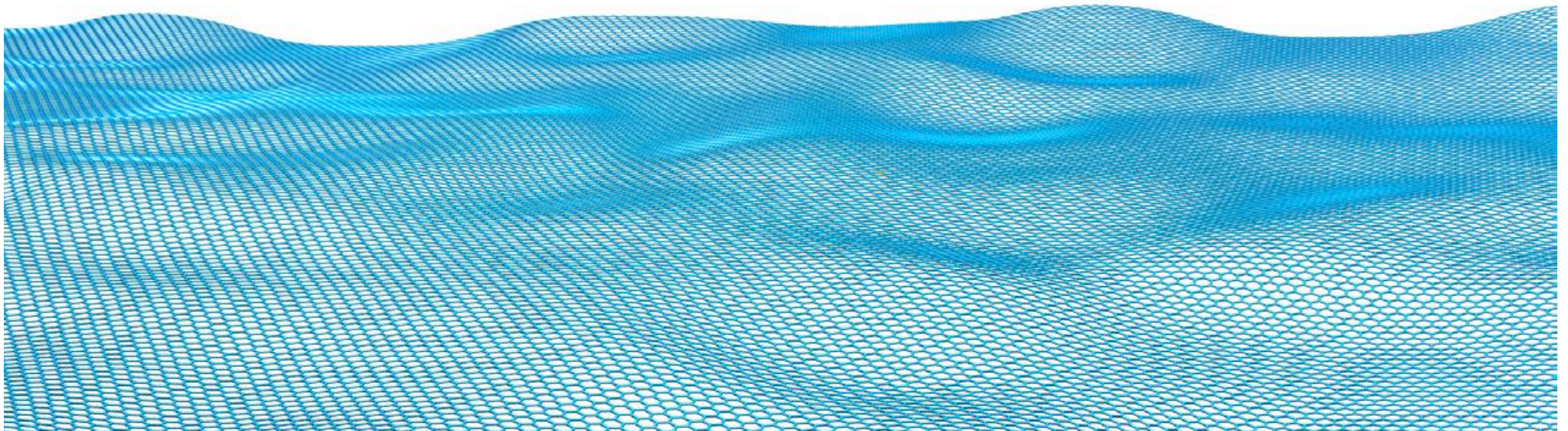
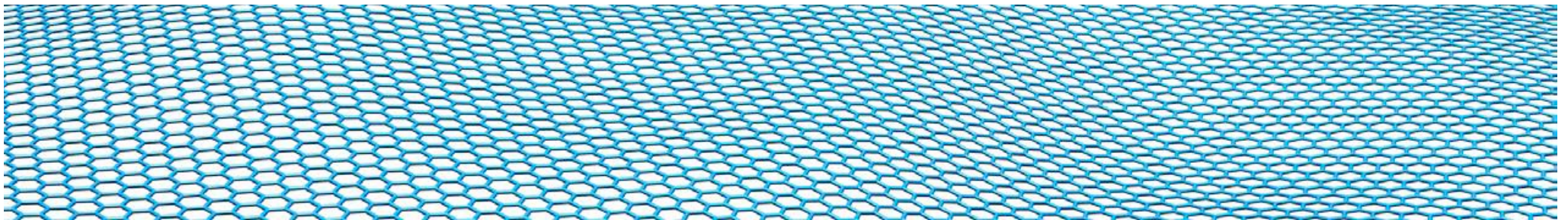


Introducing defects in wet-chemically prepared graphene as structural motifs



27 June 2018 – AG Eigler – FU Berlin



WELCOME TO THE GRAPHENE AGE



George Osborne on a visit to the Manchester University lab of Professors Geim and Novoselov

SOLAR PANELS

MIT professors have shown how graphene could be used to make the electrodes in organic solar cells cheaper, lighter and more flexible than in current systems



AIR TRAVEL

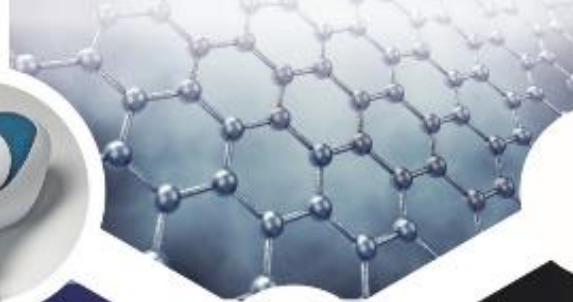
Using graphene would enable aeroplane manufacturers to develop extremely strong, yet light components – bringing down weight and therefore reducing fuel costs

