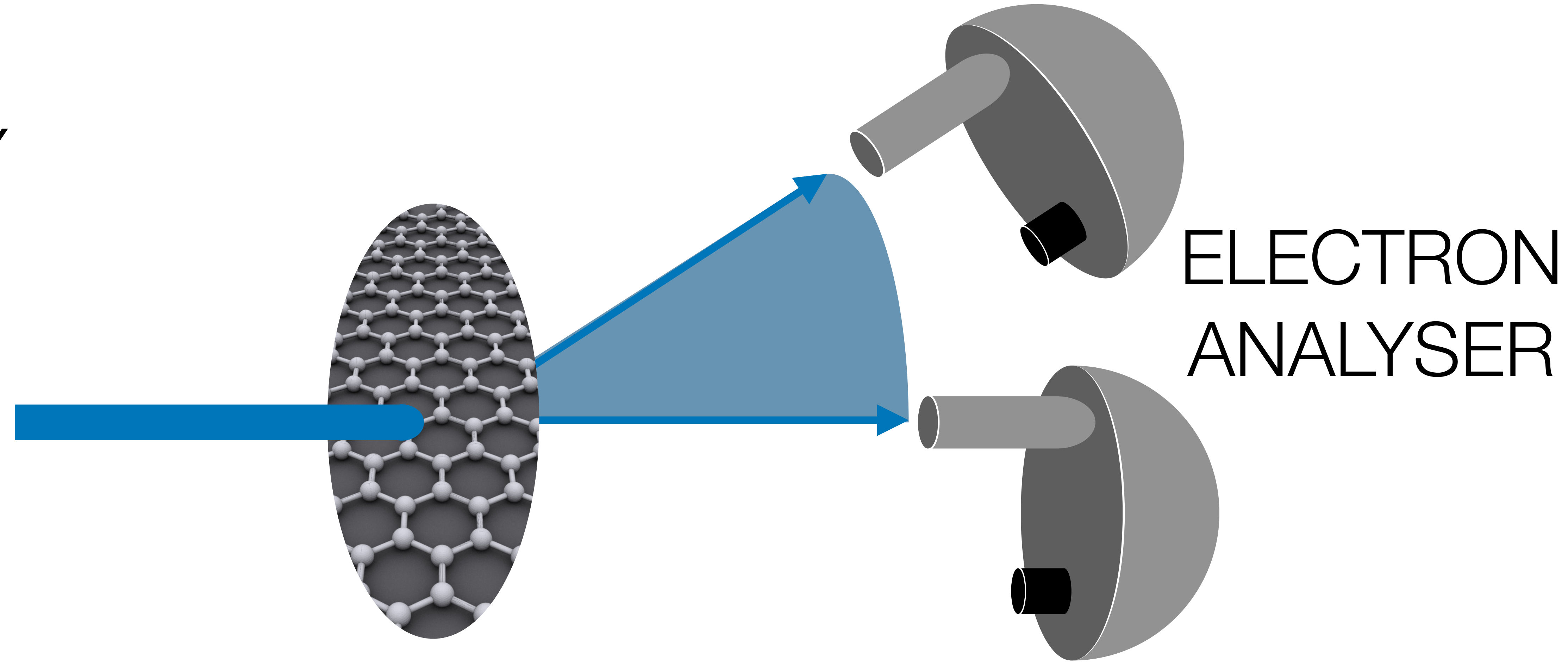
For the total cross-section evaluation:

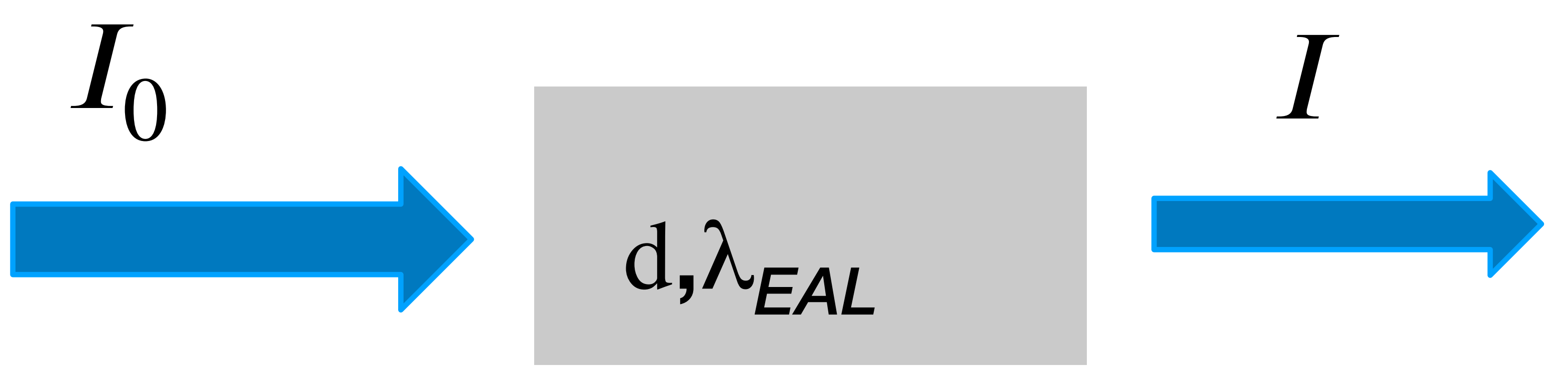
- n_G = carbon atom surface density in graphene
- σ_{tot} = total cross-section
- All and only the non-scattered electrons $I(E)$ should be measured

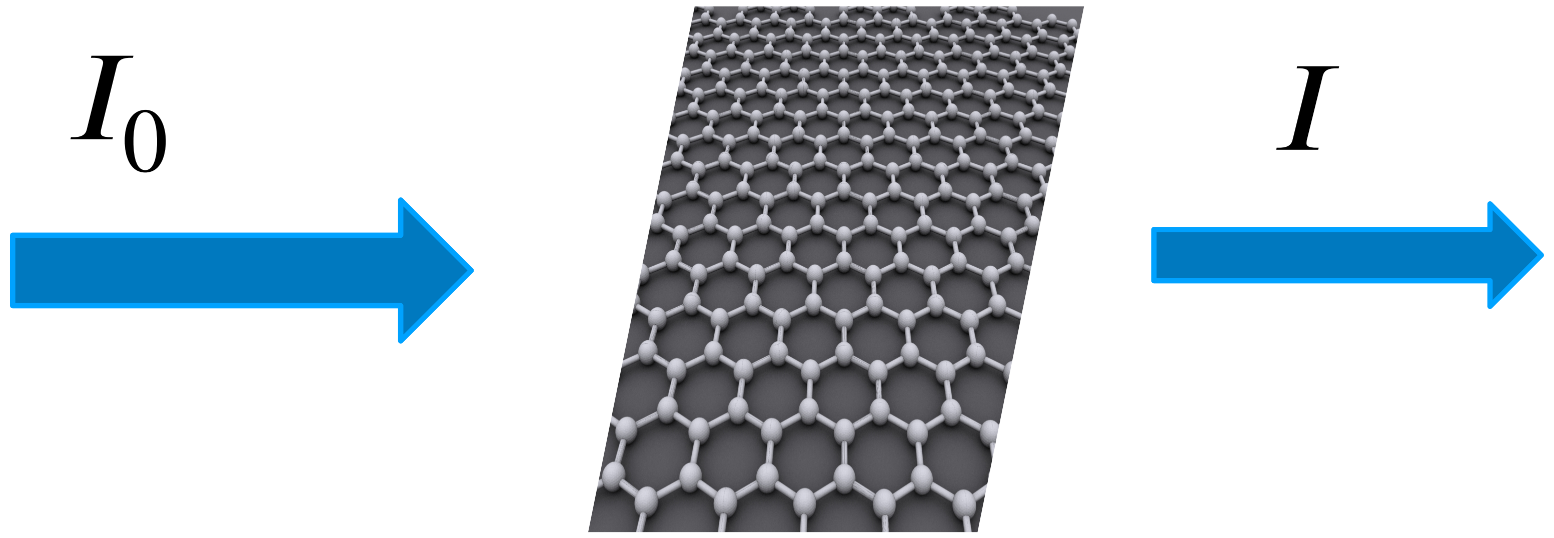


$$I(E) = I_0 e^{-n_G \sigma_{tot}(E)}$$









$$I(E) = I_0 e^{-\frac{d}{\lambda_{EAL}}}$$

$$I(E) = I_0 e^{-n_G \sigma_{tot}(E)}$$

Which thickness d must be used for ML graphene?

- Interplanar distance in graphite: 3.35 Å
- Twice the radius of covalent bond: 2.48 Å

The attenuation length obtained in this way is affected by the arbitrariness of the thickness choice

Where:

- n_G is the surface density of the carbon atom in graphene
- σ_{tot} is the total cross section

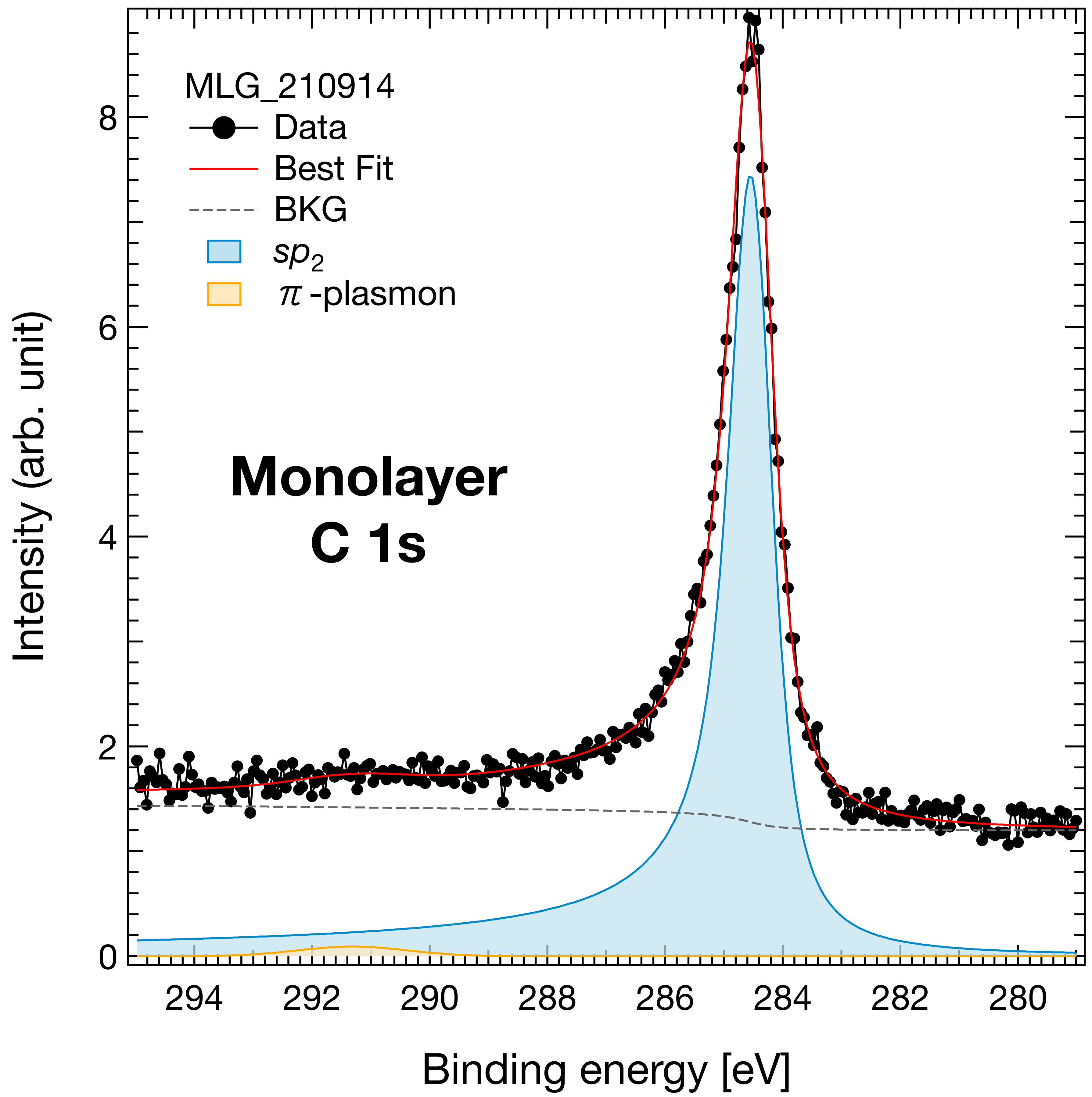
A correct measurement of the non scattered electrons $I(E)$ allows to obtain the total cross section

