Update on Preparation and Hydrogenation of Suspended Graphene

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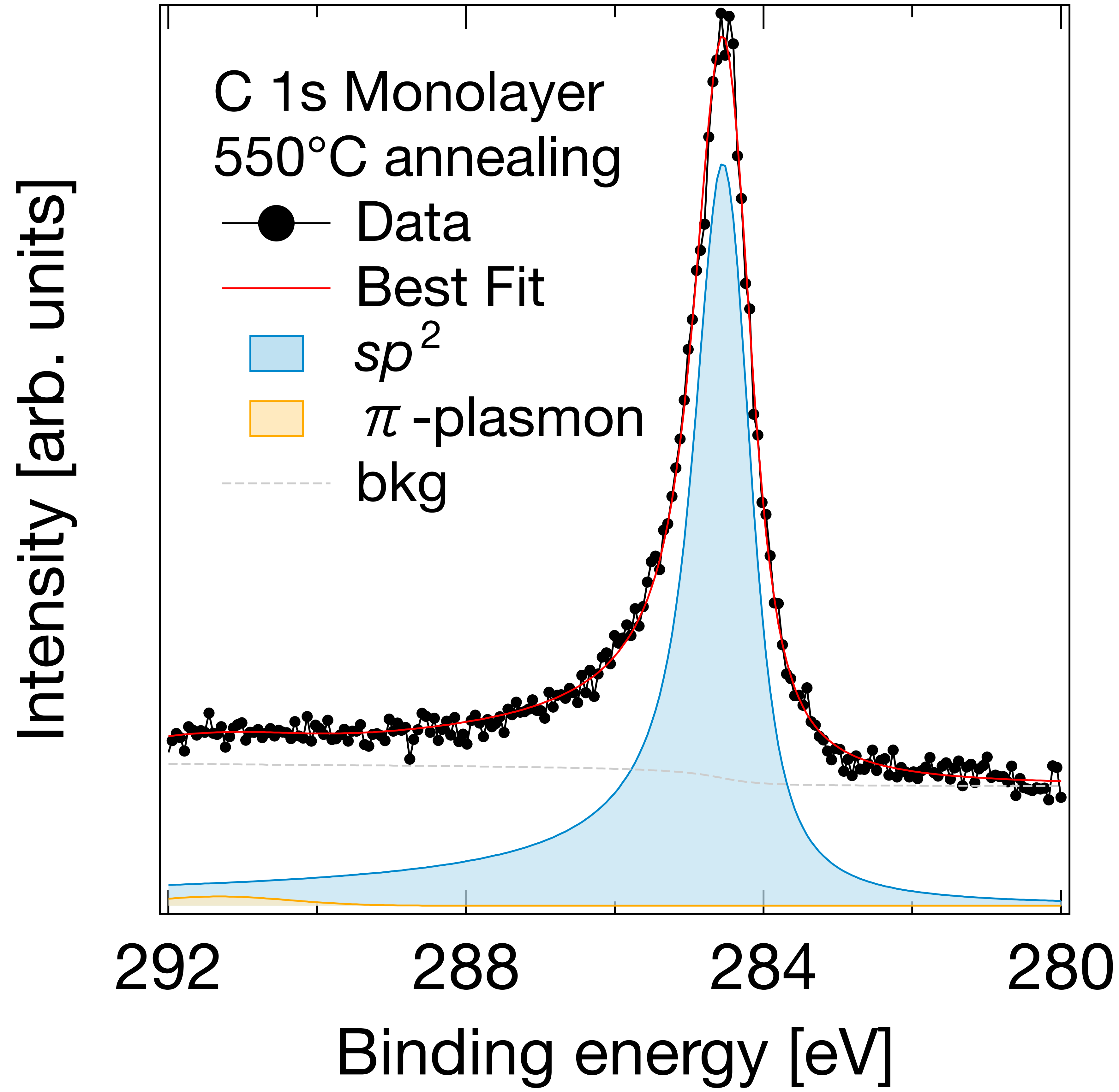
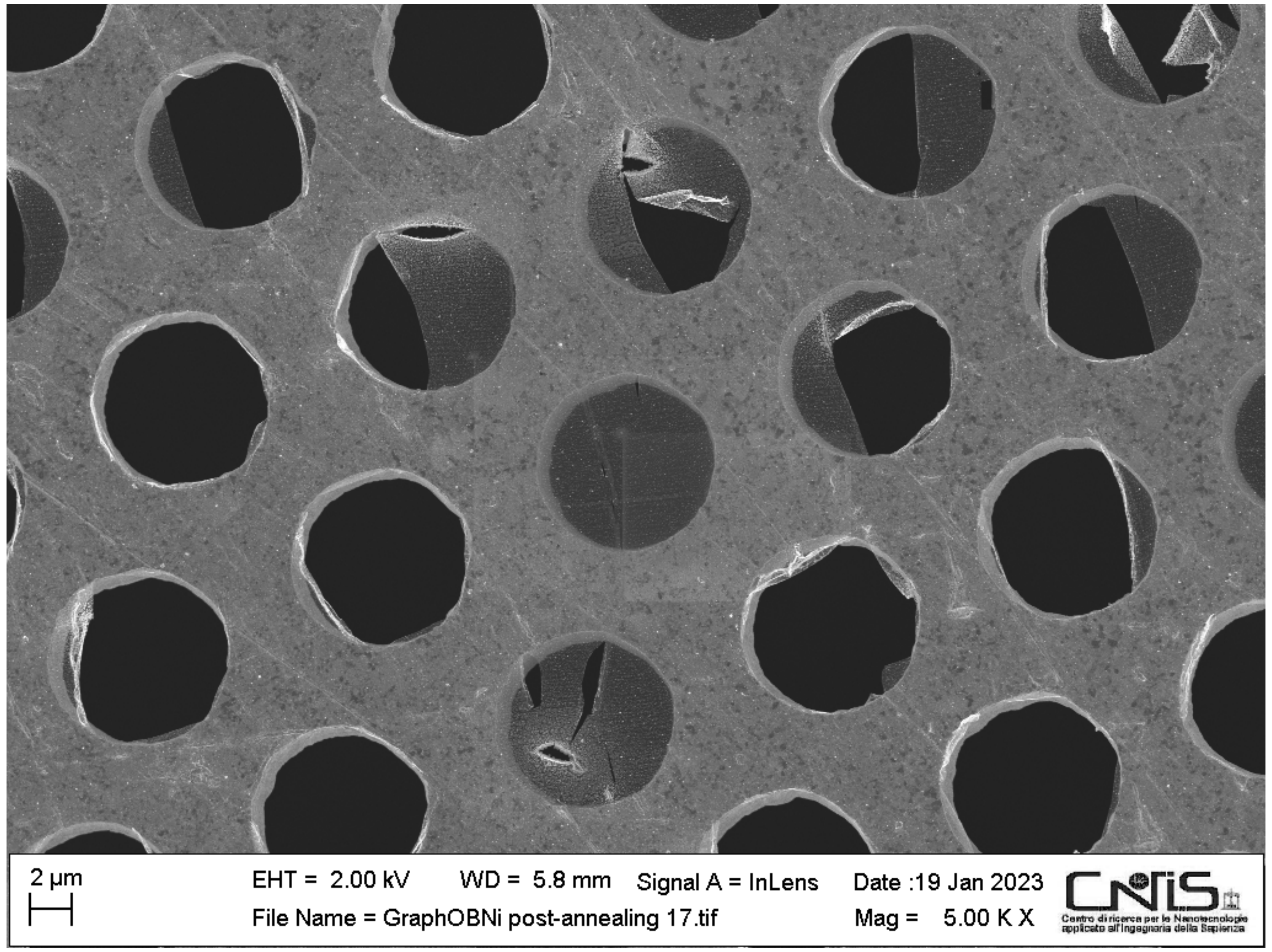
INFN Istituto Nazionale di Fisica Nucleare

High Temperature Annealing Cleans…But Damages

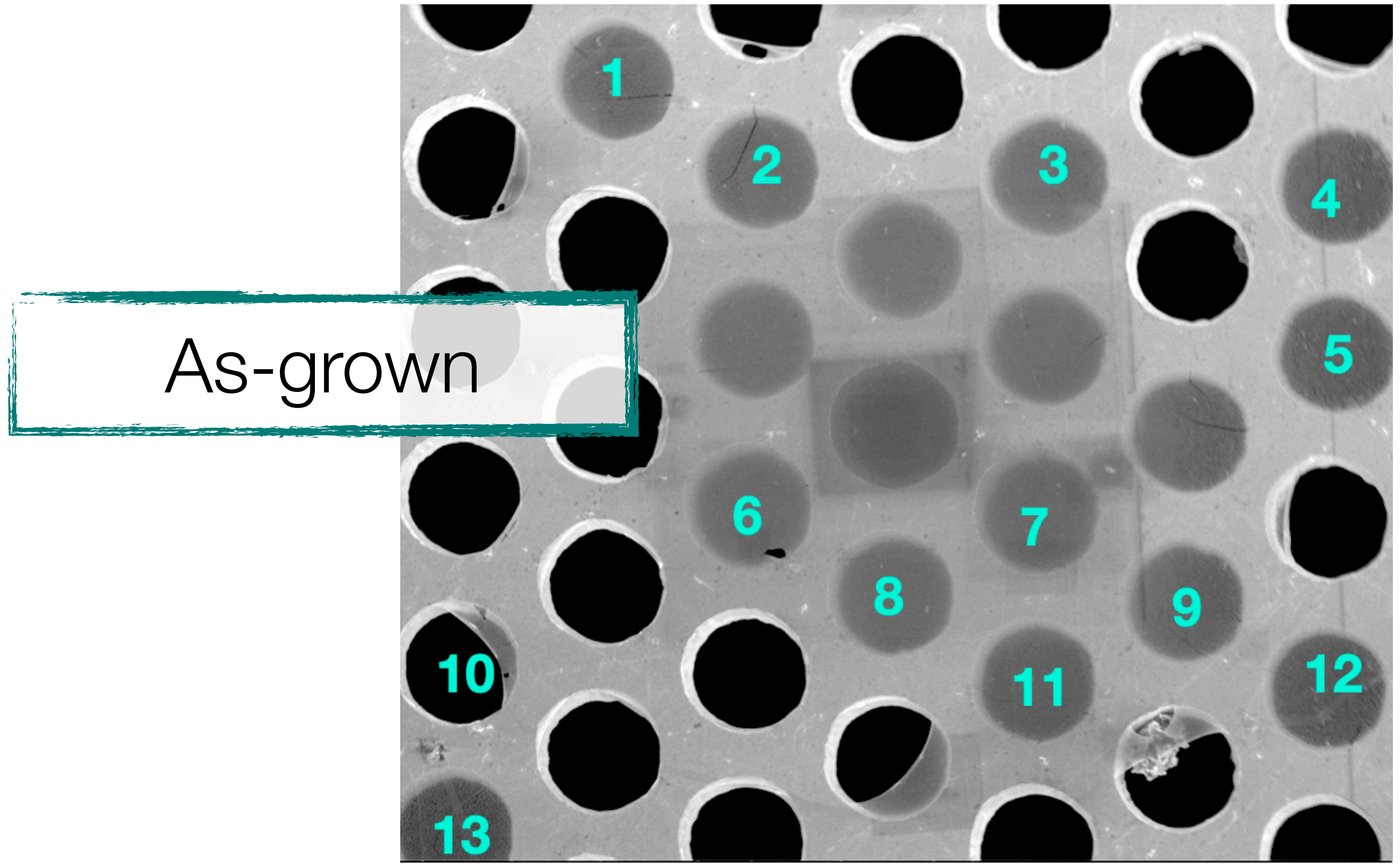
550°C annaling removes PMMA → but damages graphene





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

Looking for the Critical Temperature



Which is the critical temperature?