MOBILE PHONES

Nokia is exploring the potential uses of graphene in mobile devices. Aside from smaller, more flexible phones, it may allow built-in solar power and transparent electronics

A CLOSER LOOK AT GRAPHENE

Graphene is a one-atom thick form, or allotrope, of carbon – other allotropes include diamond and graphite. It is often described as an atomic-scale chicken wire constructed of carbon atoms and their bonds. When graphene sheets are stacked, three million sheets would be needed to create a 1mm thickness. It's been claimed that it is the strongest material known to man, that a clingfilm-thick layer could support an elephant. Despite its strength it can be stretched by 20% without being damaged. It is also an excellent conductor of electricity and the best conductor of heat that has been discovered



FLEXIBLE SCREENS

Researchers in South Korea have produced a continuous layer of graphene 63cm wide. This has opened up possibilities in electronics. "You could theoretically roll up your iPhone and stick it behind your ear like a pencil," claims one scientist

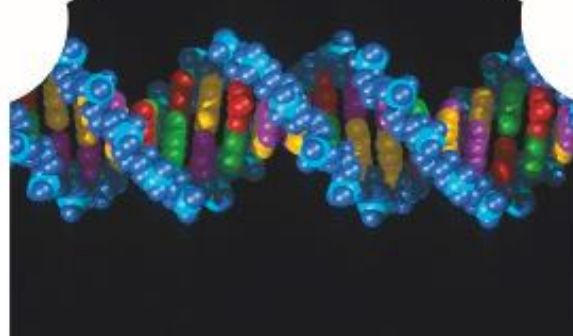


PROSTHETICS

Aside from allowing for the construction of stronger, more flexible and lighter limbs, its conductivity opens up new possibilities for its use in the electrodes used to turn brain signals into movement

COMPUTER CHIPS

Geim and Novoselov have been working on demonstrating how graphene could replace silicon as the key material in electronic circuits. IBM is one of many electronics firms experimenting with graphene conductors



DNA SEQUENCING

Researchers at British firm Oxford Nanopore, building on discoveries made at Harvard, claim that using graphene could reduce the cost and speed up the process of DNA sequencing

Synthesis of oxo-functionalized graphene (oxo-G)