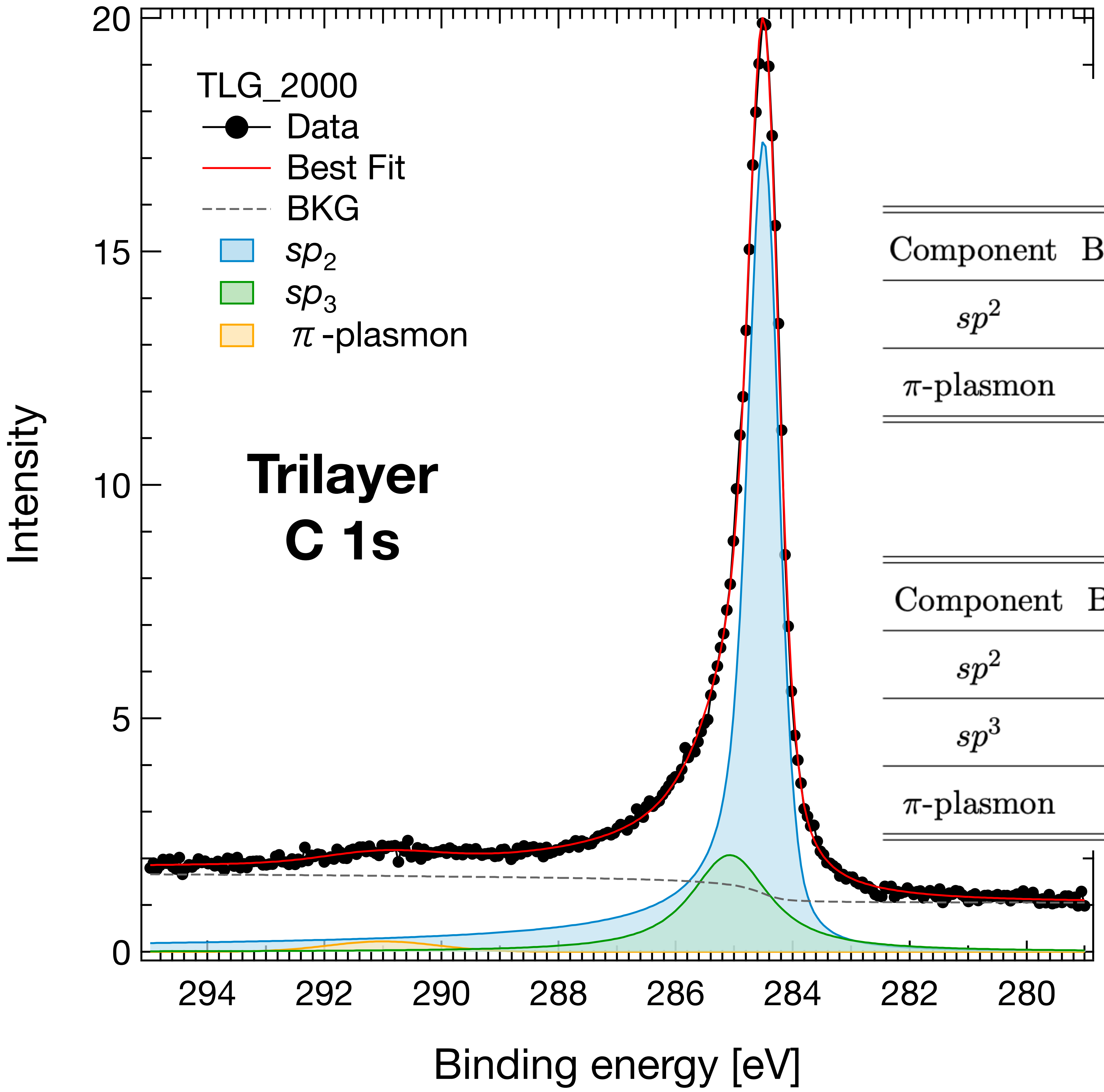
High Temperature Annealing: Good Quality Graphene

550°C annealing
in vacuum

Both C 1s spectra reveal a good quality graphene:

- ✤ Main contribution due to sp2
- ✤ Slight amount (~20%) of sp3 in the trilayer
- ✤ Lorentzian width of sp2 higher in the monolayer





Monolayer graphene

Component	Binding energy [eV]	Area	GW [eV]	LW [eV]	Asymmetry
sp^2	284.45	204	0.45	0.58	0.1
π-plasmon	290.9	4	1.9	0	0

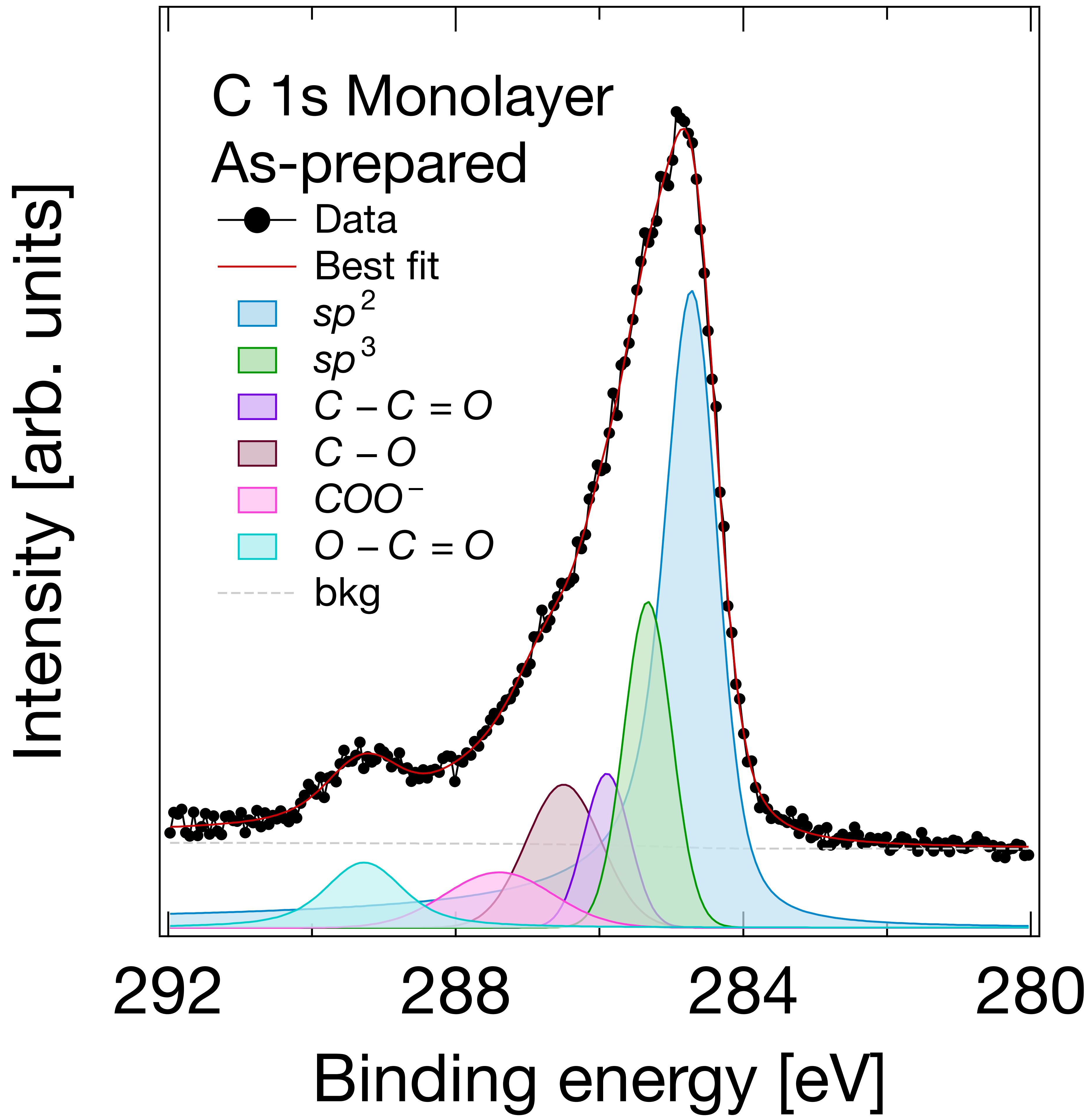
Trilayer graphene

Component	Binding energy [eV]	Area	GW [eV]	LW [eV]	Asymmetry
sp^2	284.47	311	0.46	0.24	0.1
sp^3	285.1	84	0.5	1.5	0
π-plasmon	291.0	10	2.2	0	0