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

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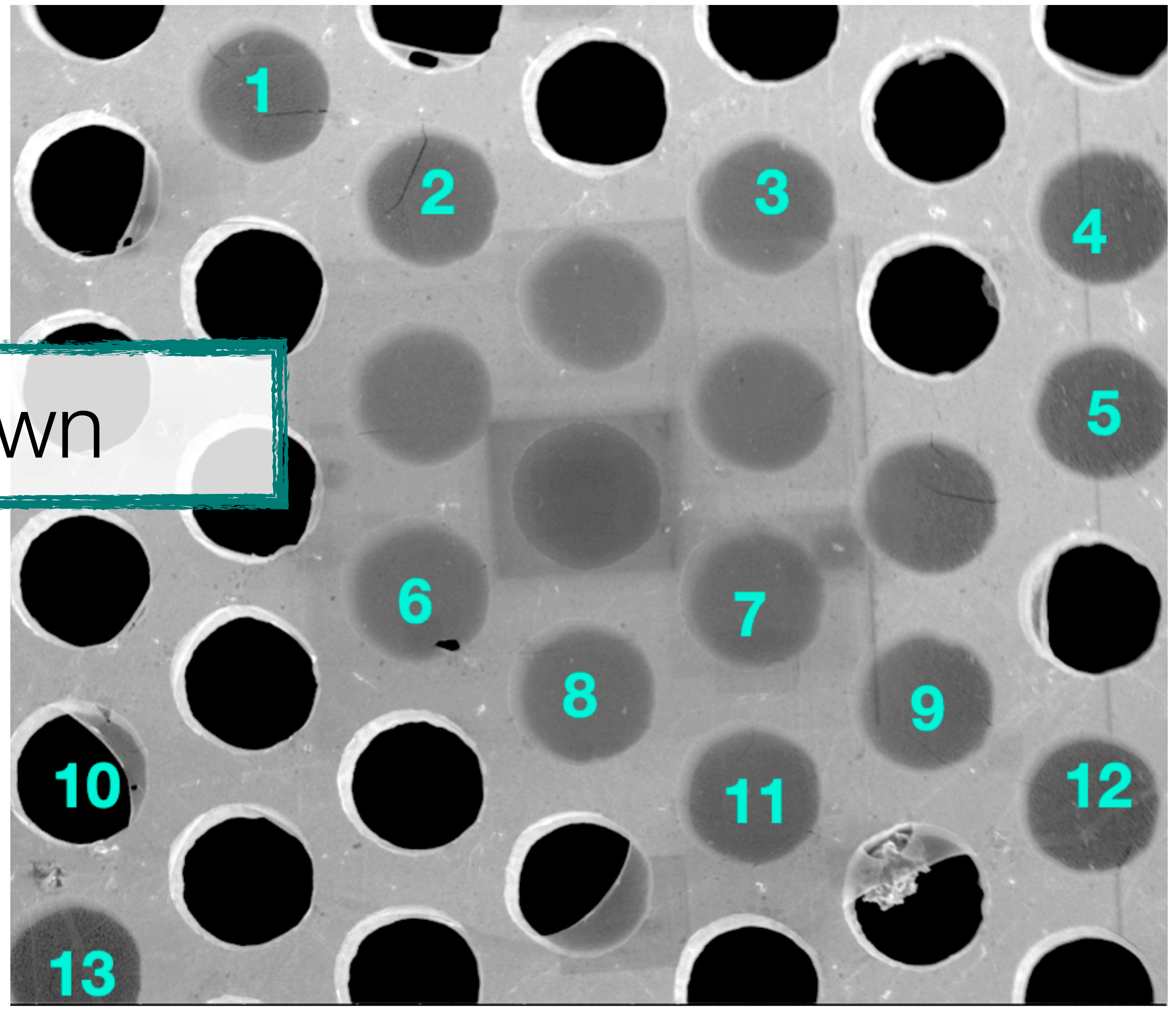
- ✤ SEM at each step
- ✤ Nothing happens

As-grown

300 °C annealing



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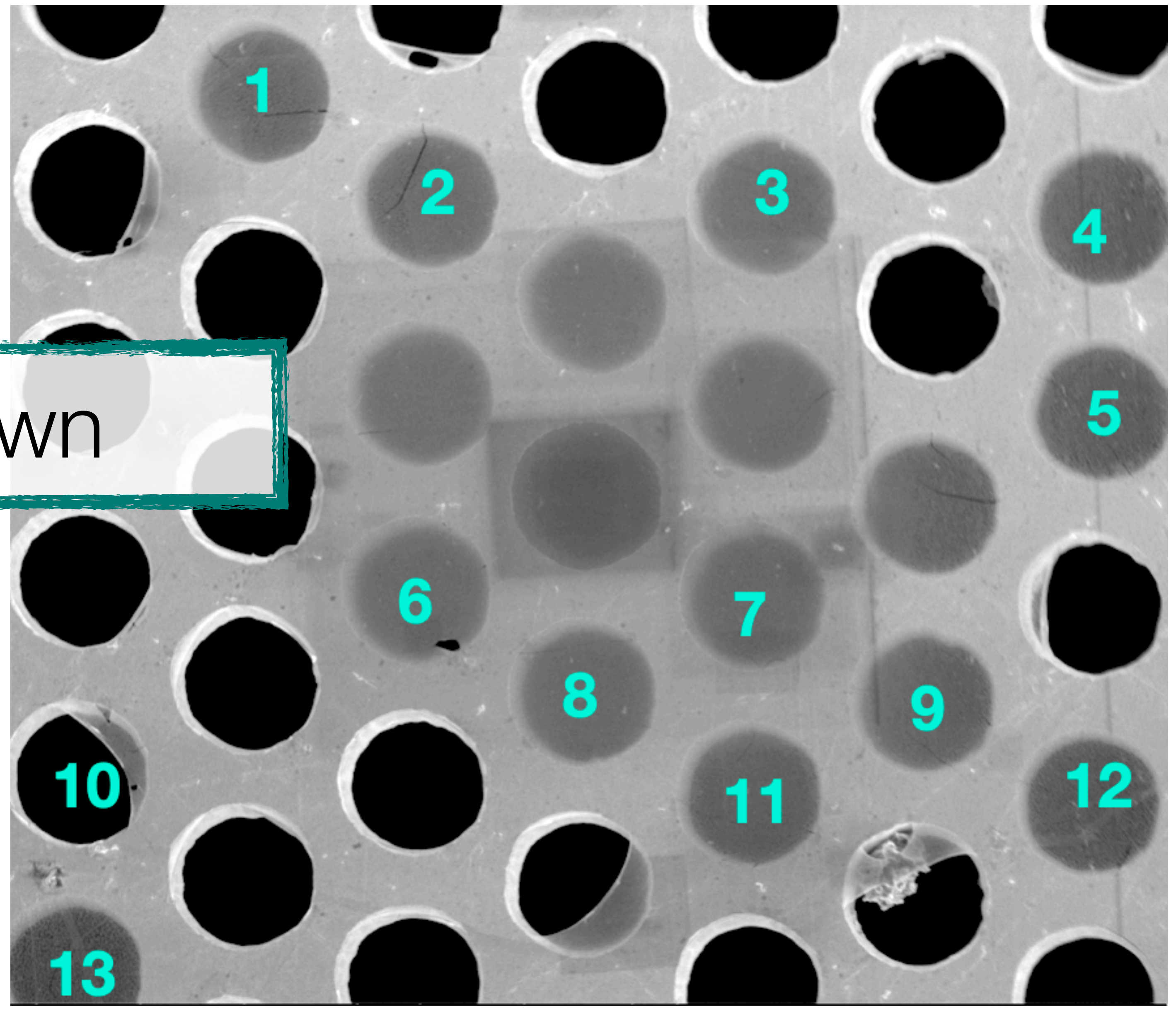
As-grown

300 °C annealing

350 °C annealing



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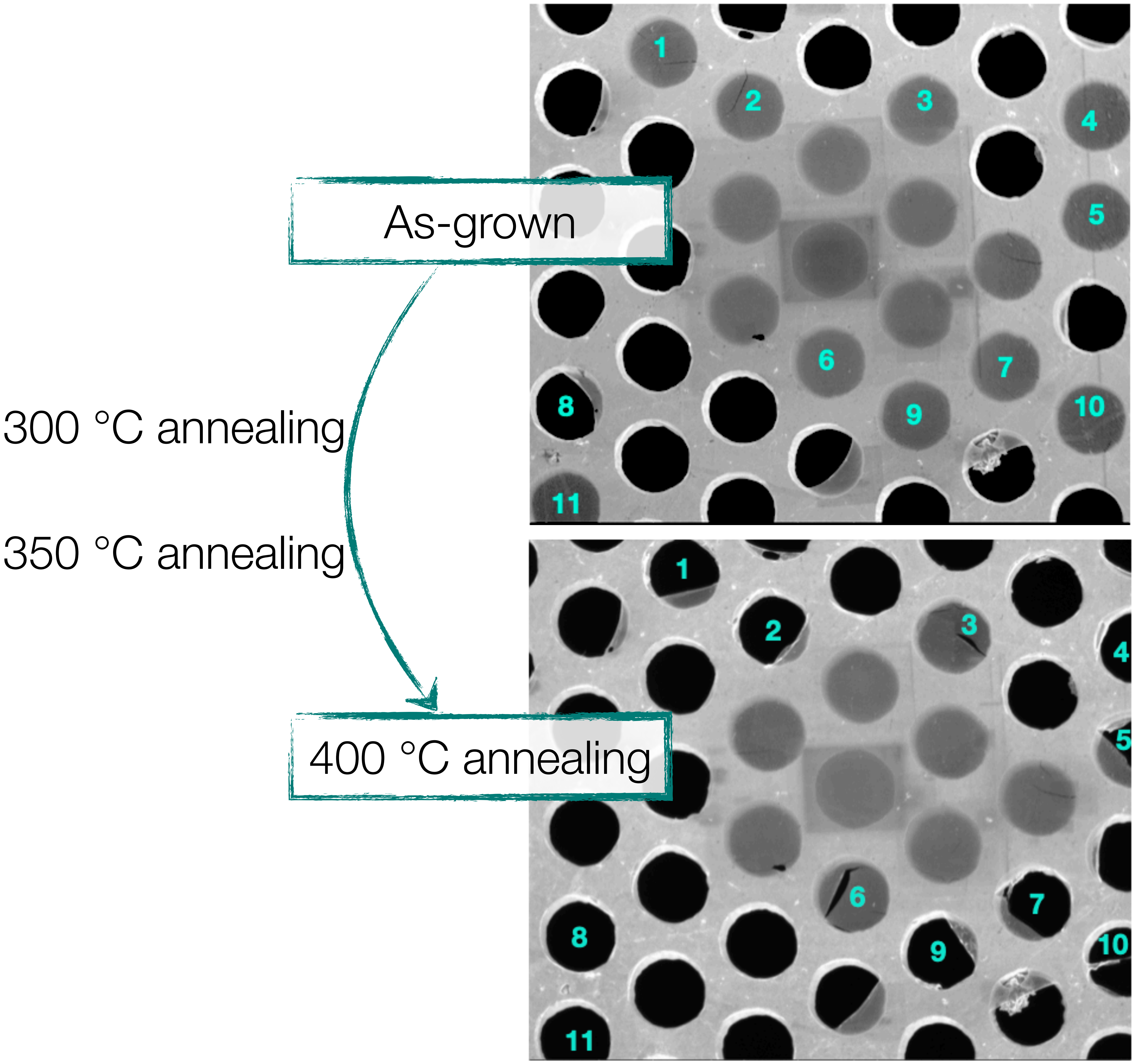