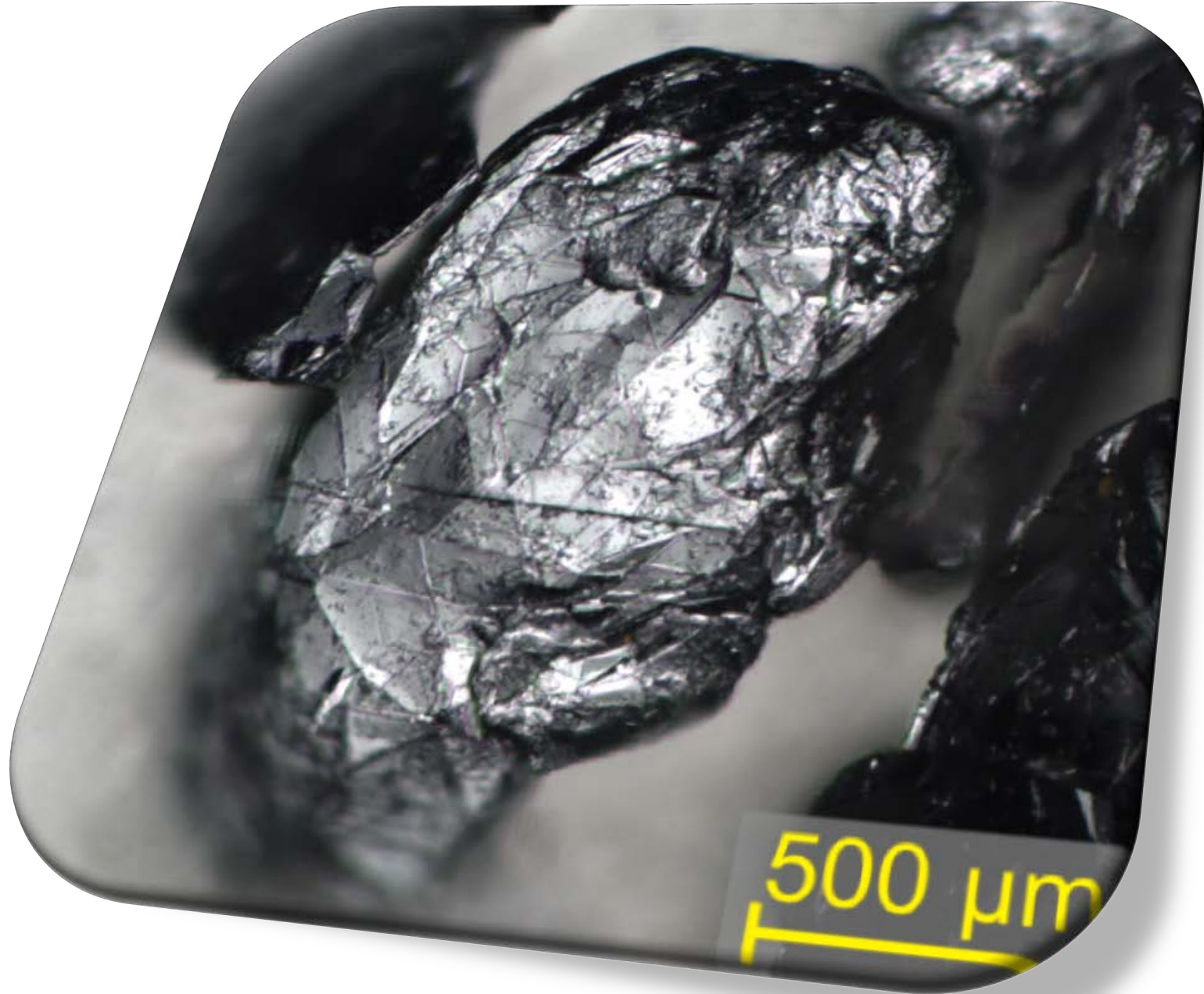
Quality of carbon framework

Certain control over defect formation