High Temperature Annealing Cleans…

Full covered, few spots no graphene

but PMMA contamination



High Temperature Annealing Cleans…

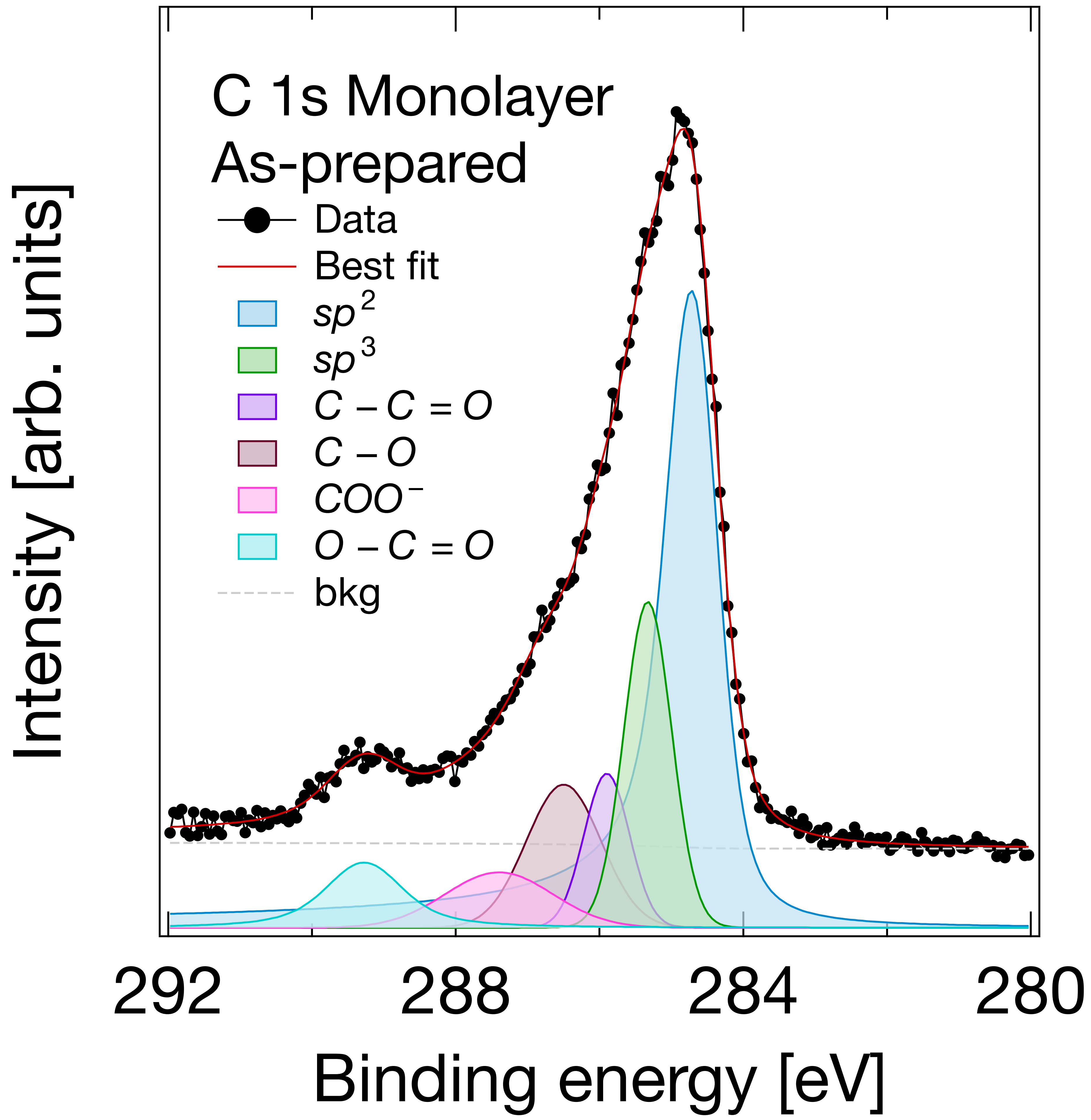
Full covered, few spots no graphene

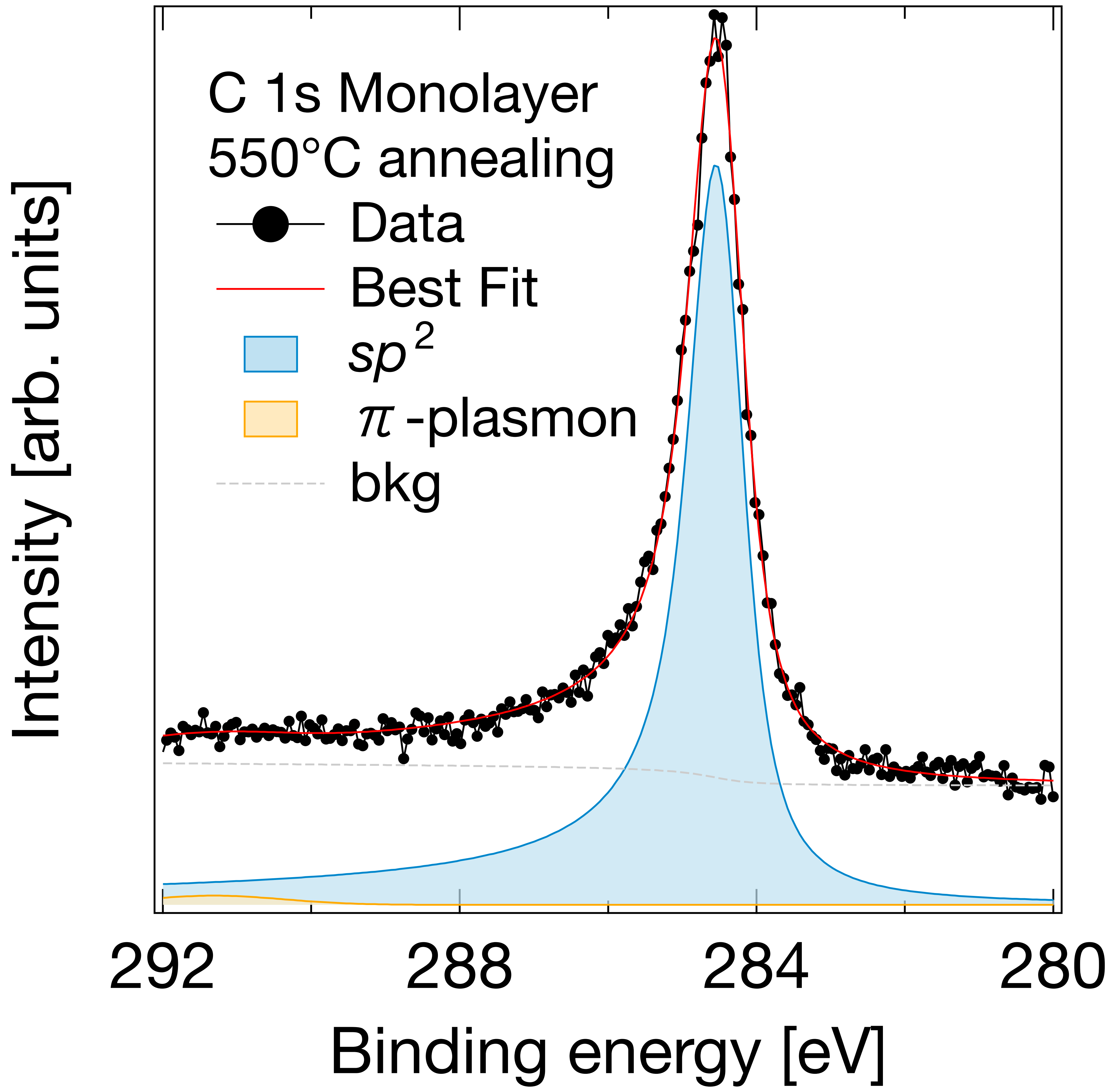
but PMMA contamination

550°C annealing →

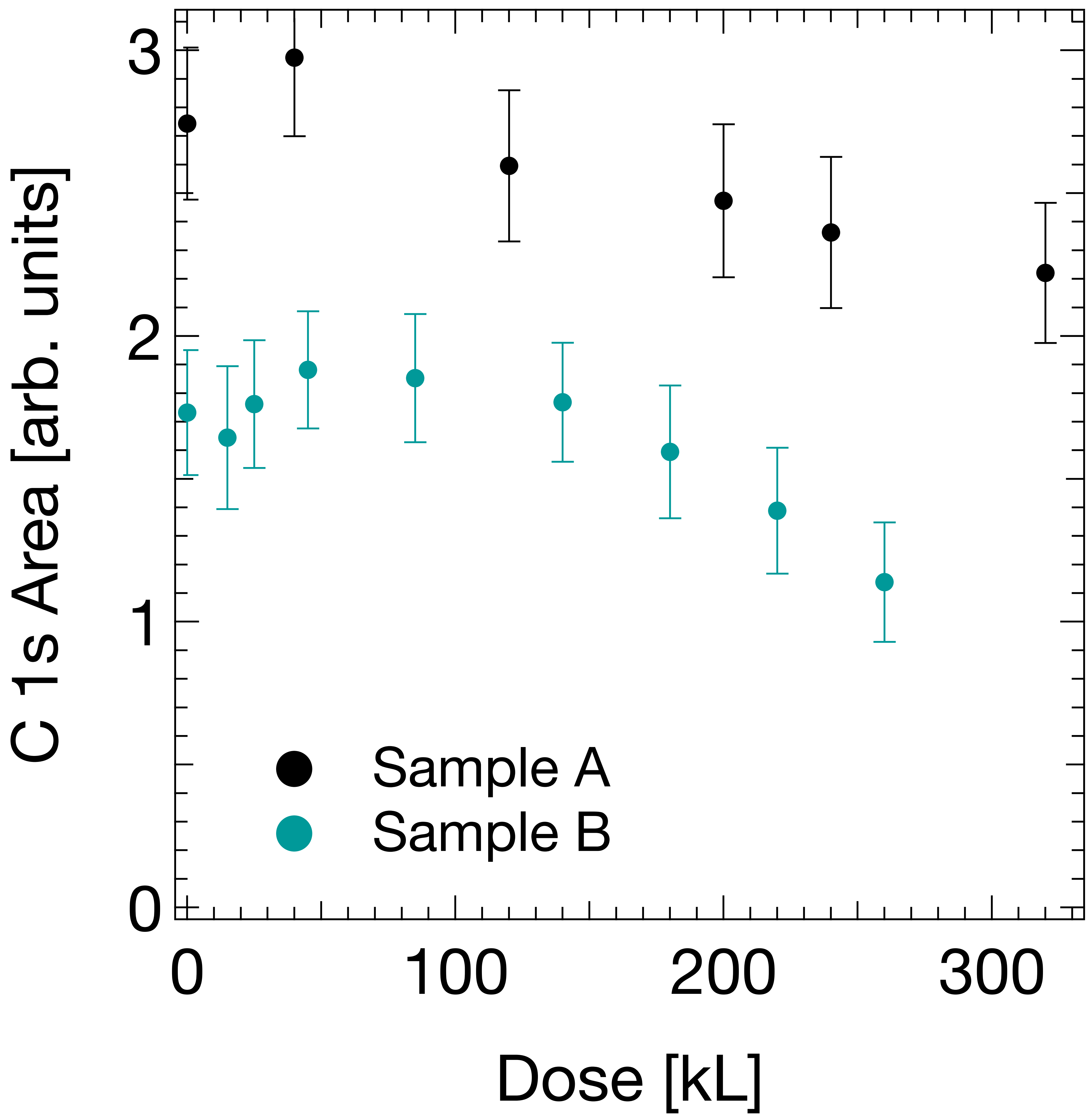
Effective for cleaning, high quality

graphene with sp^2 contribution only



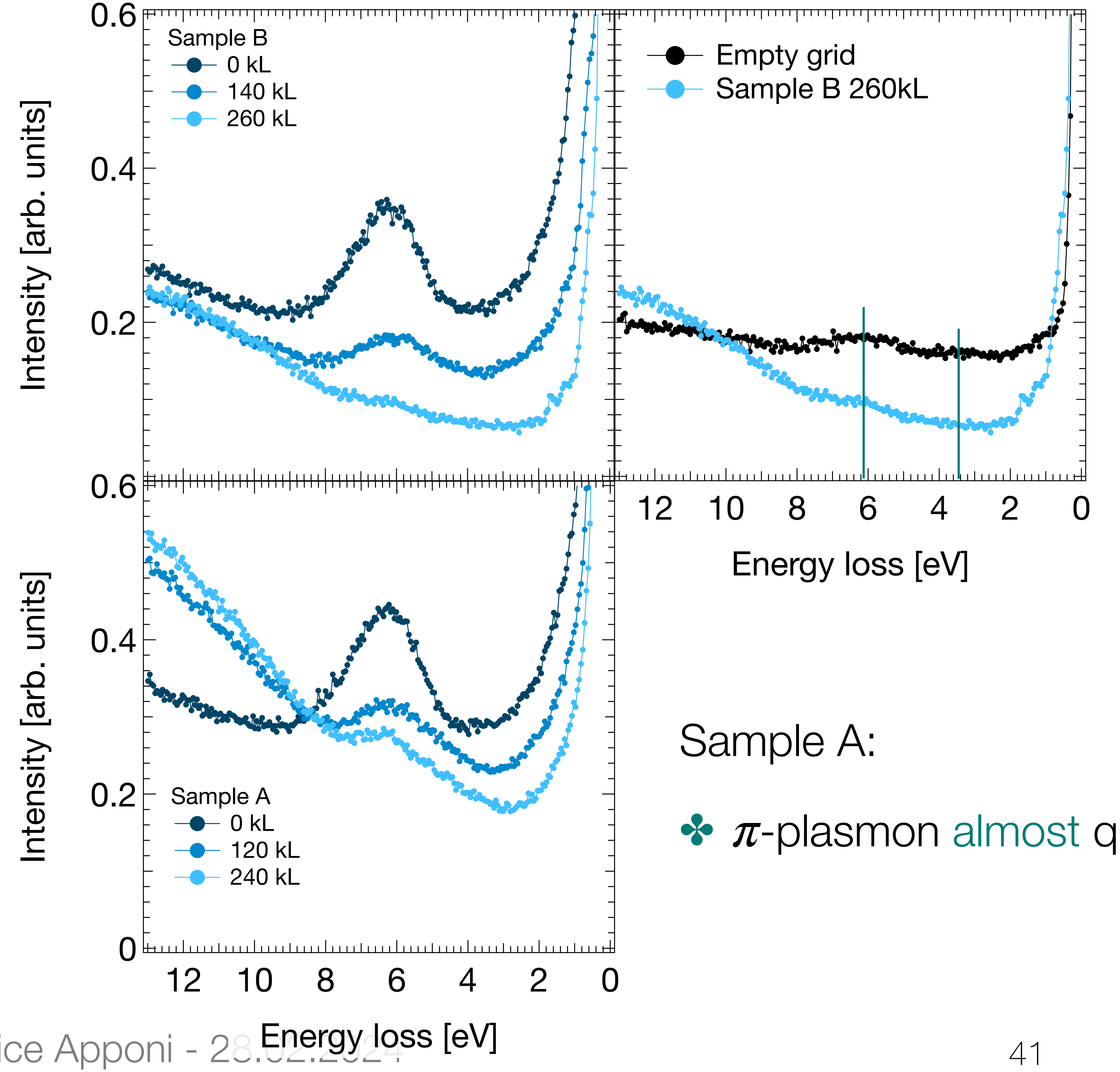


Total C 1s Area



Quenching of π-Plasmon: Ni Losses Is What's Left

PRELIMINARY



Sample B:

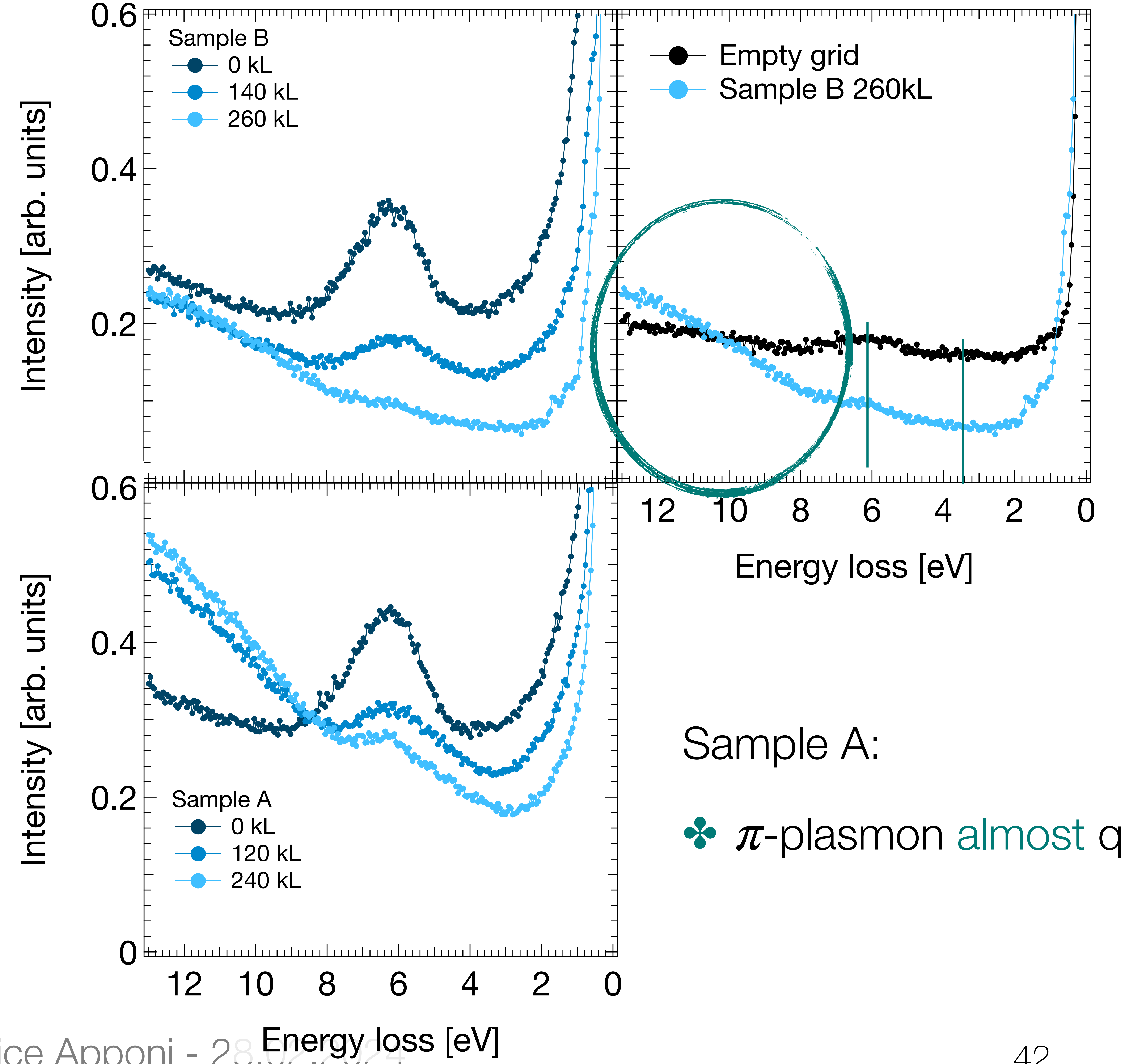
- π-plasmon ~completely quenched
- Ni has losses at ~6 eV and ~3.5 eV