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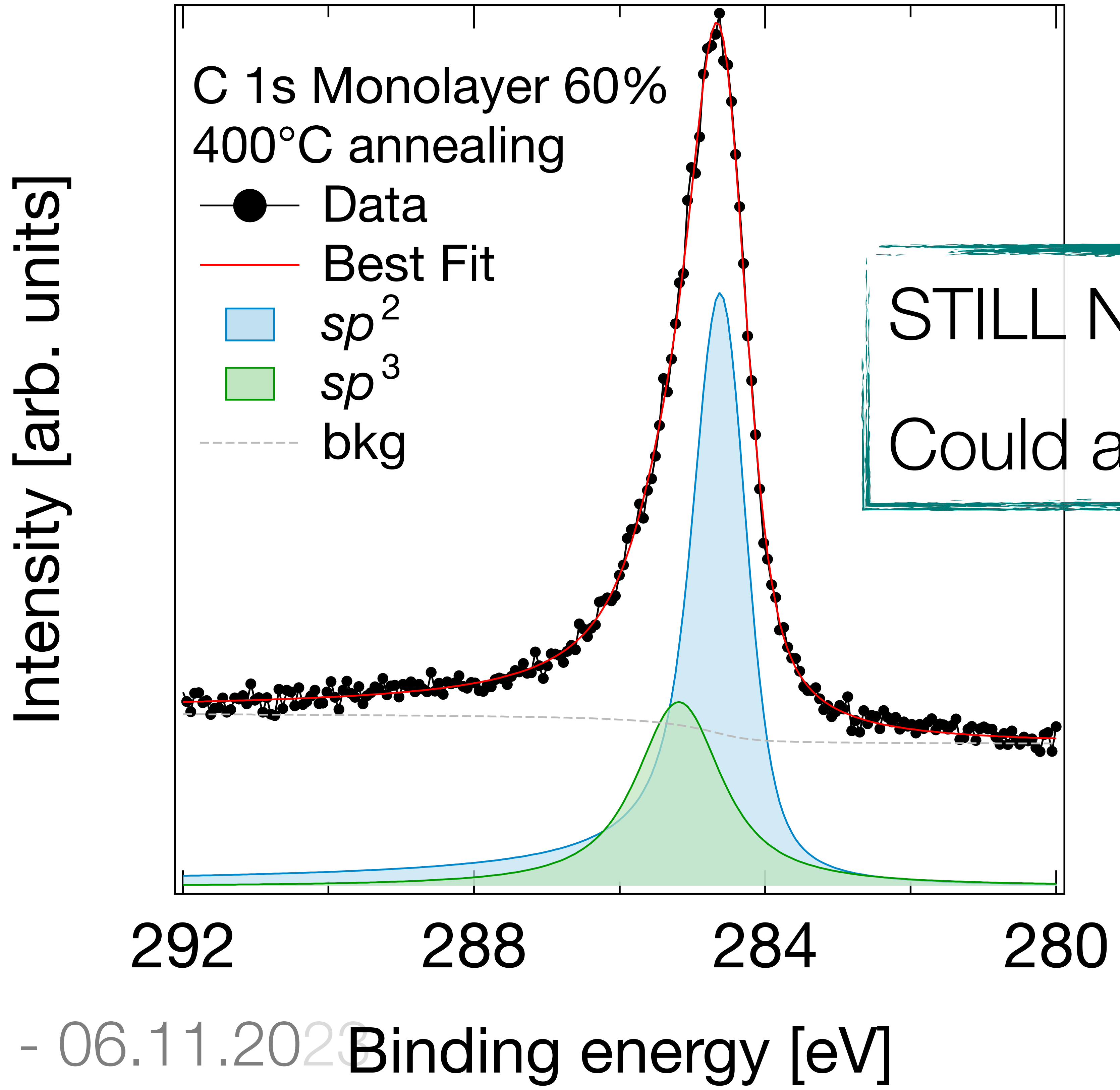
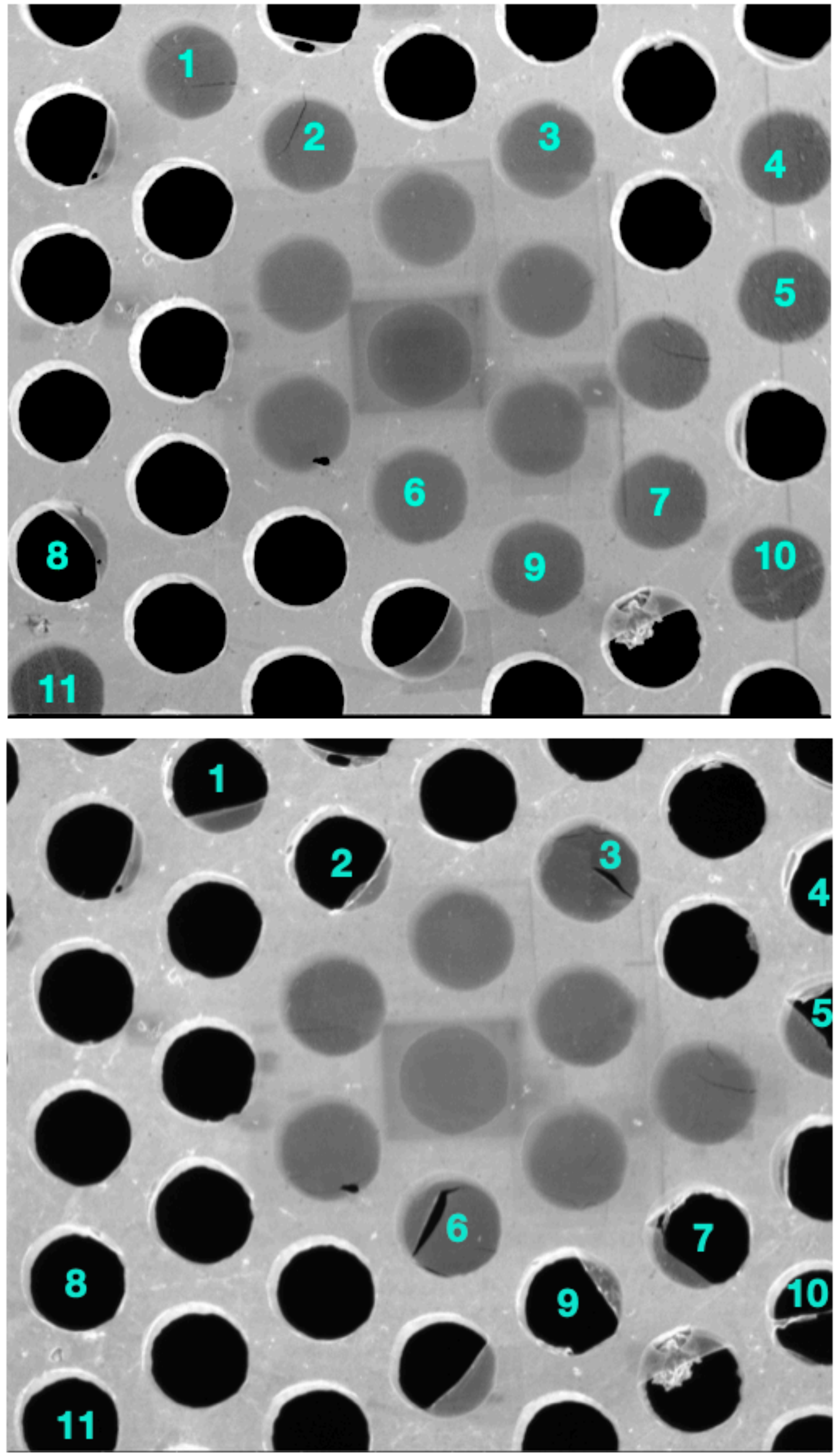
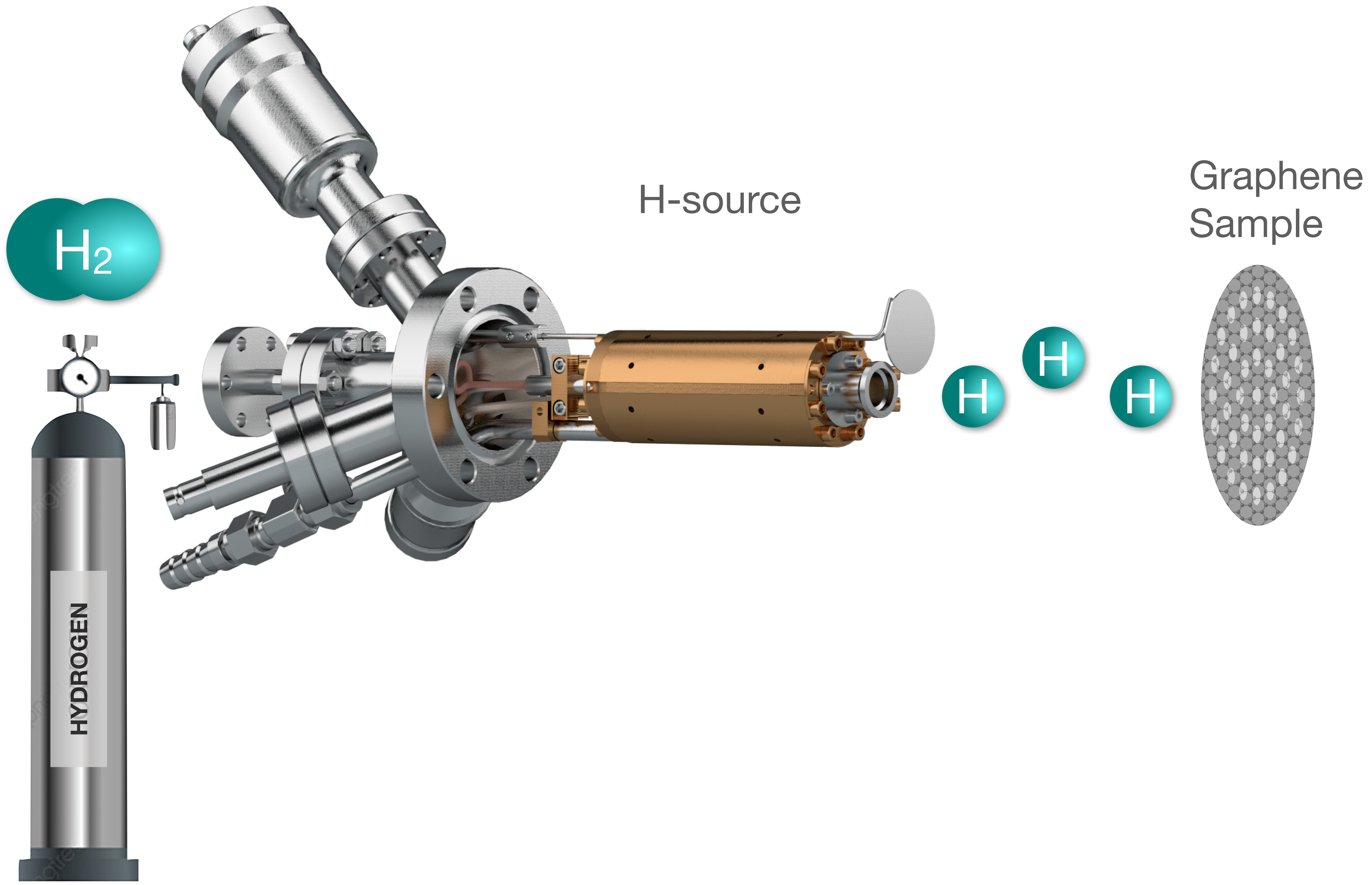


STILL NOT ENOUGH…..

Could a bad sample be misleading?

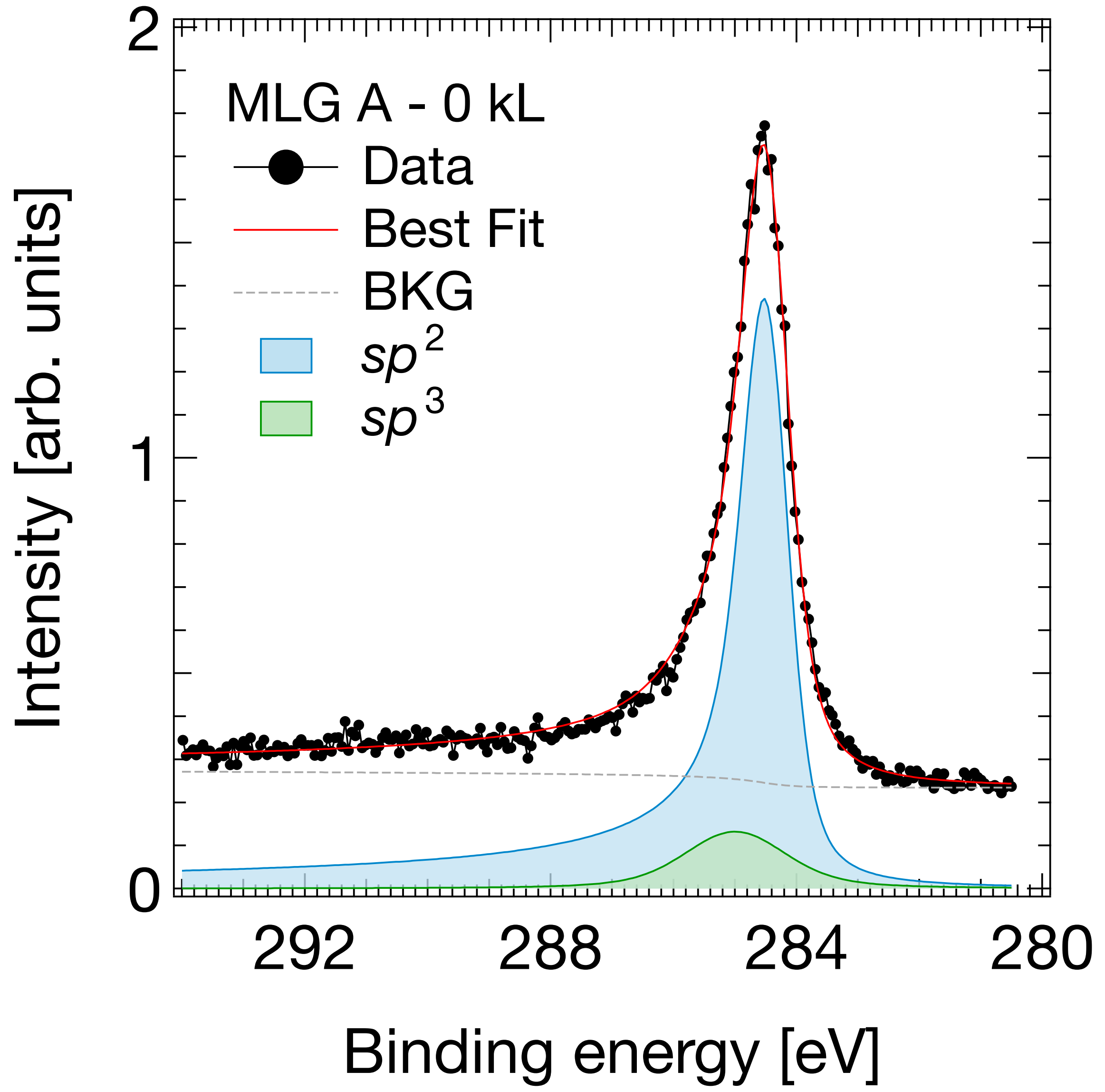


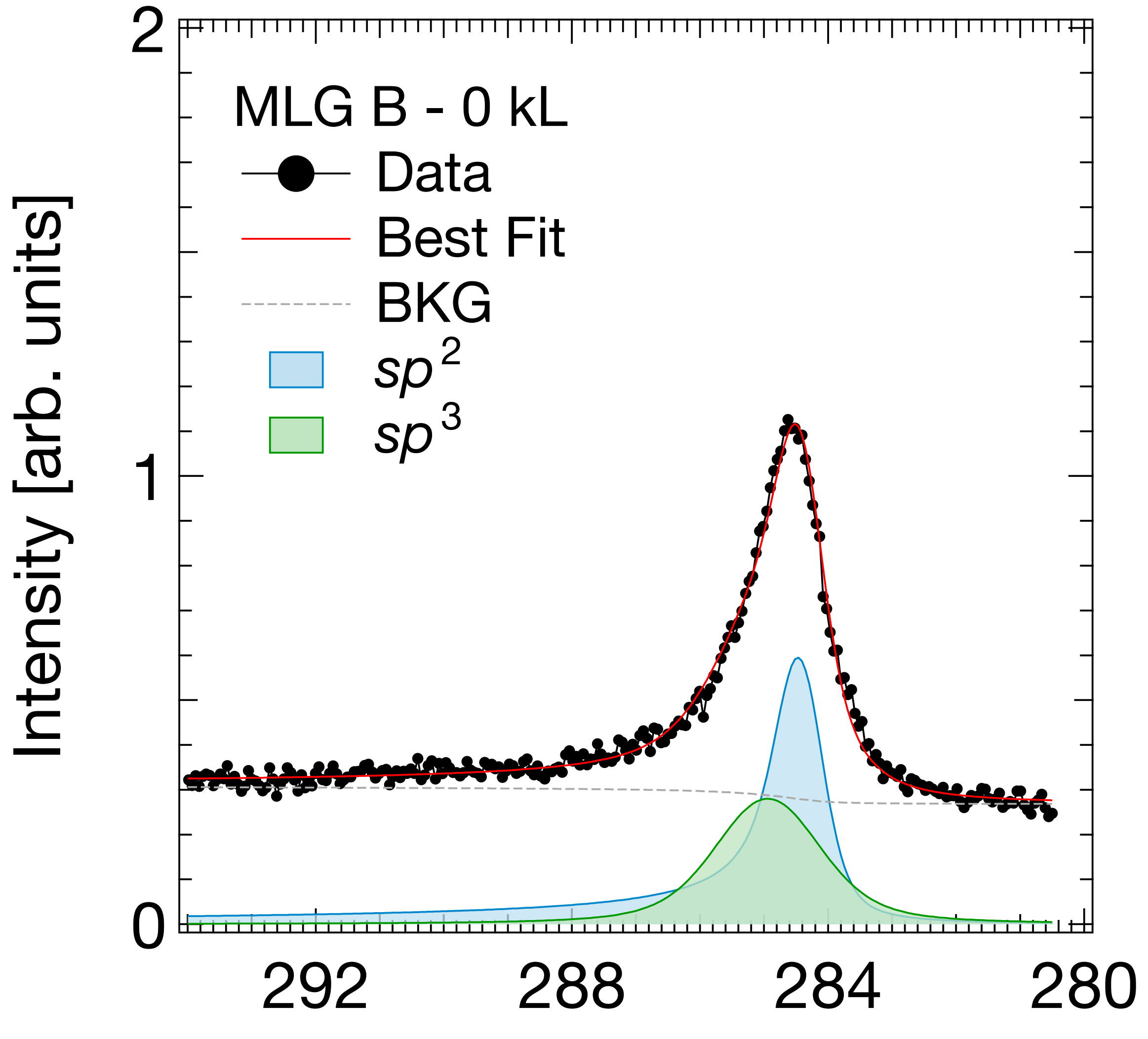
Let's Try to Hydrogenate Graphene on TEM