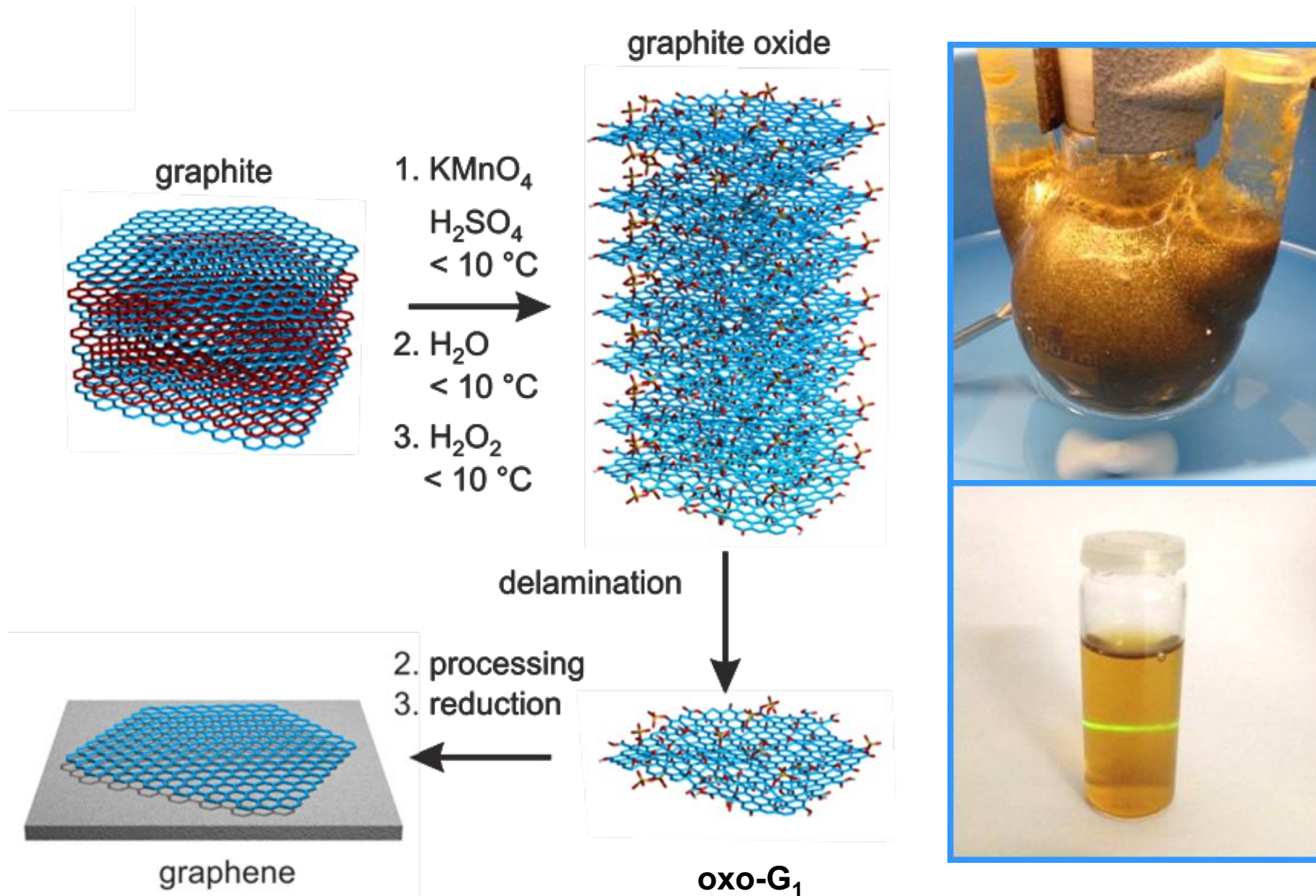
Defects as structural motifs