Sample A:

- π-plasmon almost quenched despite 59% sp^3 saturation

Quenching of π-Plasmon: Ni Losses Is What's Left

PRELIMINARY



Sample B:

- π-plasmon ~completely quenched
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Sample A:

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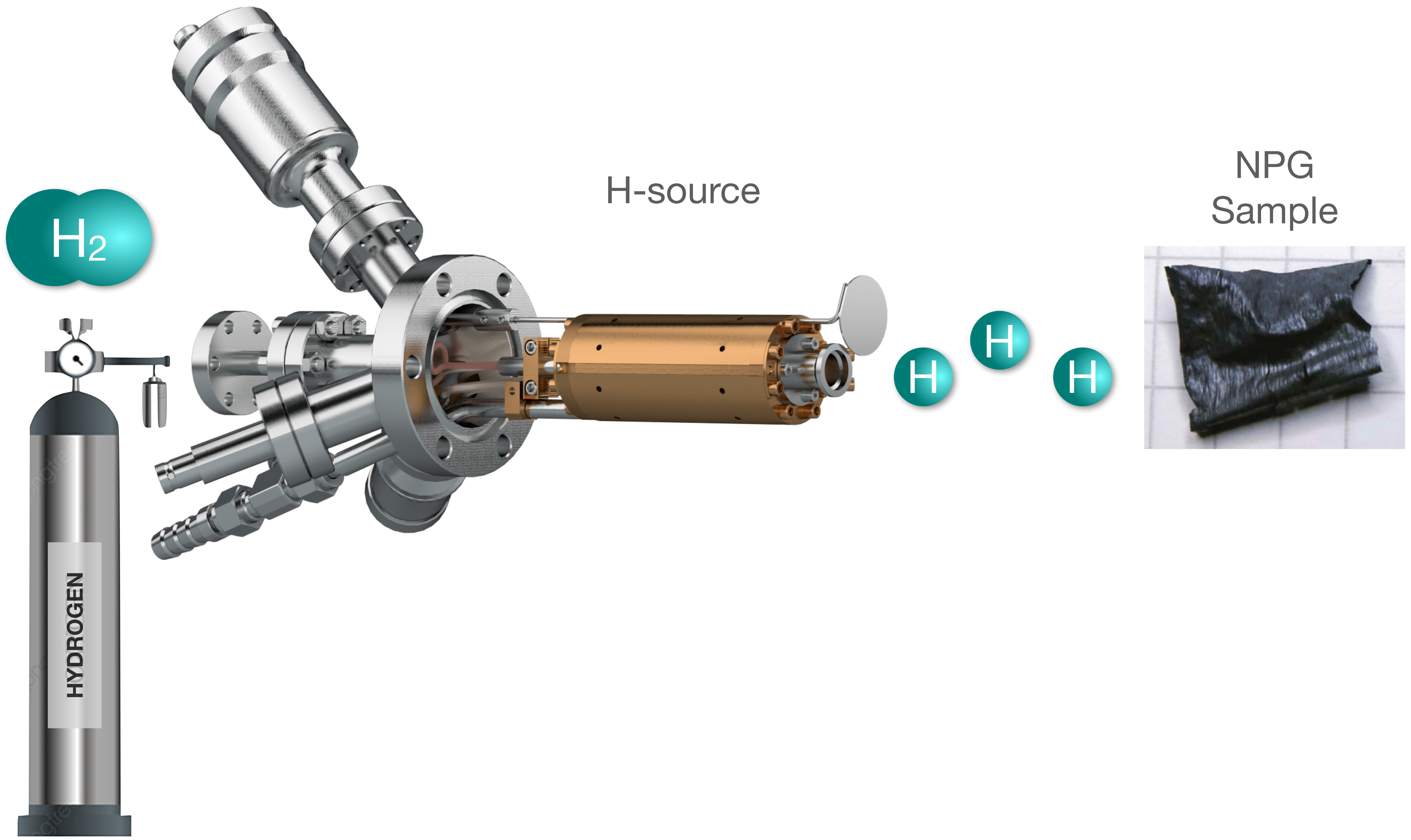
Hydrogenation of NPG: Different Depth Sensitivity



Hydrogenated nanoporous graphene (NPG):

- Synchrotron micro-XPS experiment
- hν = 350 eV (C 1s E_K = 60 eV)
- $sp^3/(sp^2+sp^3) \approx$ 90% achieved

Betti, M.G. *et al.*, *Nano Letters* (2022),
https://doi.org/10.1021/acs.nanolett.2c00162

What's new then?