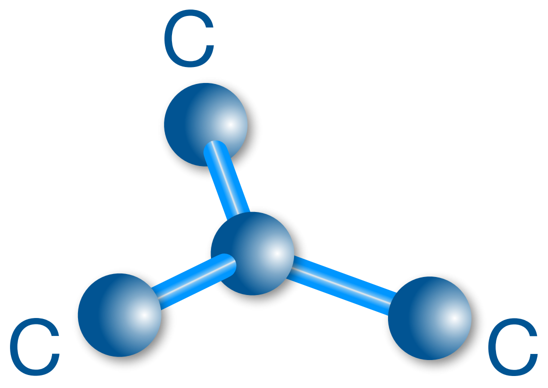


Two Graphene on TEM Samples From Same Growth

PRELIMINARY

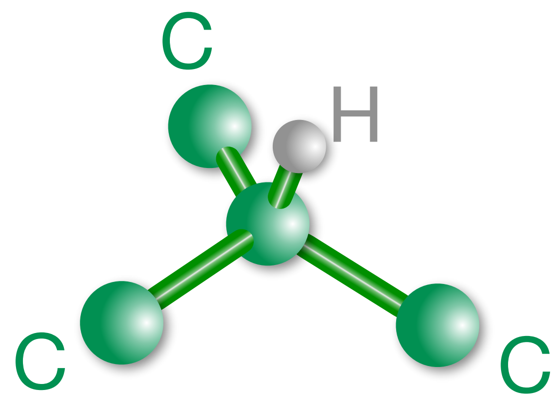






Carbon hybridization

changing from sp^2 to sp^3



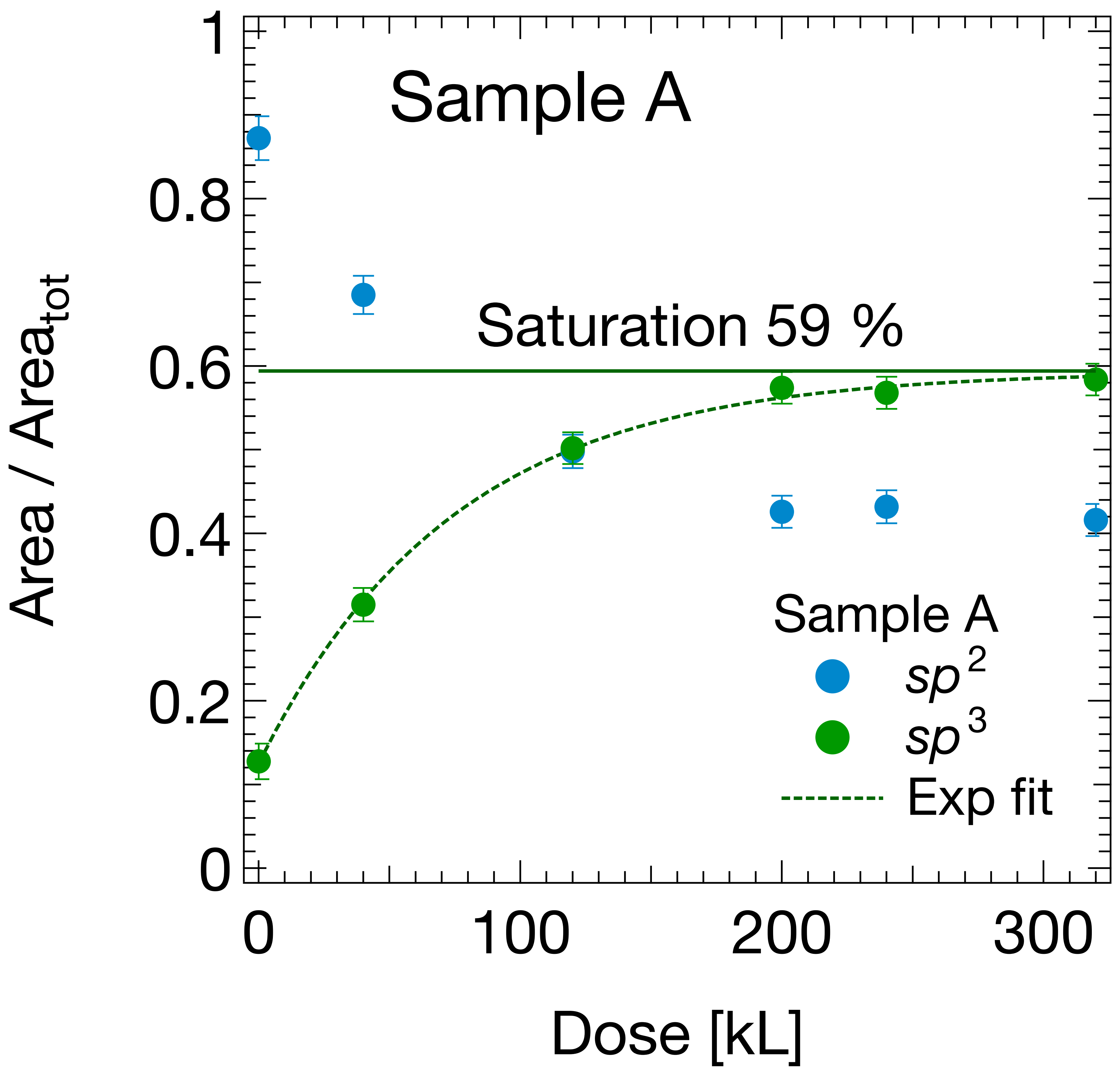
Different Starting Point, Different Saturation Point

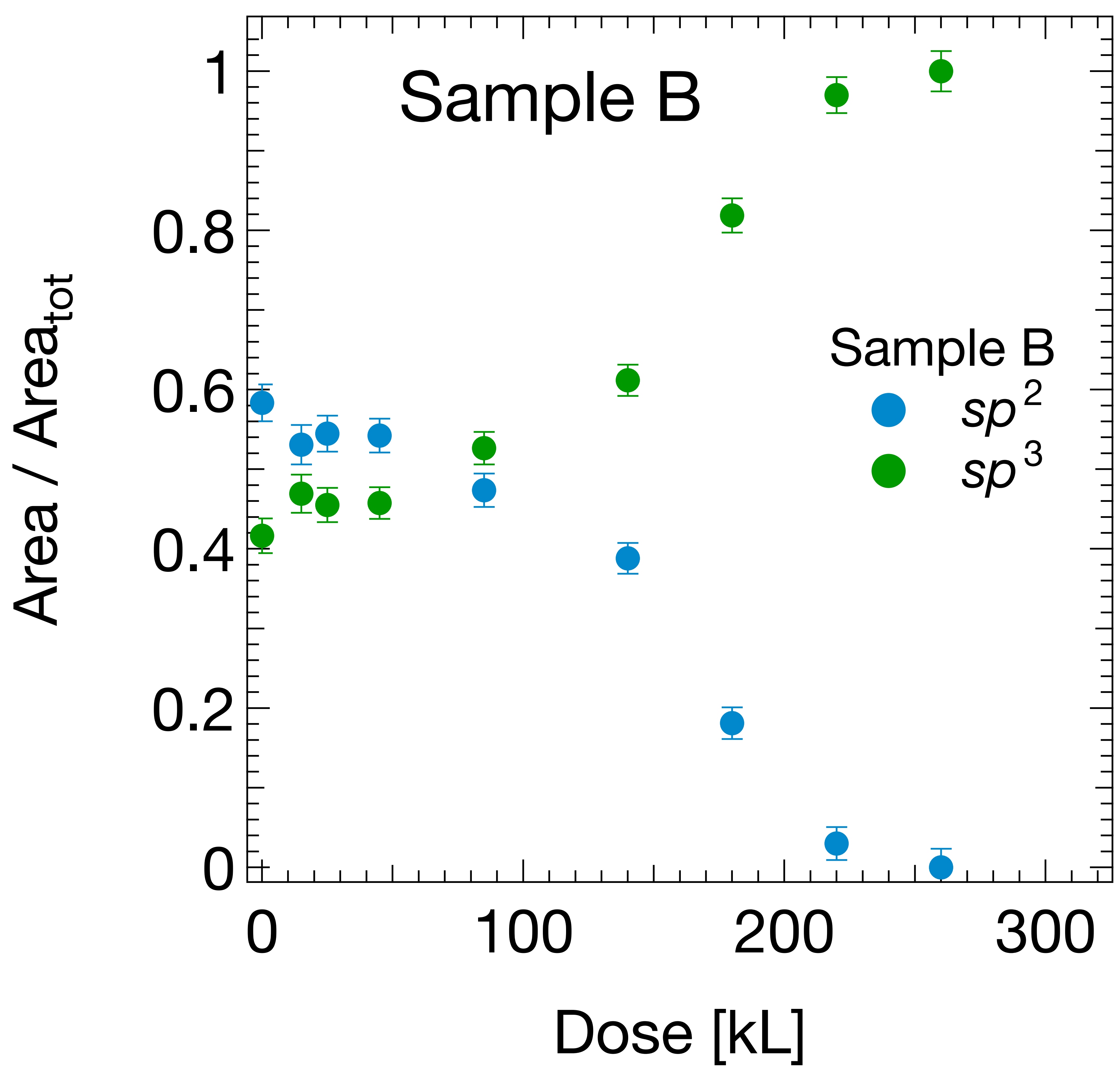
PRELIMINARY

ALREADY SEEN IN JUNE AT GS

The More Is sp^3, the Higher Will Be H-Uptake

PRELIMINARY





Sample A result:

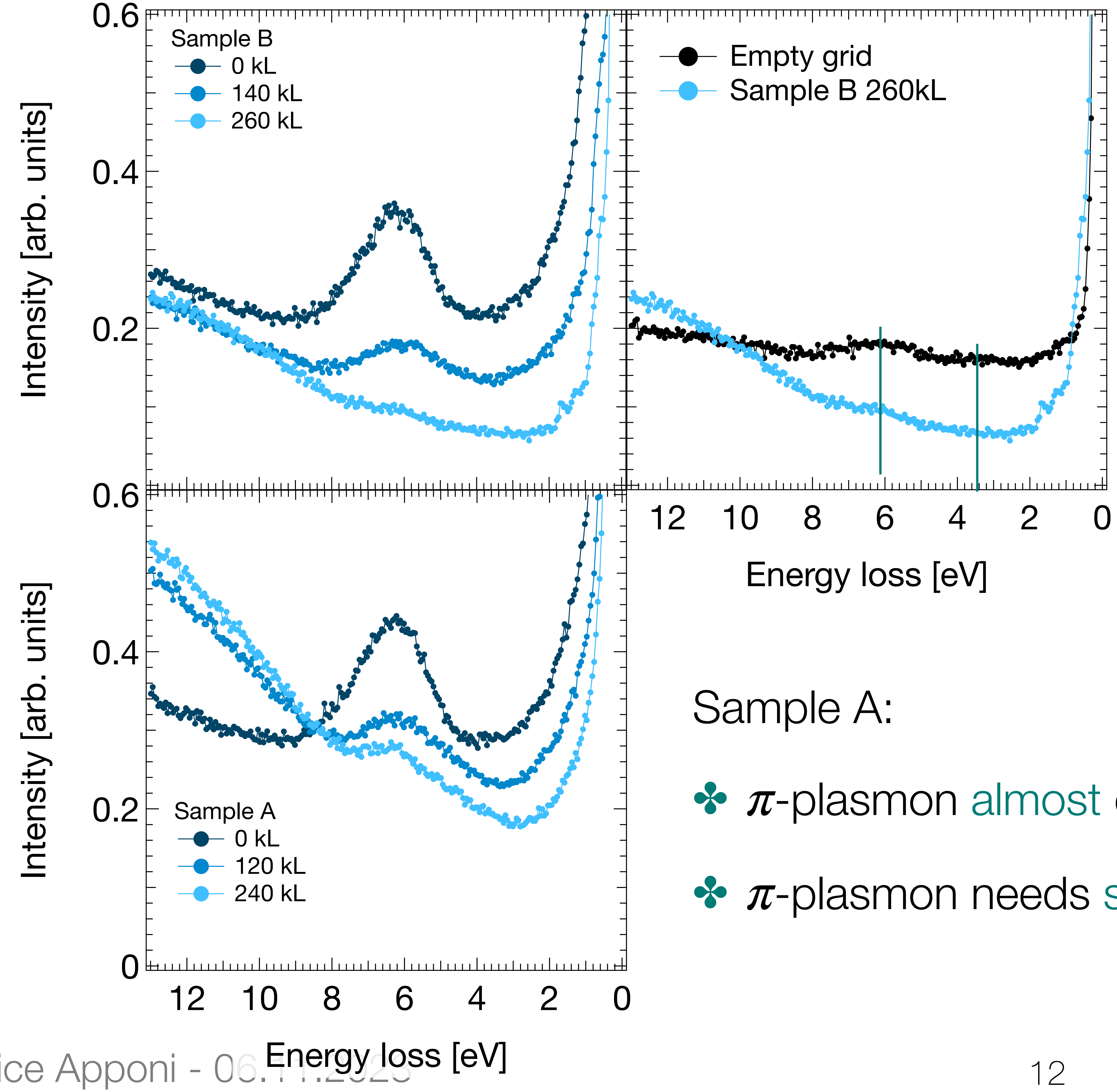
- Start with ~13% sp^3
- 59% sp^3 saturation after 320 kL dose