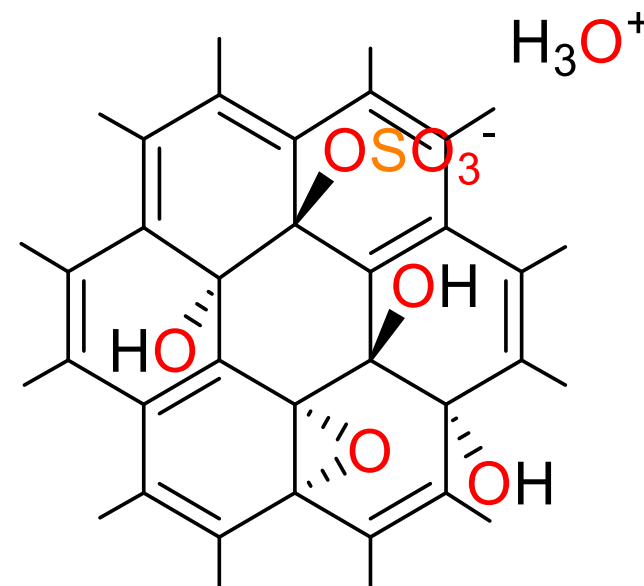
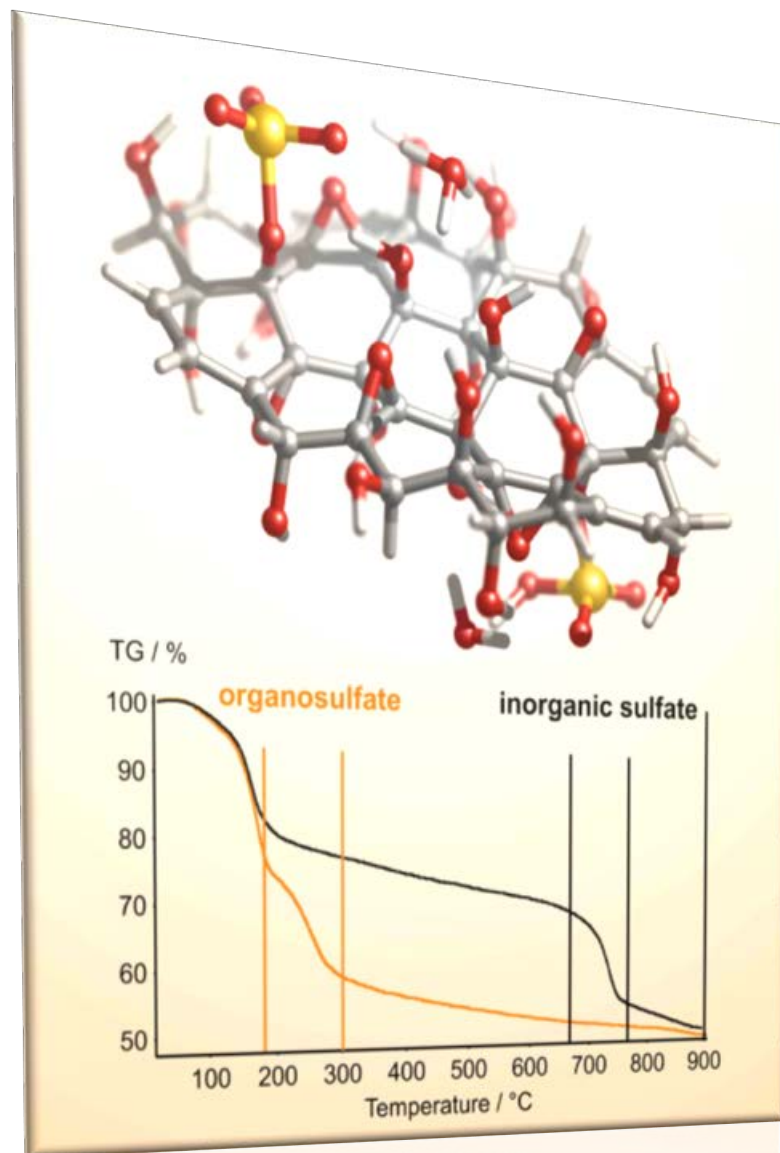
Graphite @ Sri Lanka