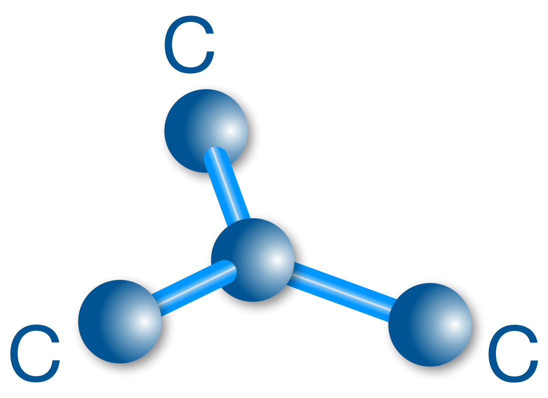
- hν = 1486.7 eV (C 1s E_K = 1200 eV)
- Electron energy loss spectroscopy (plasmon investigation)

Different depth sensitivity

E_K = 60 eV depth ~ 9 Å

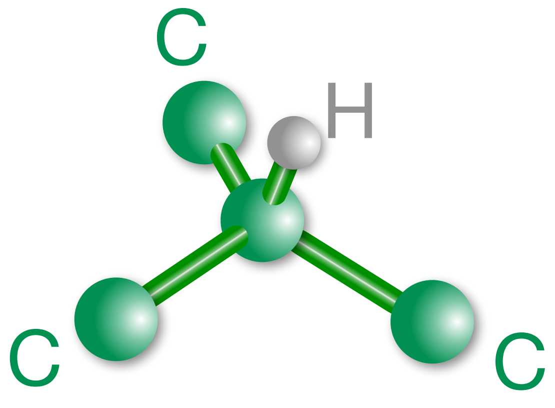
E_K = 1200 eV depth ~ 90 Å

Increase of sp^3: XPS Footprint of Hydrogenation



Carbon hybridization

changing from sp^2 to sp^3

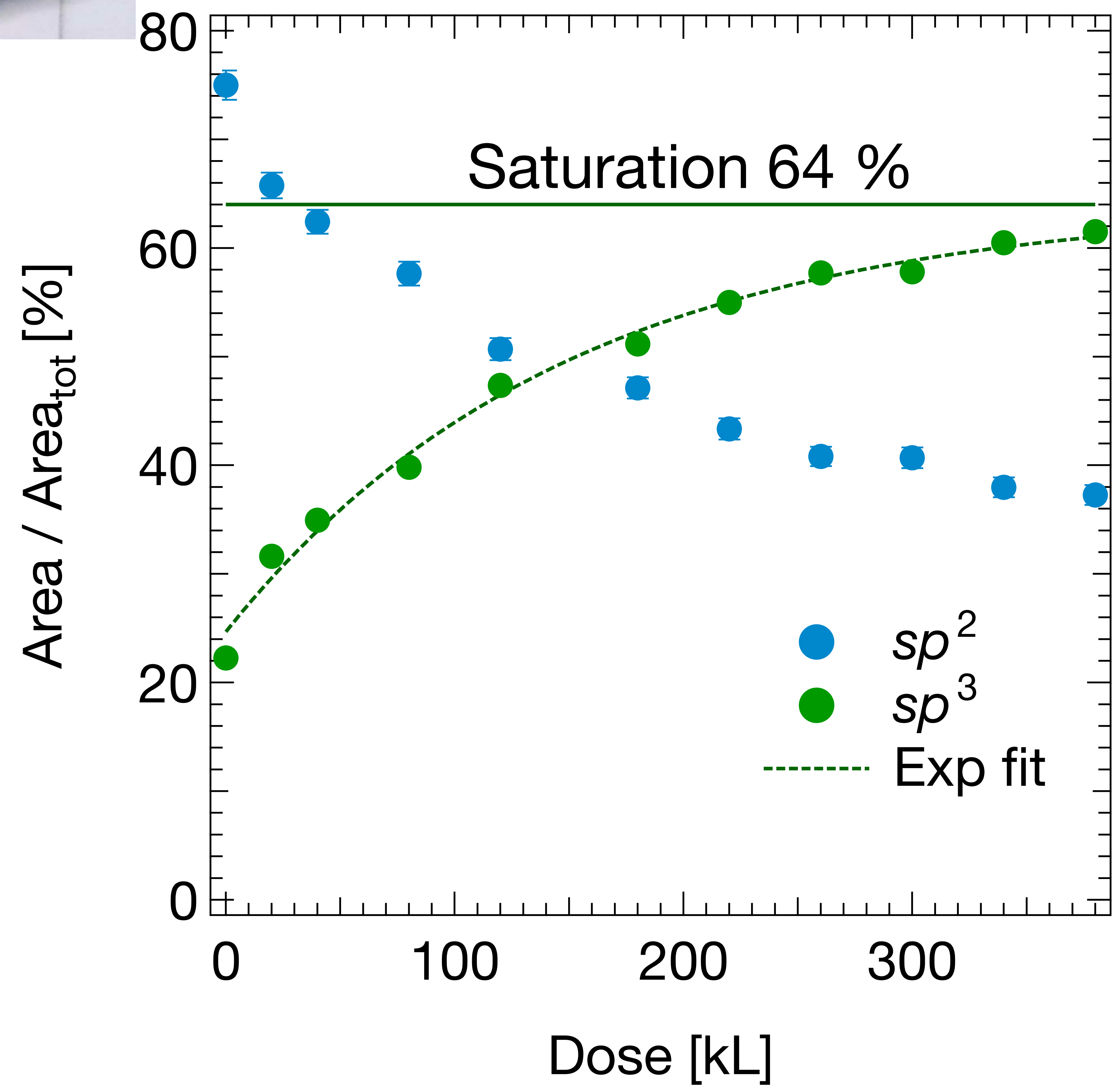


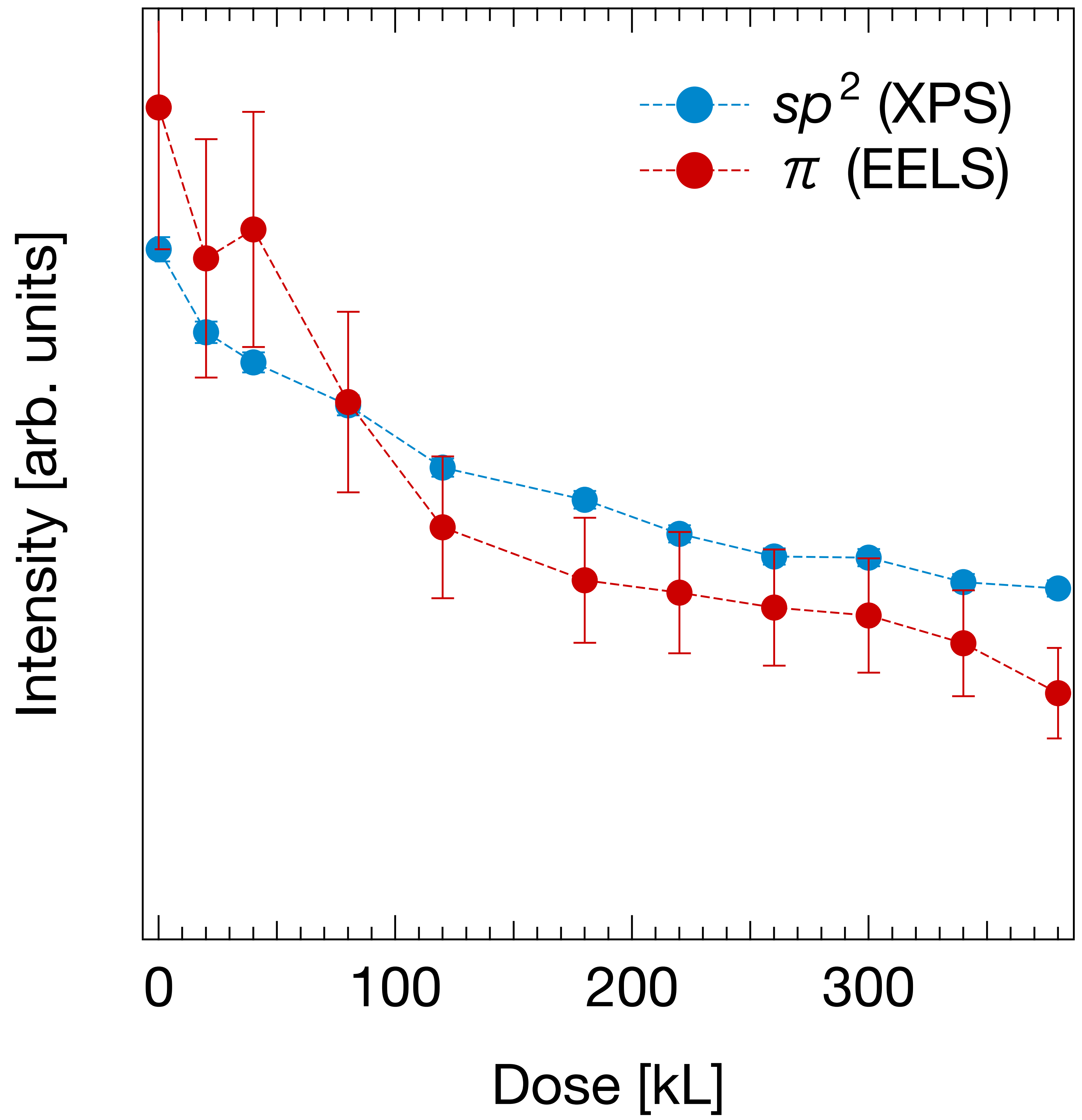
Quenching of π-Plasmon: EELS Footprint of Hydrogenation

π-plasmon:

- ✤ Excitation associated to sp^2
- ✤ Quenching due to sp^3 changing

We Reached the 64% Saturation





XPS result:

- Decrease of sp^2
- Exponential increase of sp^3
- 64% saturation seems to be ~reached

XPS-EELS comparison:

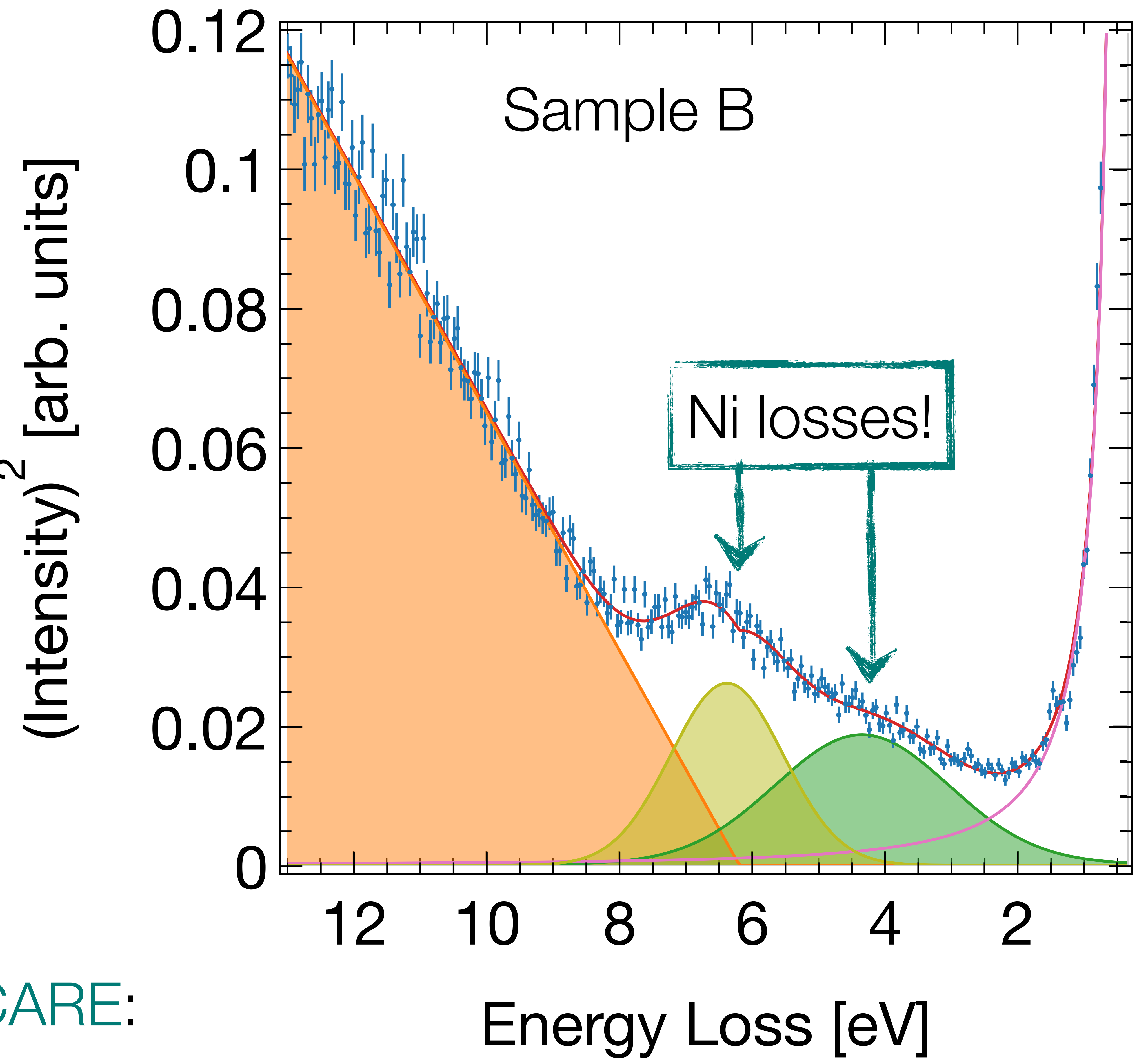
- Behaviour seems compatible
- π-plasmon not completely quenched
- sp^2 still there

~6.2 eV Band Gap Measured With EELS

PRELIMINARY

Hydrogenated graphene:

- sp^2 to sp^3 distortion
- Band gap opening
- Electronic transition onset $\propto (E - E_g)^{1/2}$ for direct gap semicondutors
- EELS measurement [2] and fit with a straight line
- With this analysis E_g = 6.2 eV



HANDLE WITH CARE:

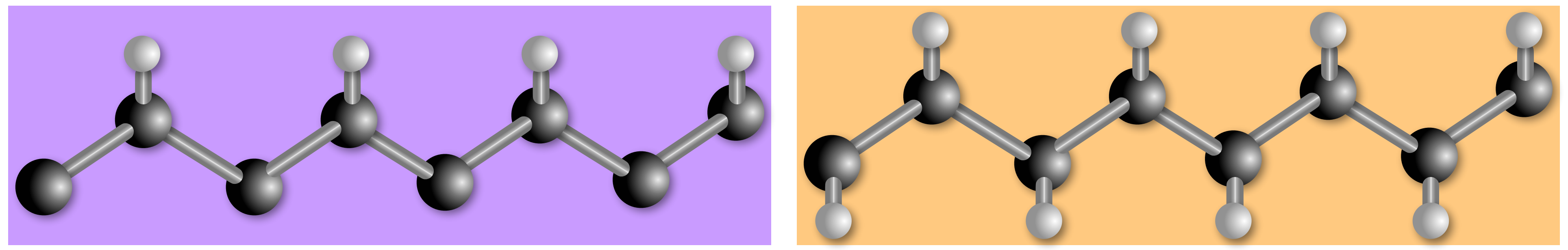
- Background
- Excitons

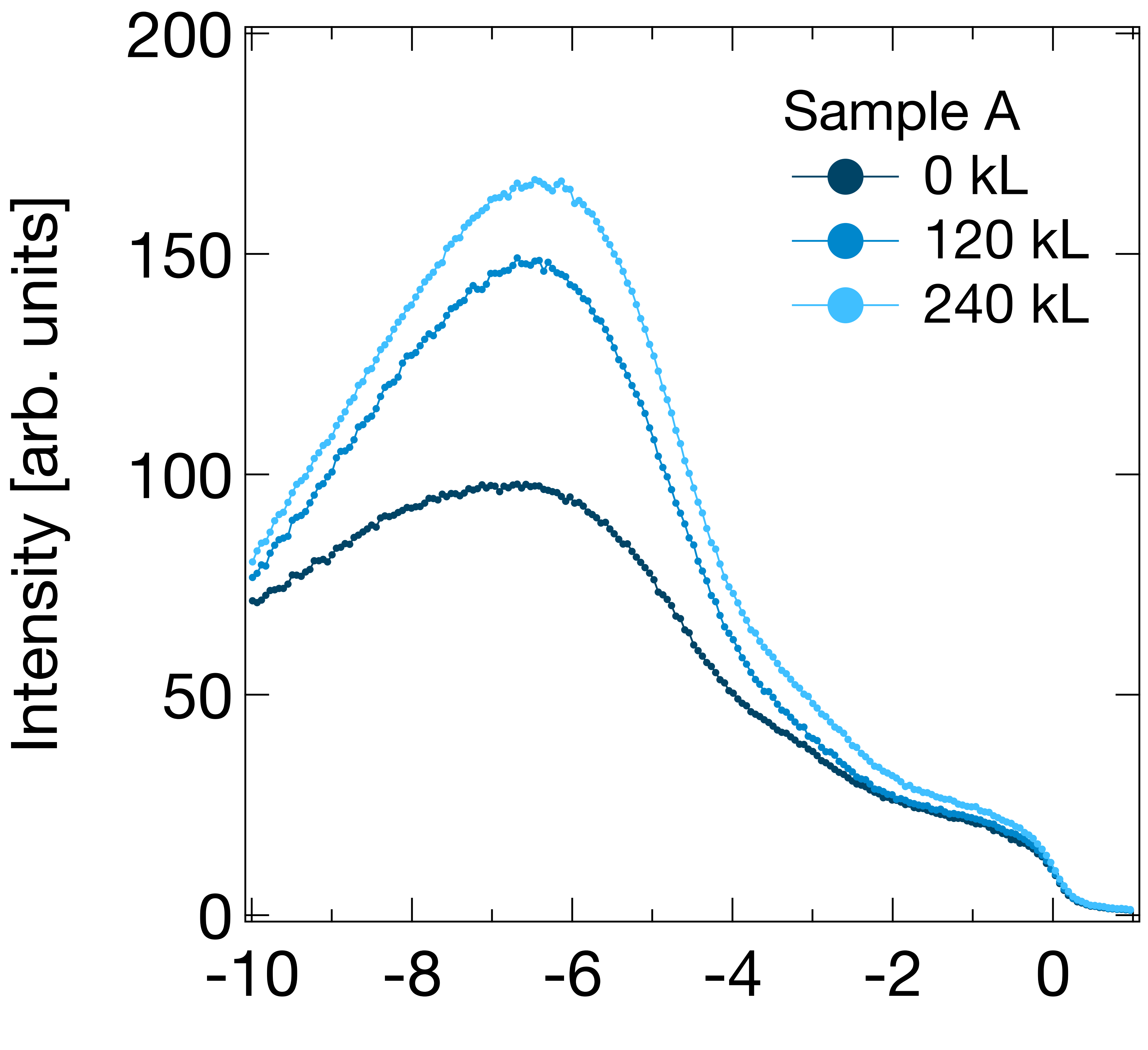
Valence Band to Understand CH Bonding

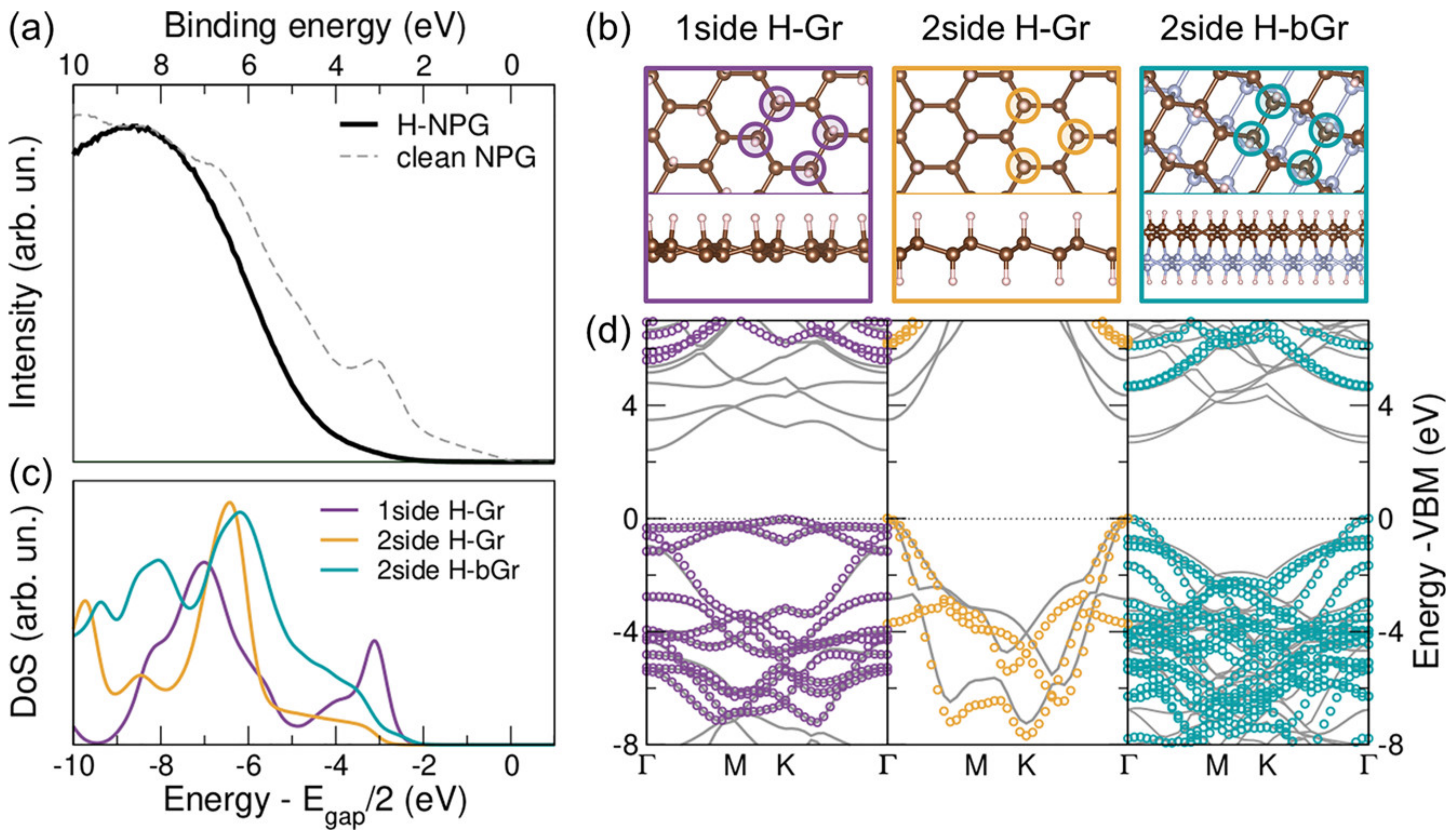
PRELIMINARY

How many sides?