Sample B result:

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

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
- π-plasmon needs sp^2 domains comparable to its 5 nm wavelength

G. Di Filippo et al., App. Surf. Sci. (2020), https://doi.org/10.1016/j.apsusc.2020.145605

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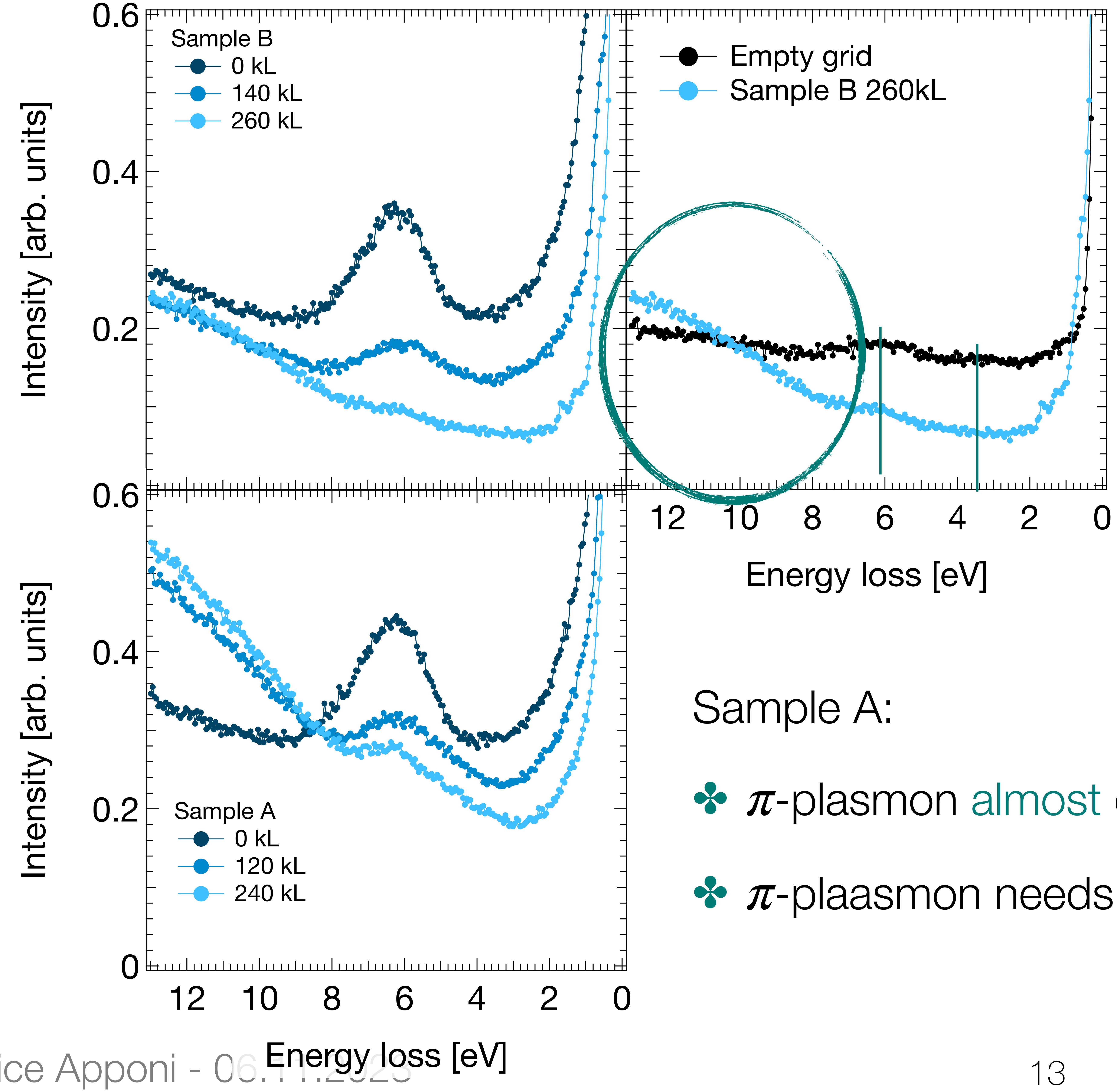

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~6.2 eV Band Gap Measured With EELS

PRELIMINARY

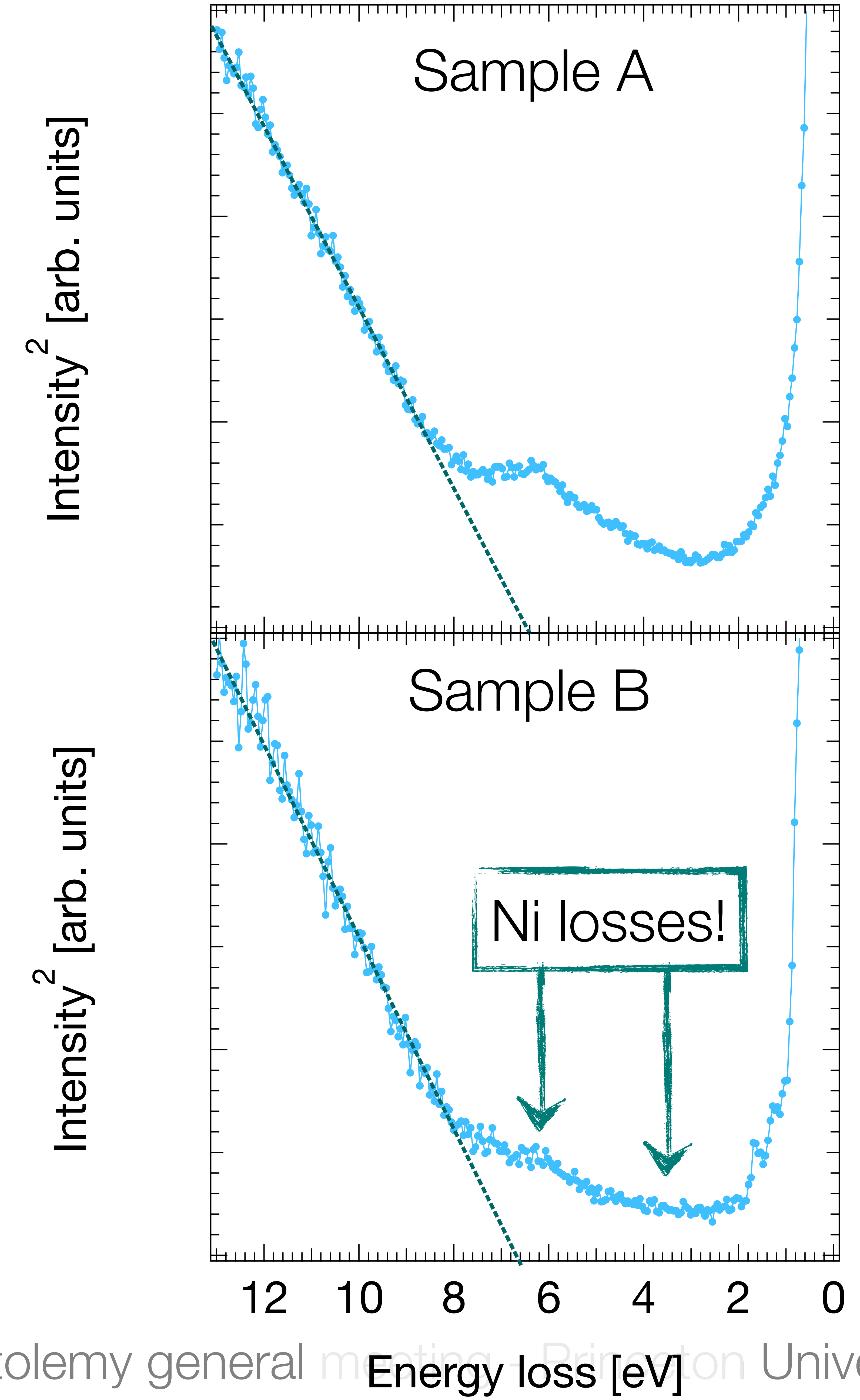
Hydrogenated graphene:

- sp² to sp³ 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 sample A and E_g = 6.3 eV for sample B

100% sp³ saturation   59% sp³ saturation

Take it as a lower bound:

- Background
- Excitons

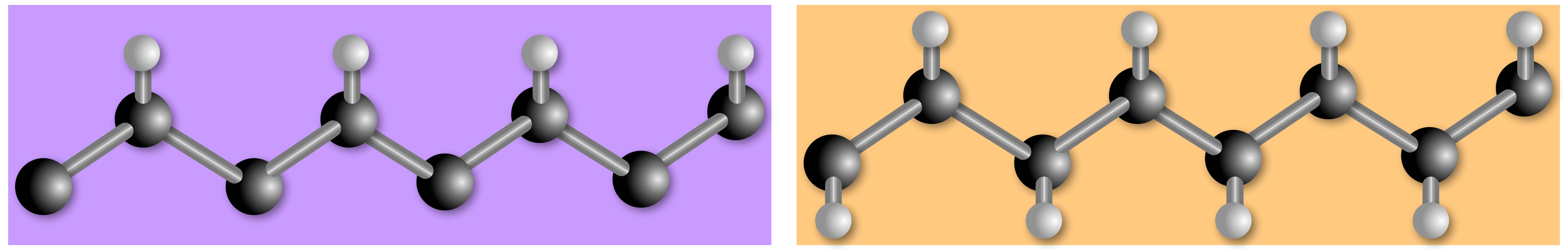


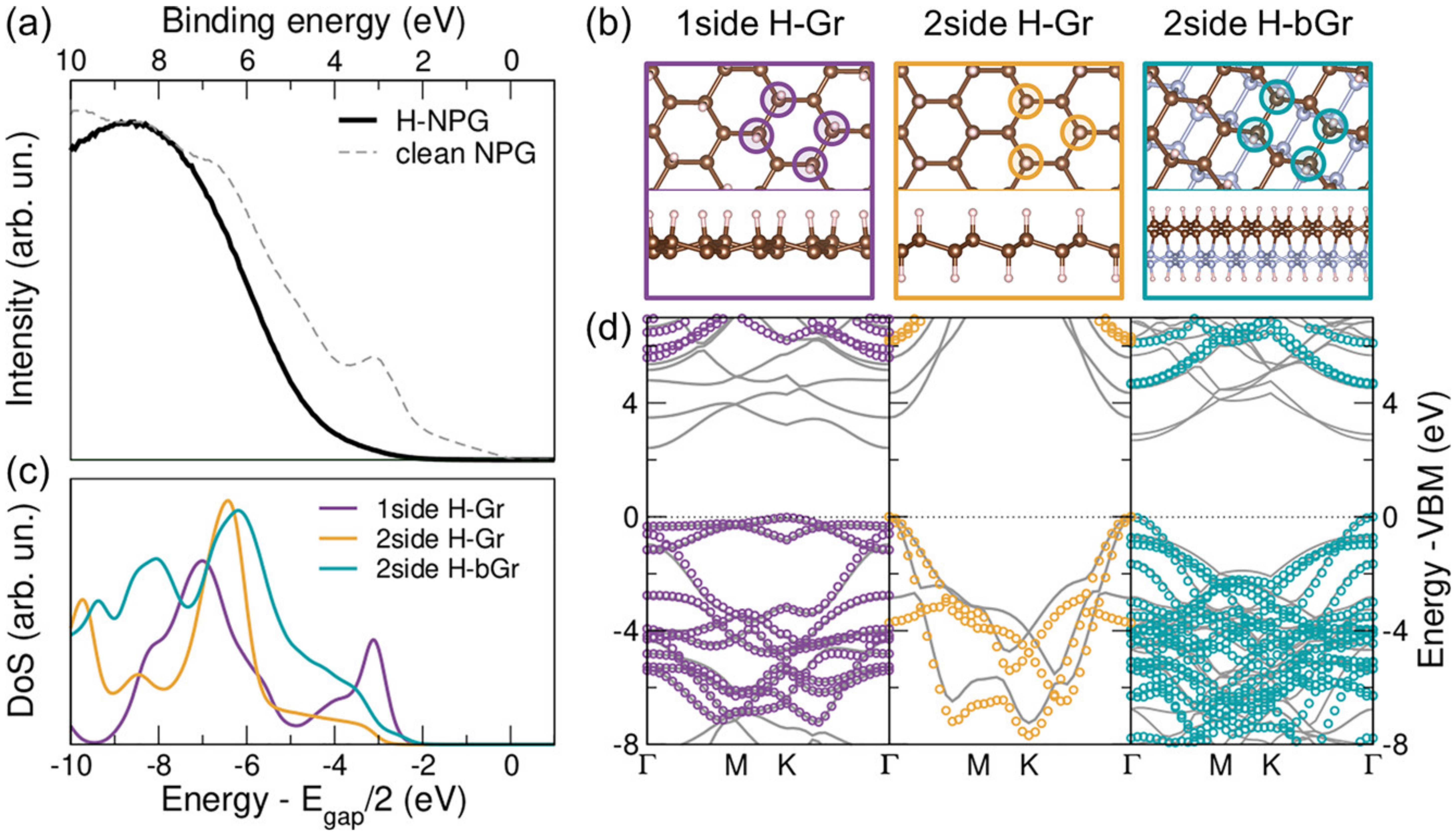
Valence Band to Understand CH Bonding

PRELIMINARY

How many sides?