- ✤ C 1s not an unambiguous marker
- ✤ UPS: valence band *features* and angular resolution







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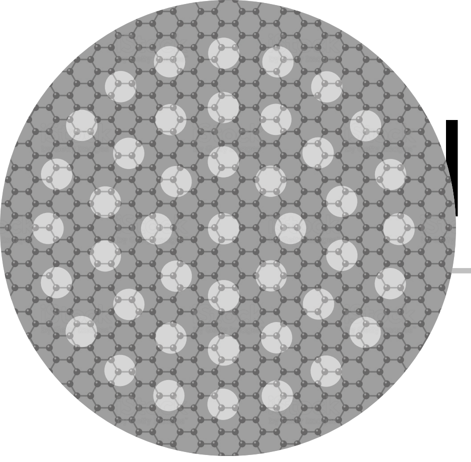
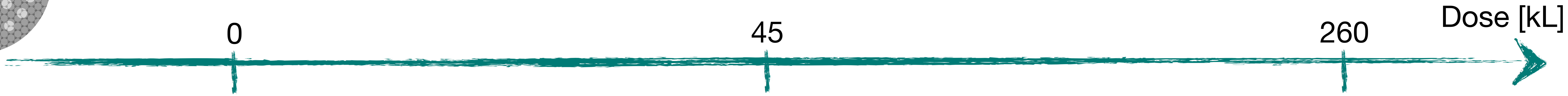
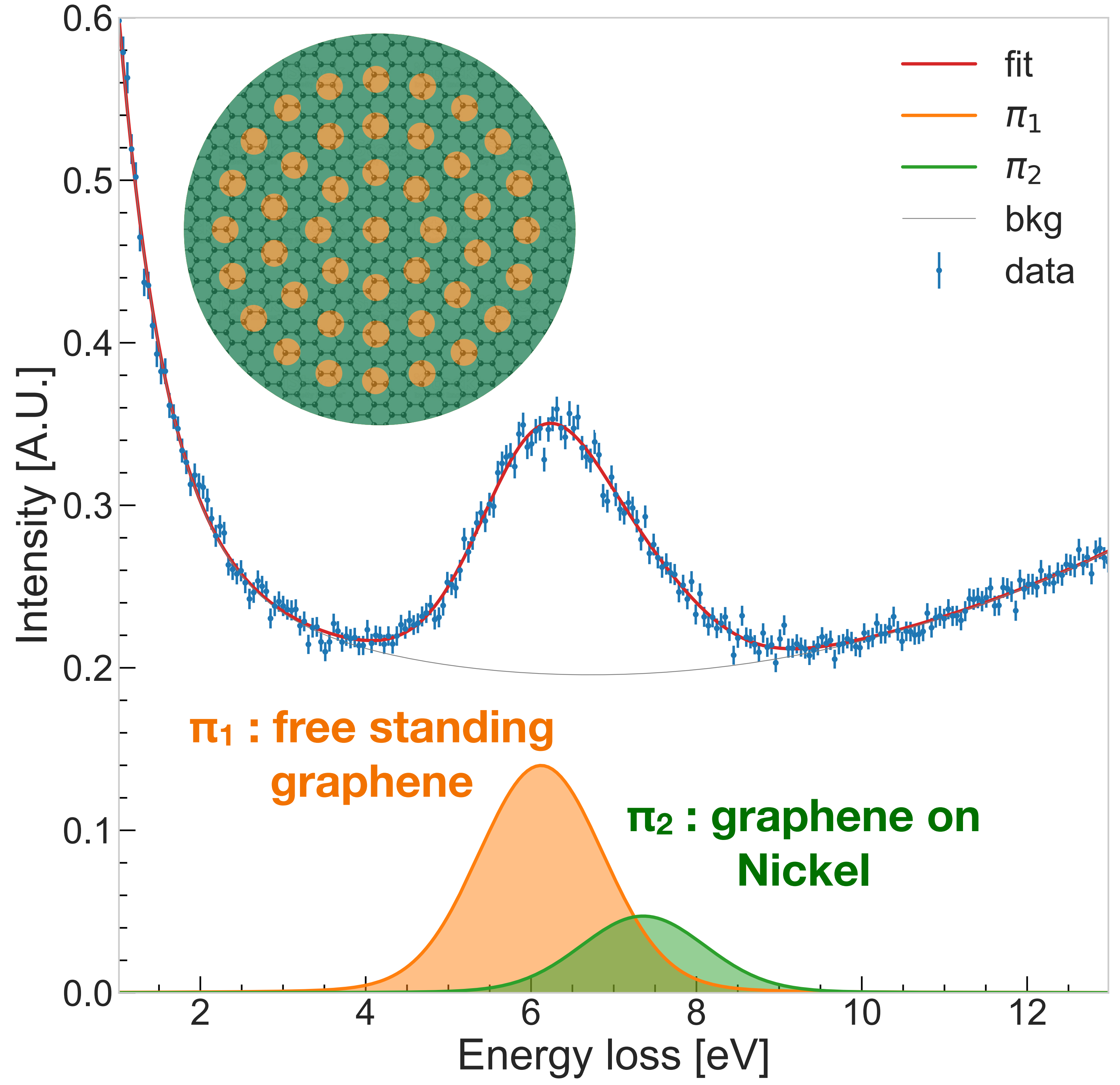
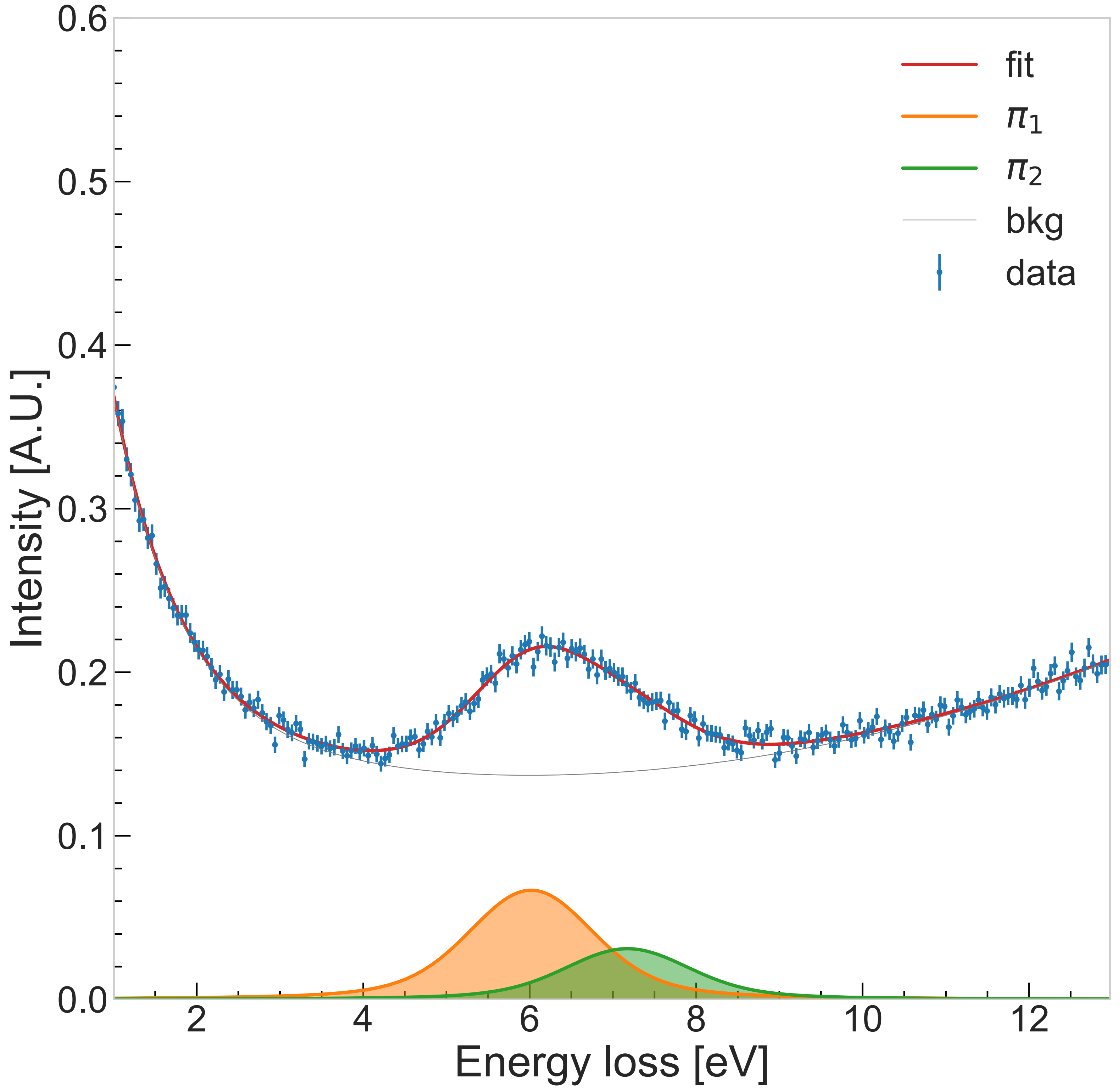
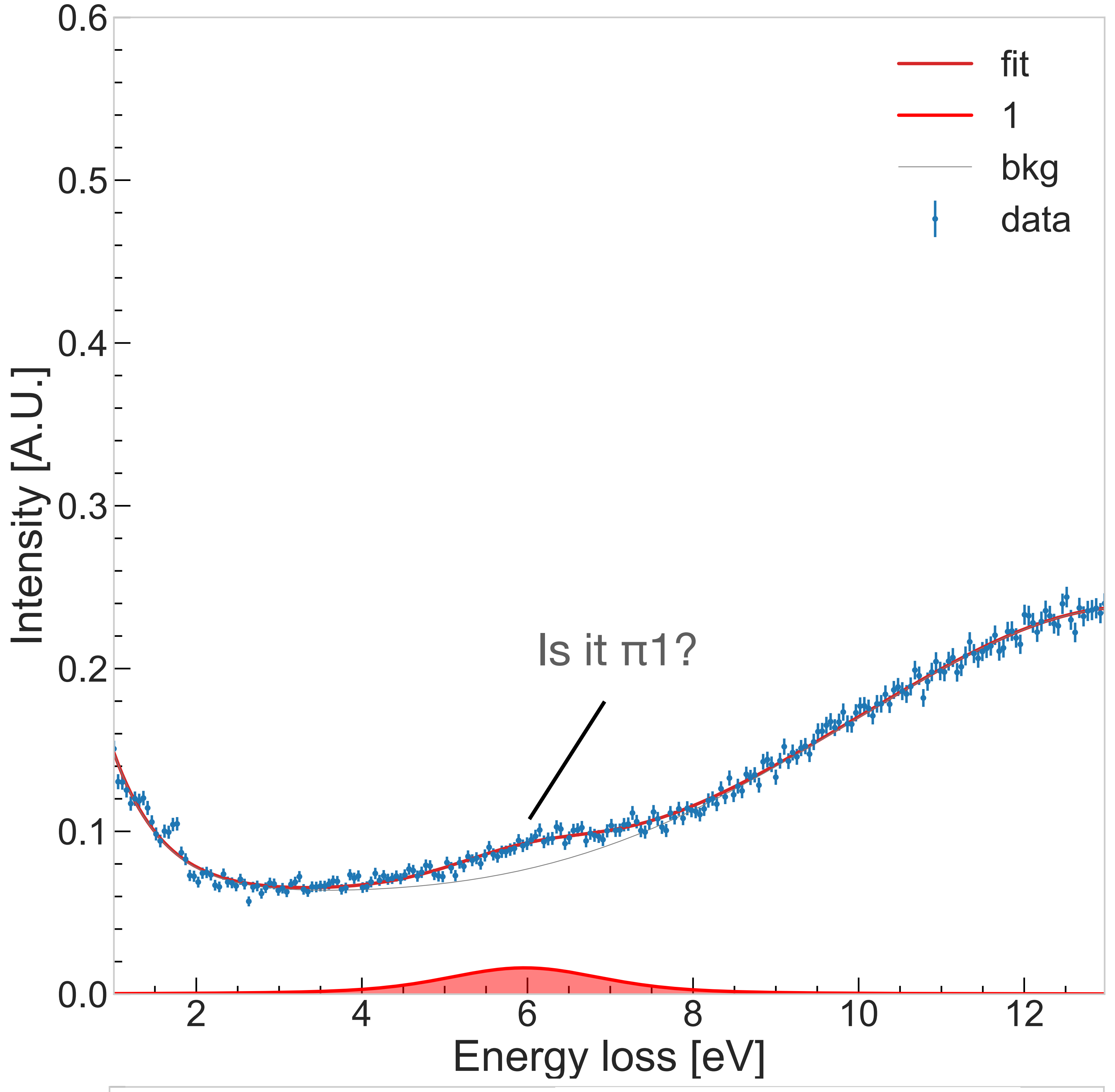