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





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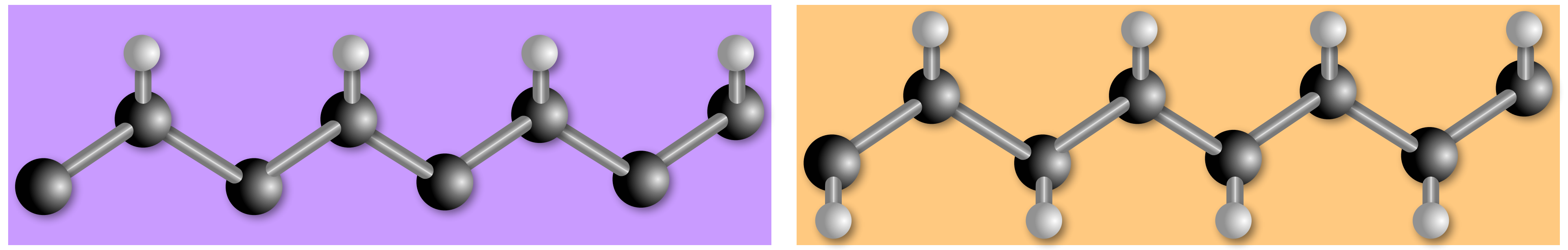

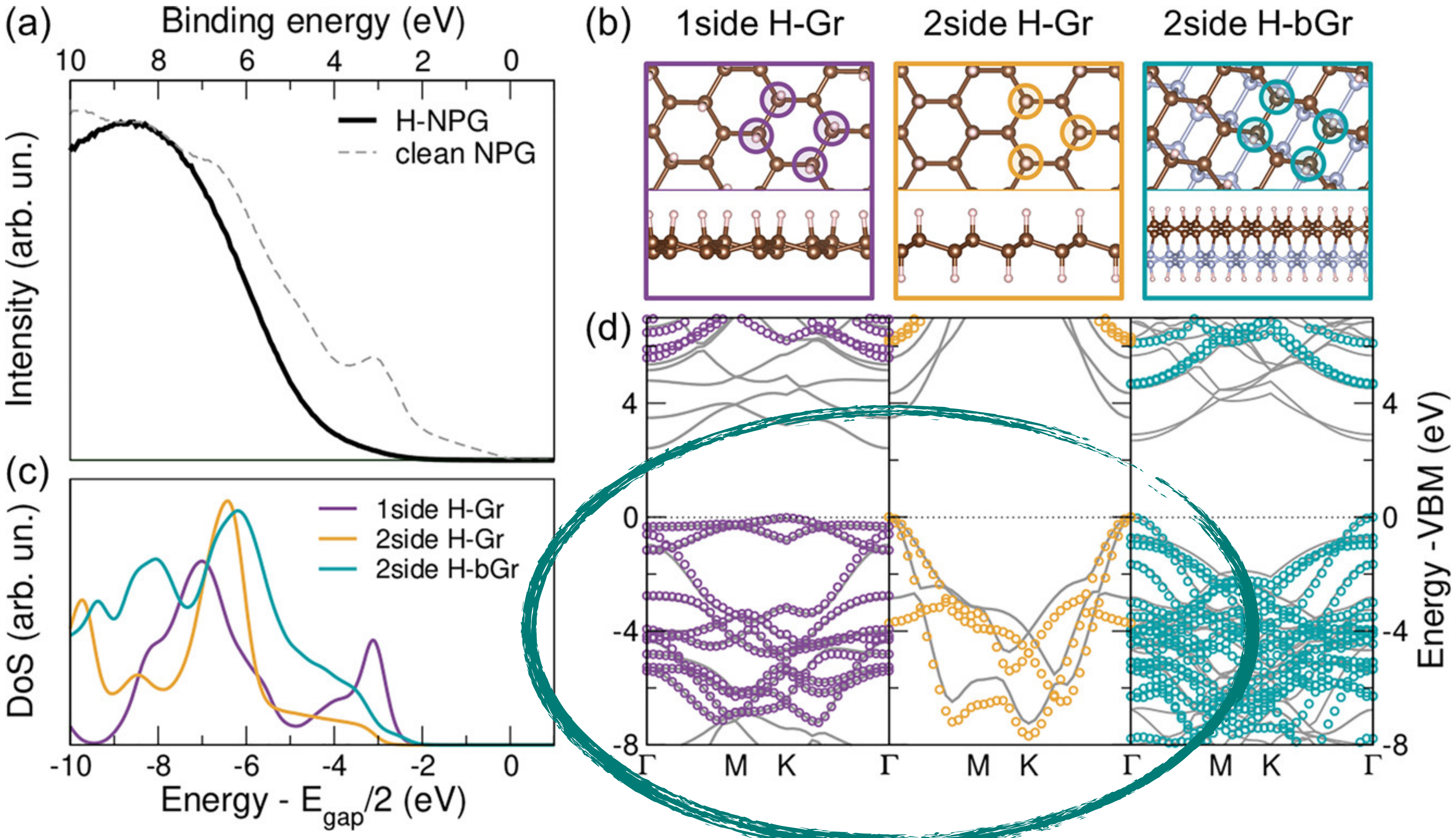

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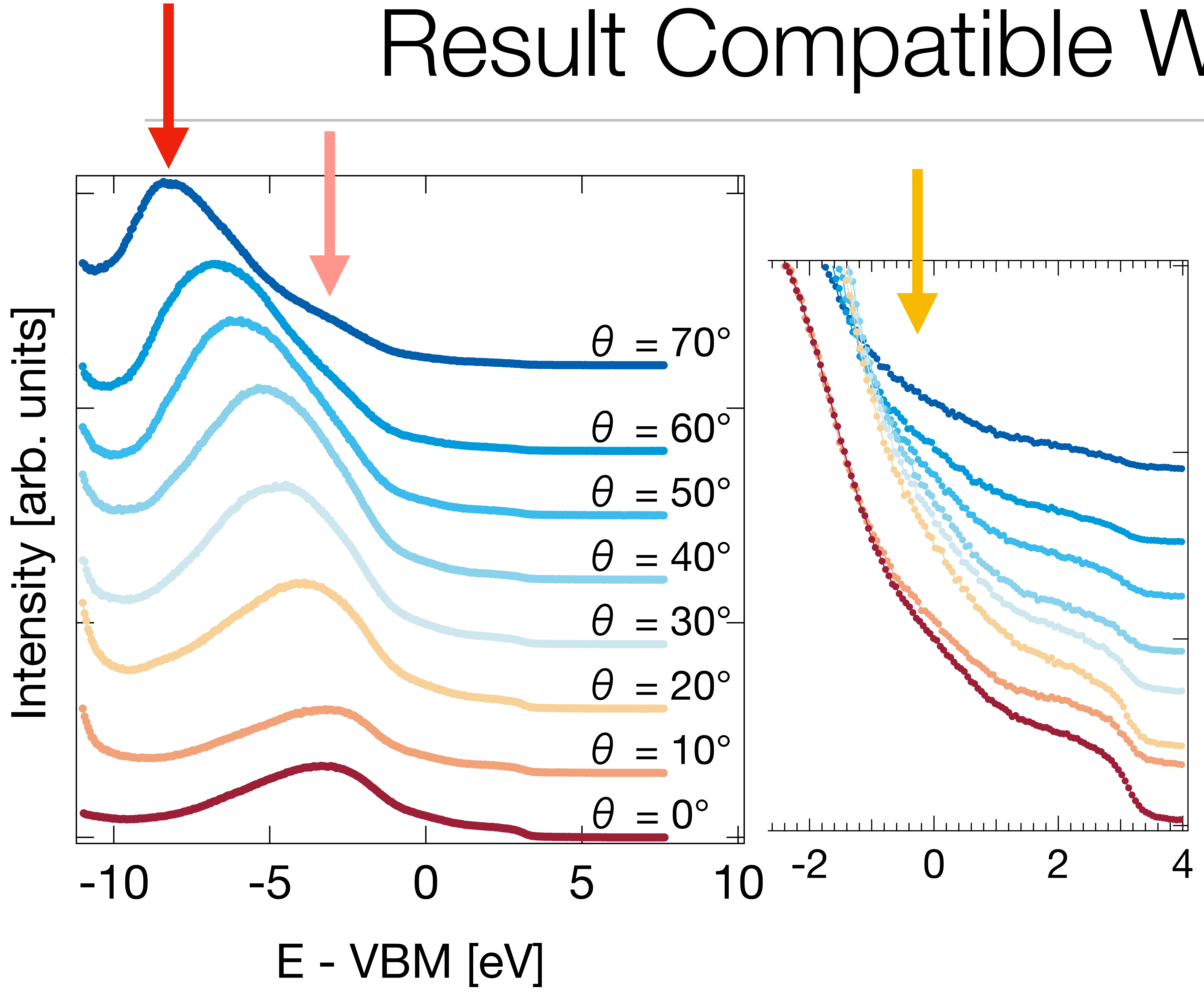
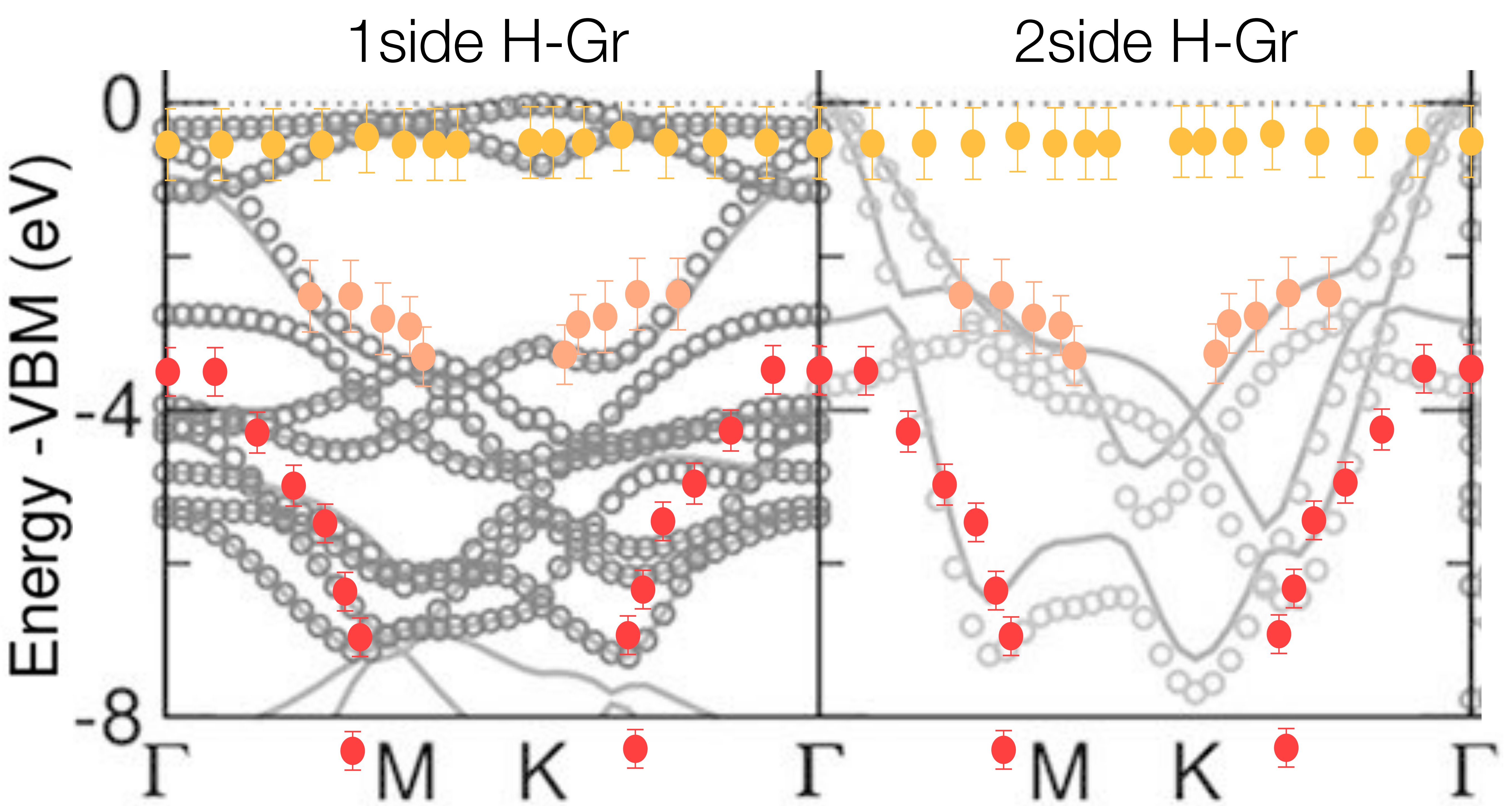
Result Compatible With 1side Hydrogenation

PRELIMINARY





He discharge lamp:

- Spot diameter 300 μm

- VBM = E_F - $E_g/2$, with E_g = 6.2 eV
- Γ-M Γ-K non distinguished due to azimuthal disorder
- Clue of 1side hydrogenation

To Conclude

Graphene cleaning:

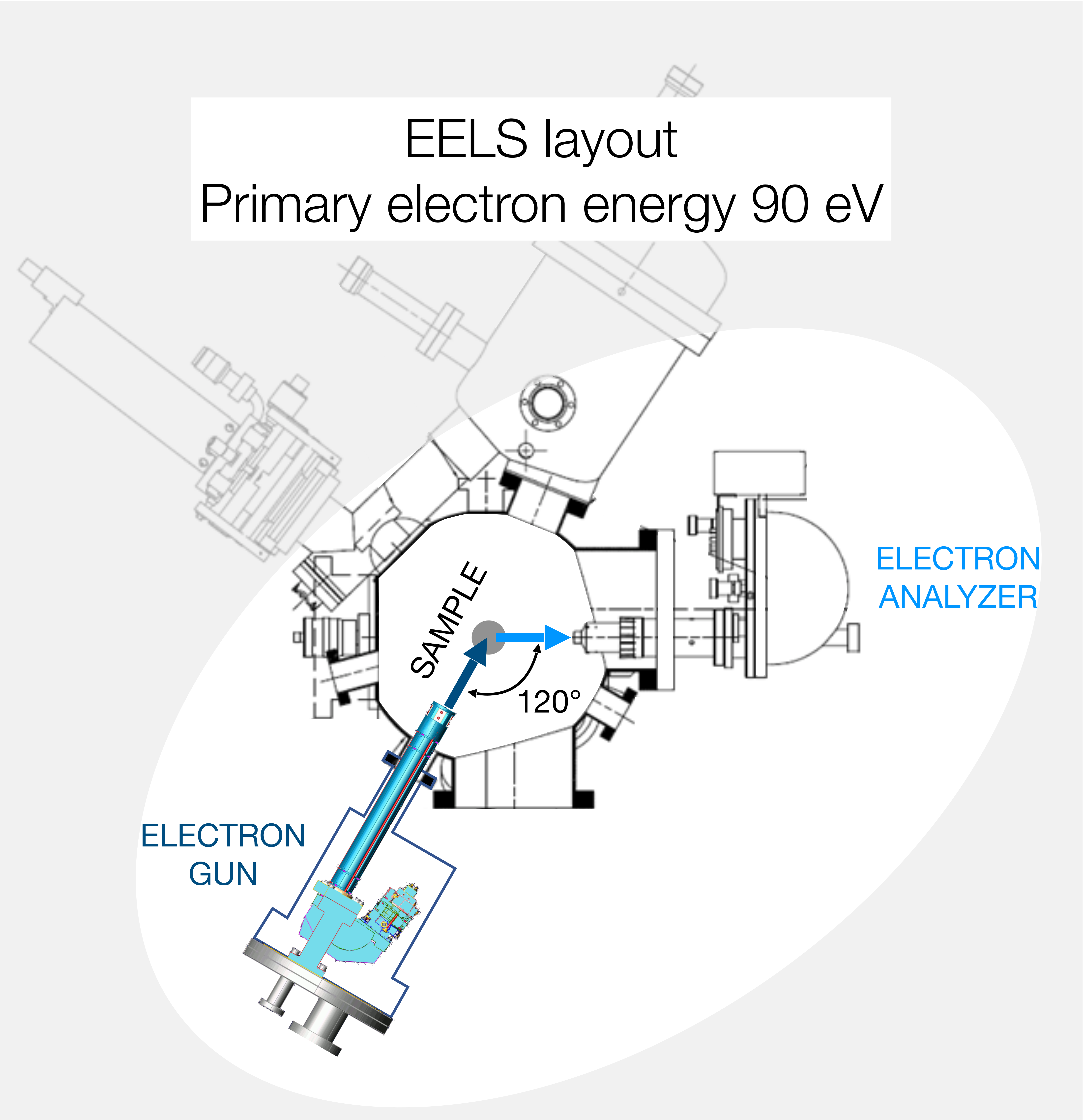
- ✤ Contaminants removed with 550°C annealing but suspended grahene breaks
- ✤ Nothing happens up to 400 °C but it seems not enough (bad sample misleading?)

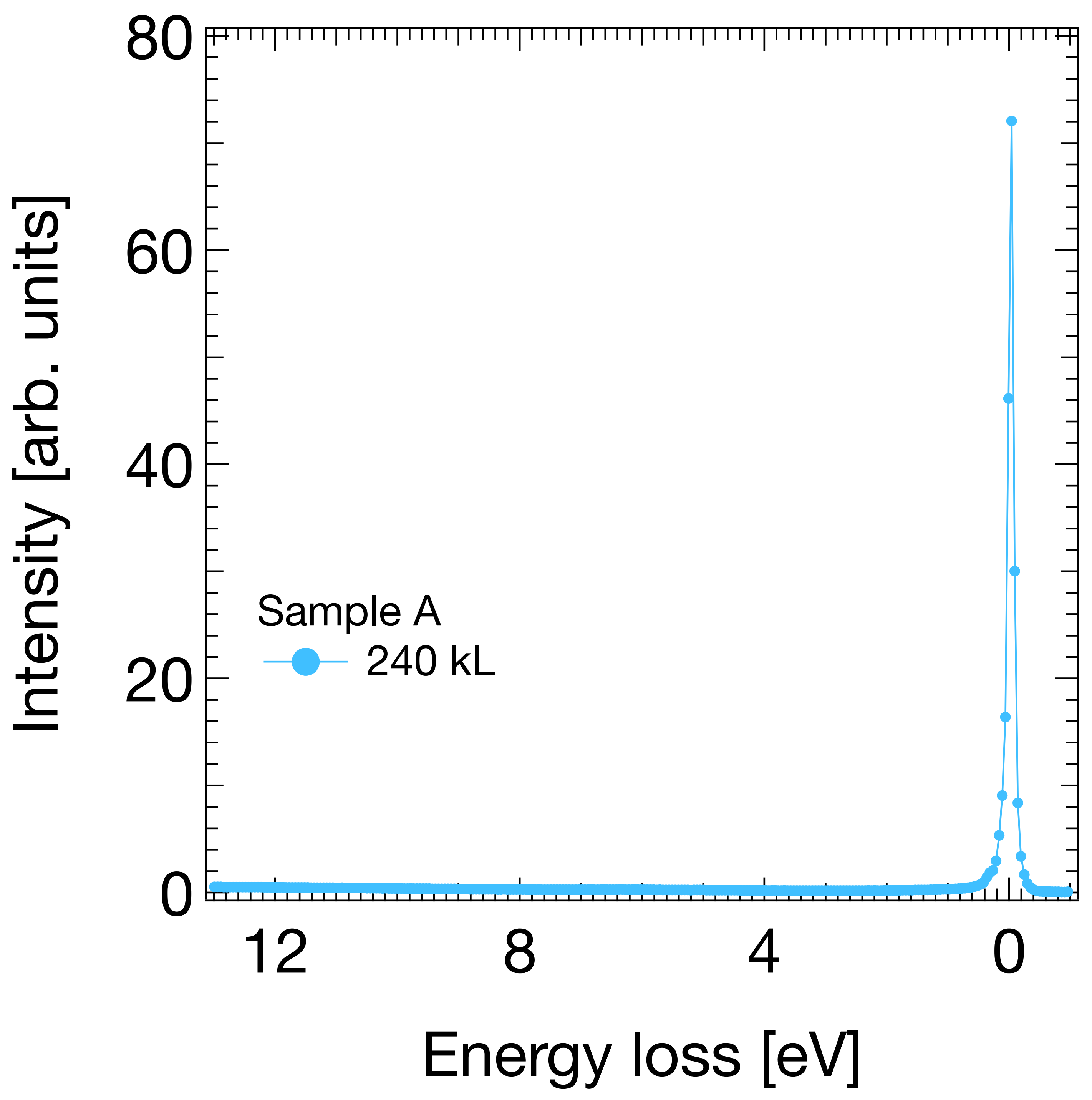
Hydrogenation of graphene:

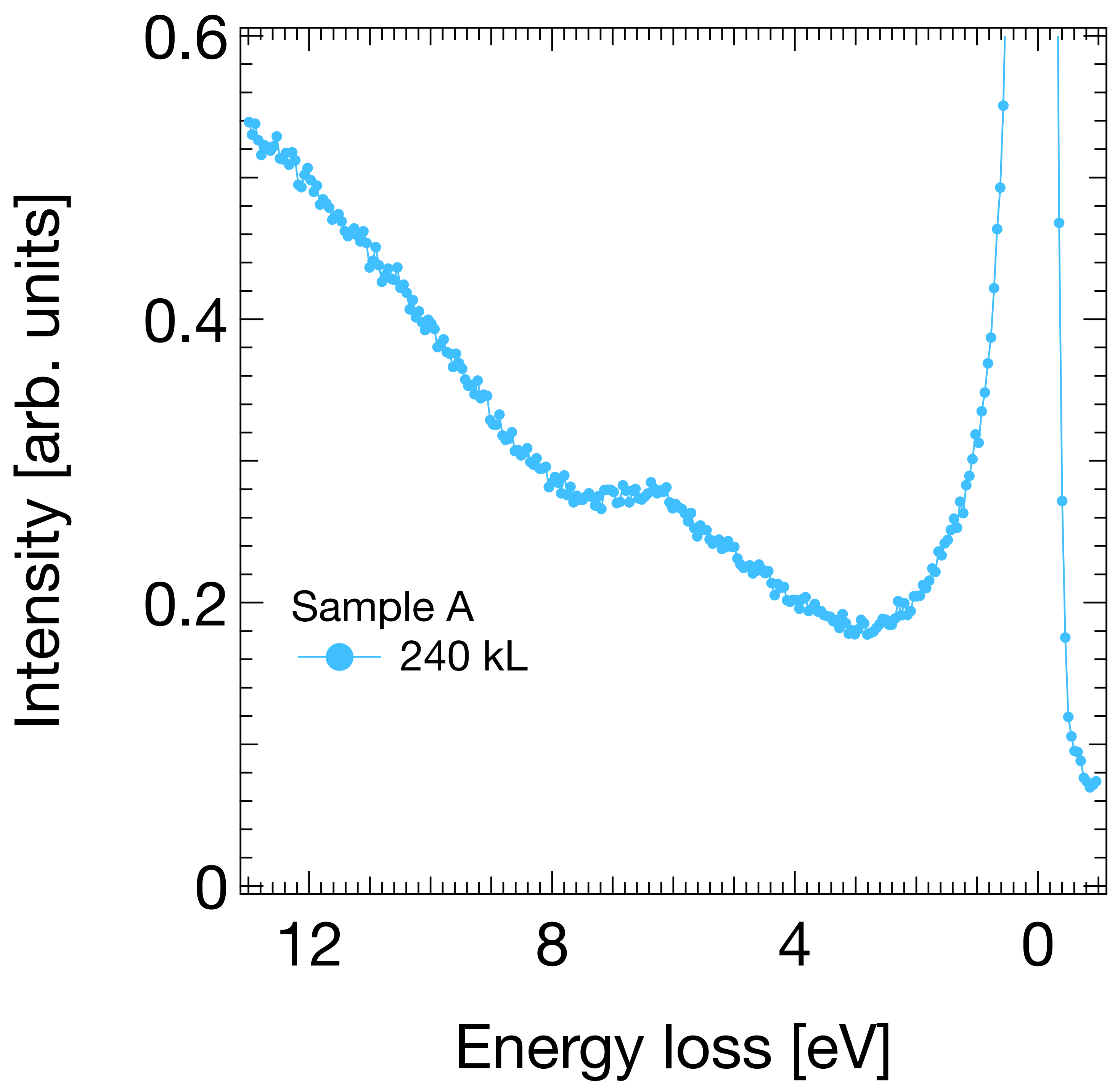
- ✤ Monolayer graphene saturation seems to depend on sp^2/sp^3 ratio
- ✤ Band gap measurements with EELS
- ✤ Angular resolved UPS gives a clue of 1side hydrogenation

BACK-UP

Electron Energy Loss Spectrum





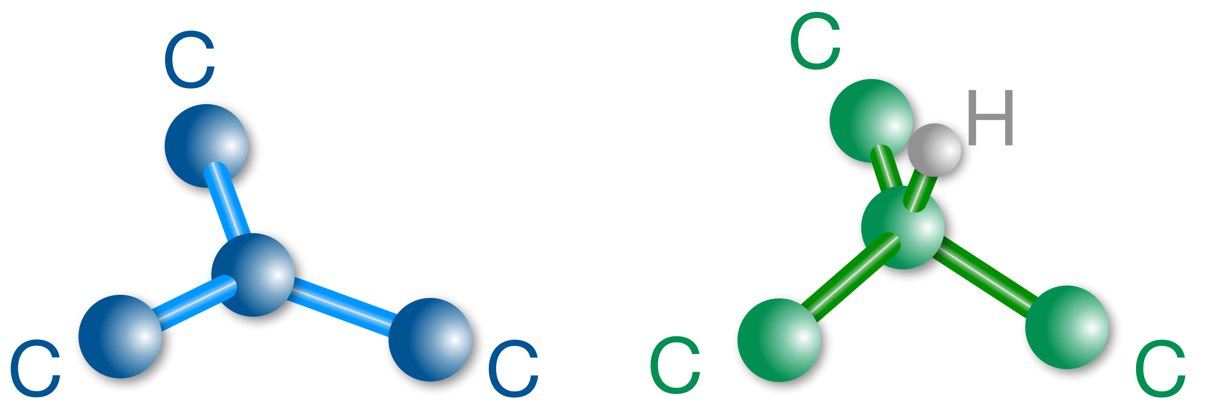


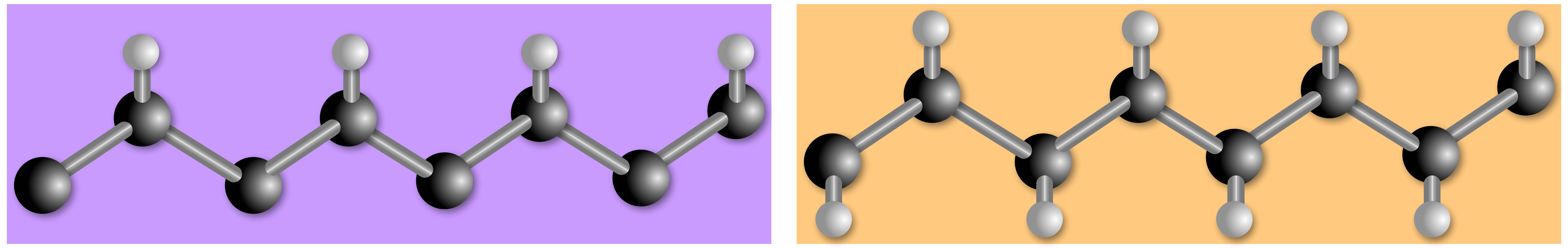
Losses are a factor 100 lower wrt elastic peack even at 90 eV of primary electron