uenching of π-plasmon: EELS footprint of hydrogenation



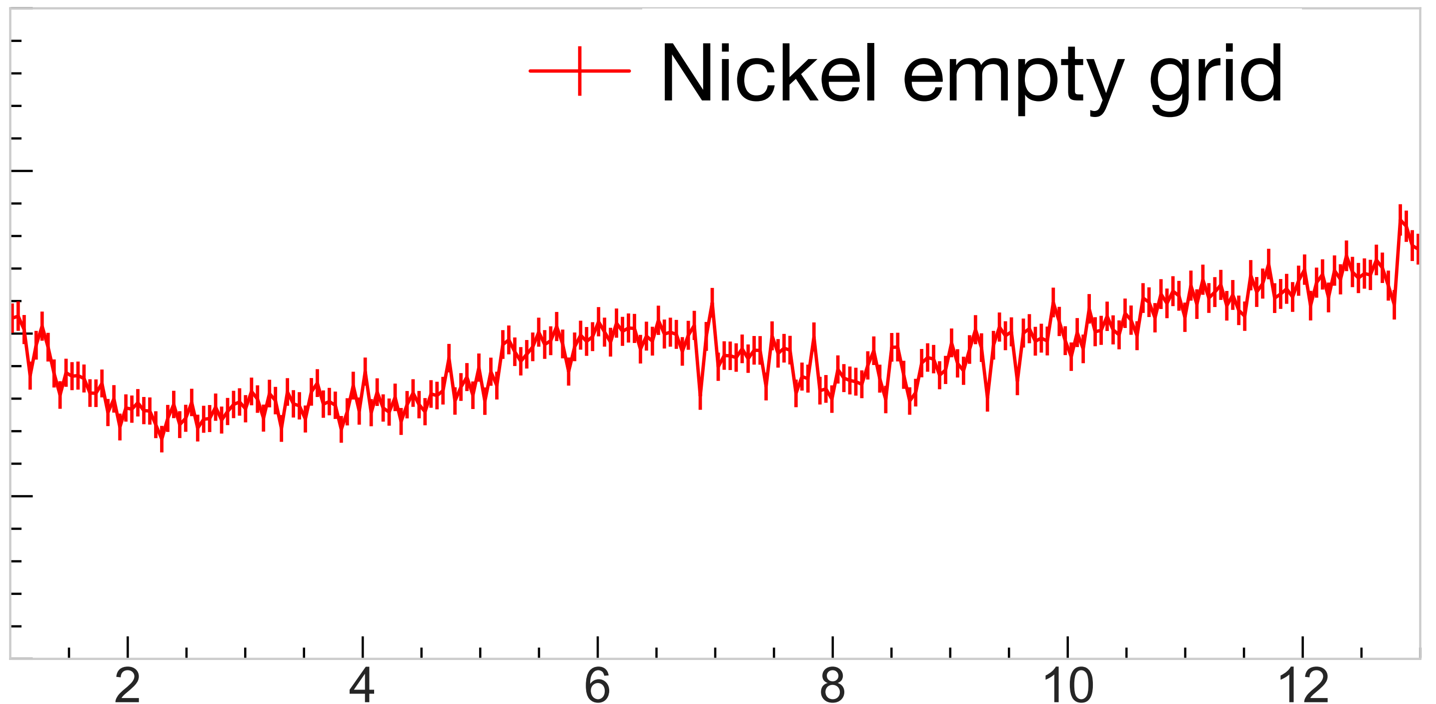




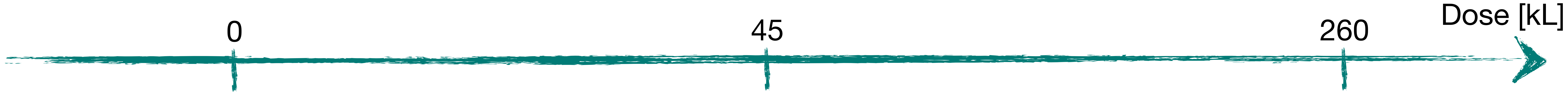


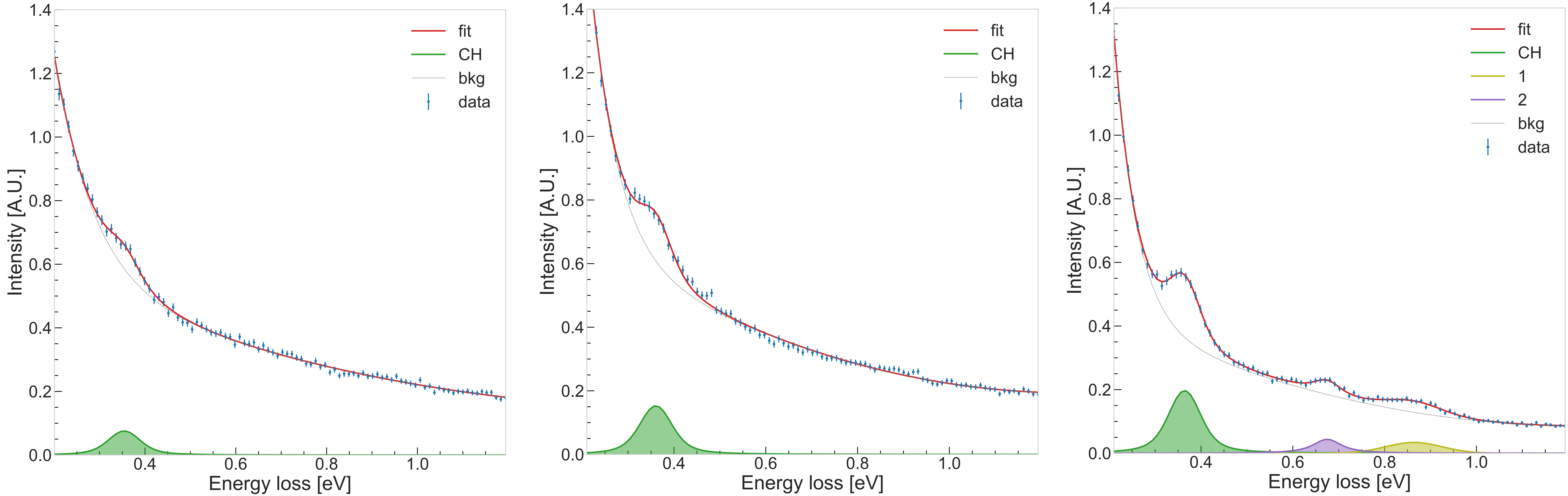
π-plasmon:

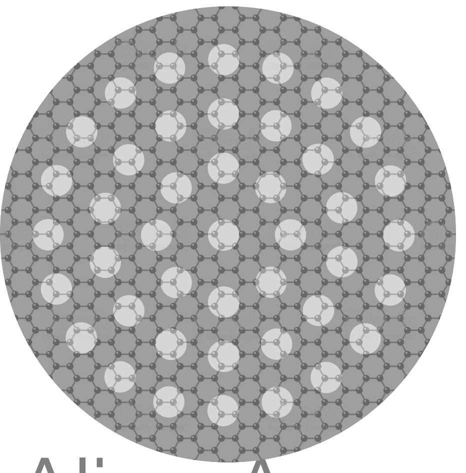
- Excitation associated to sp[2]
- Quenching due to sp[3] changing

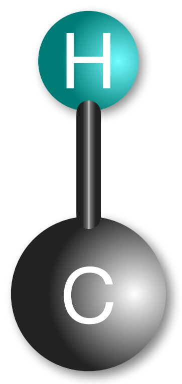


Growth of C-H stretching: EELS footprint of hydrogenation









C-H stretching mode ~360 meV

To Conclude

Graphene characterisation with spectroscopy:

- Contaminants removed with 550°C annealing but suspended grahene breaks
- C 1s only sp_2 and evidence of suspended monolayer graphene

Transmission of low-energy electrons (30-900 eV):

- Graphene coverage and geometrical transmission evaluated with SEM image analysis
- Measured tranmission corrected with coverage to obtain graphene transmission

Hydrogenation of C-nanostructures:

- Saturation of NPG achieved but H-uptake in depth should be studied
- Monolayer graphene saturation seems to depend on sp^2/sp^3 ratio

Stil lots of fun to be had:

- Non-damaging cleaning treatment
- Total cross-section for electron-graphene interaction
- Deeper understanding of suspended graphene hydrogenation (band gap, CH bonding)