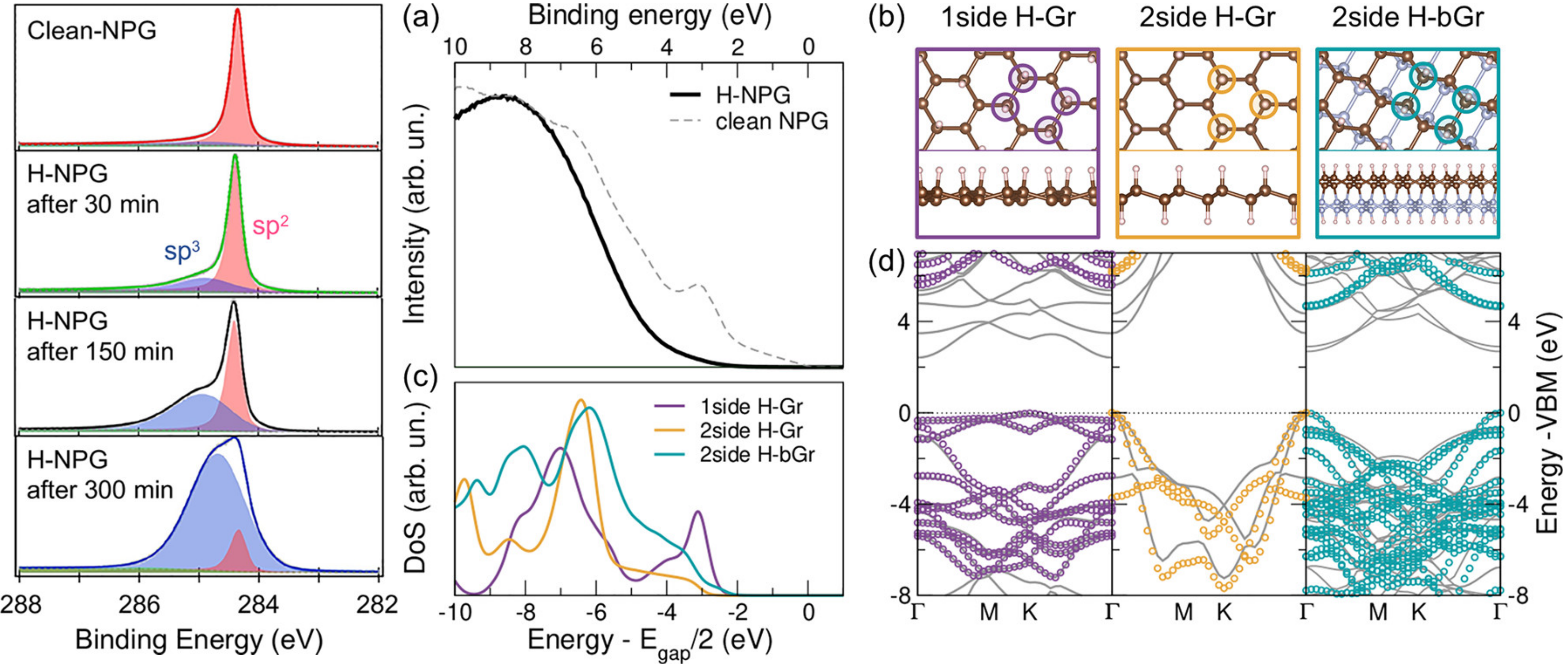
Hydrogenation of Suspended Graphene to Undestrand CH Bonding

Hydrogen bonding to graphene:

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







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

Hydrogenation of suspended graphene to better understand

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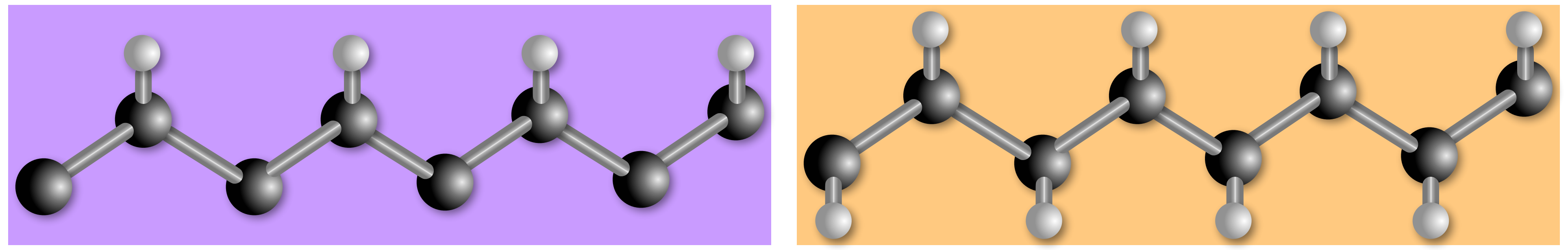

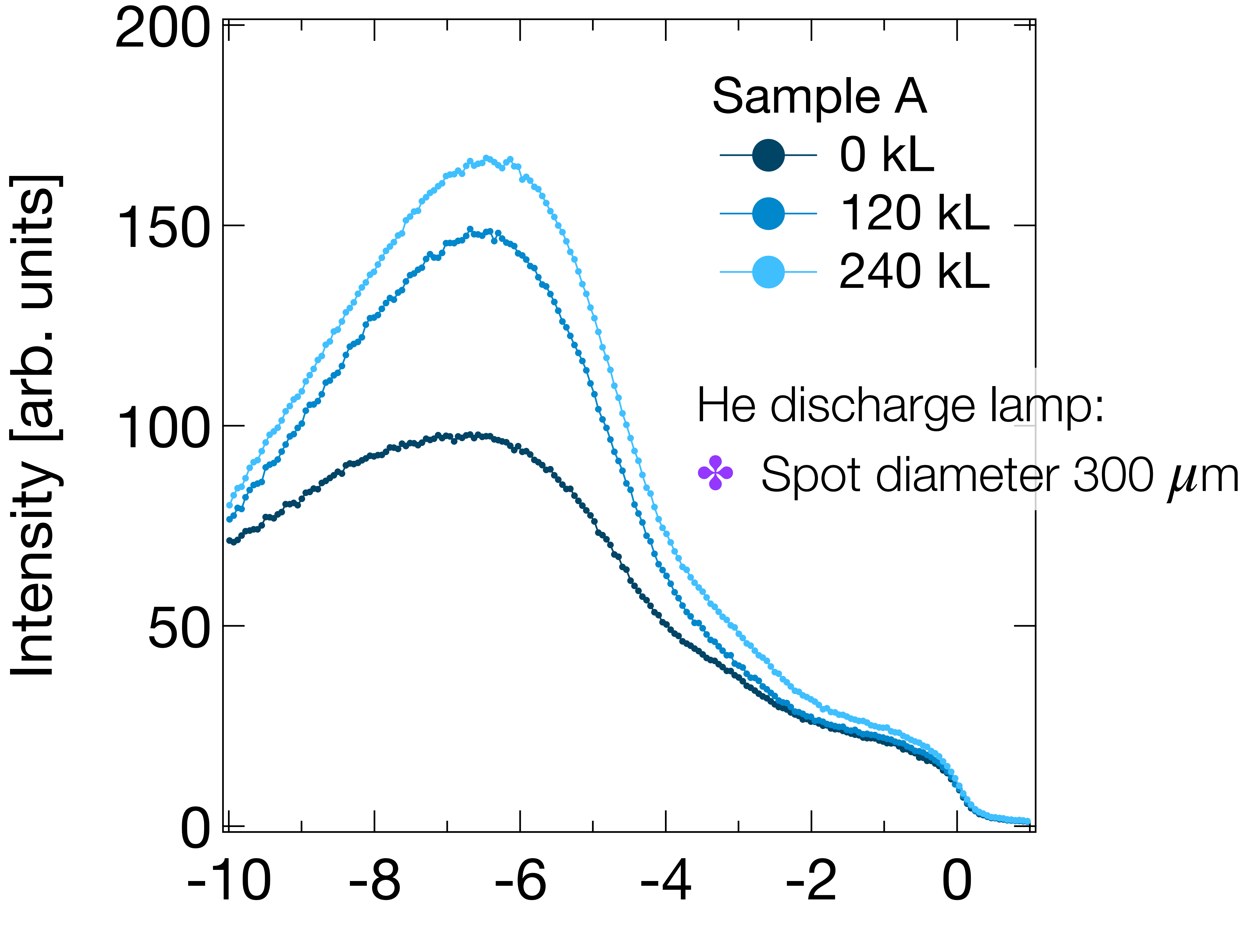

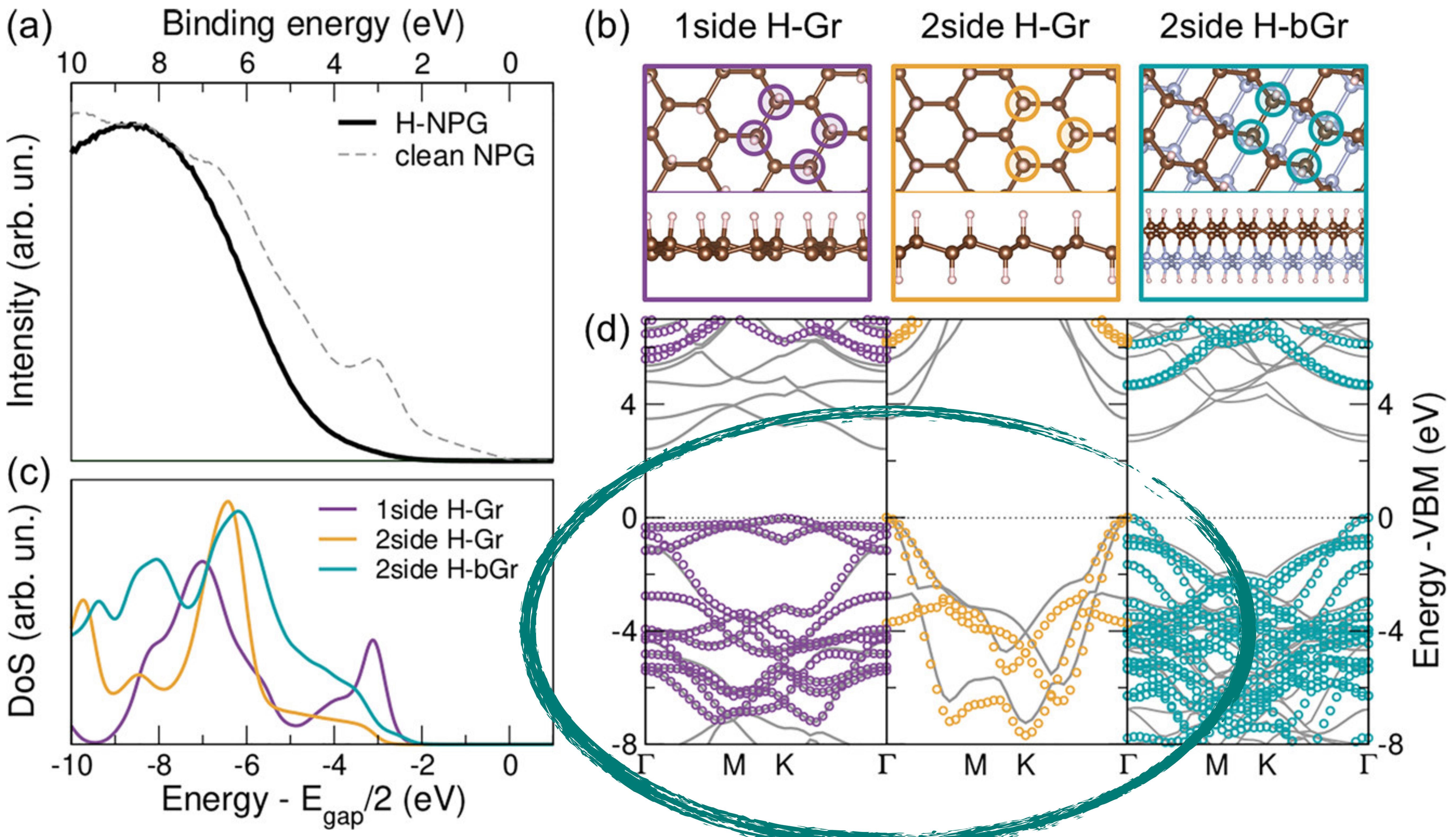

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