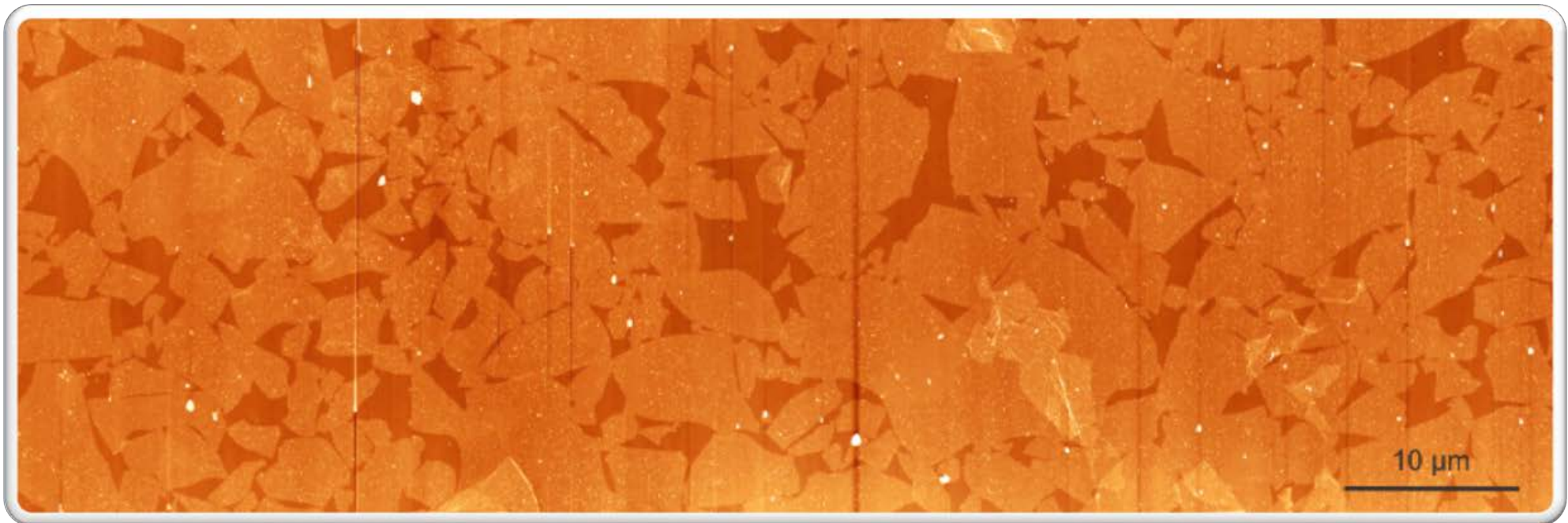
Synthesis of oxo-G₁: no CO₂ formation





**molecular architectures
based on electrostatic interactions**

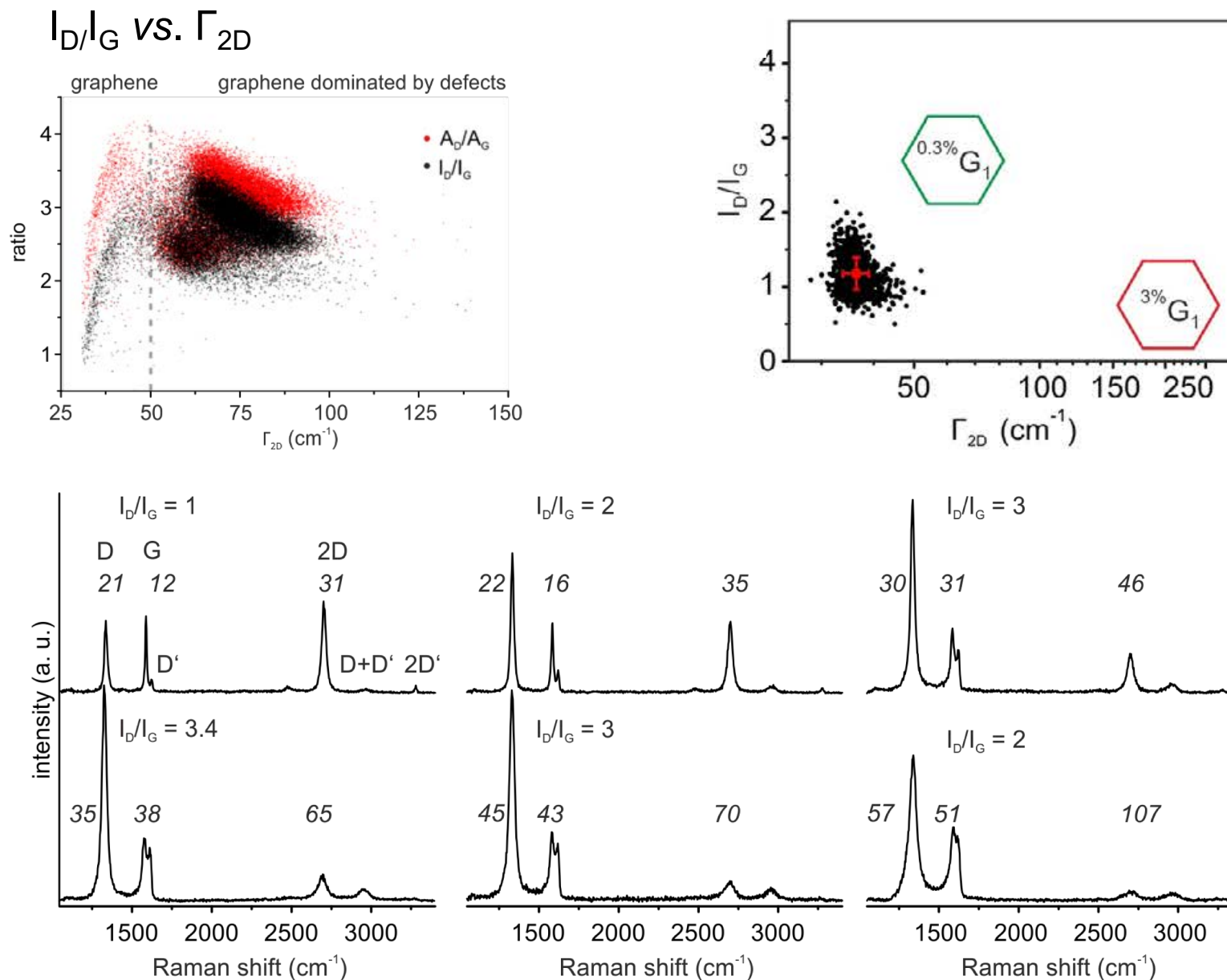
**1 organosulfate
on 30 C-atoms**

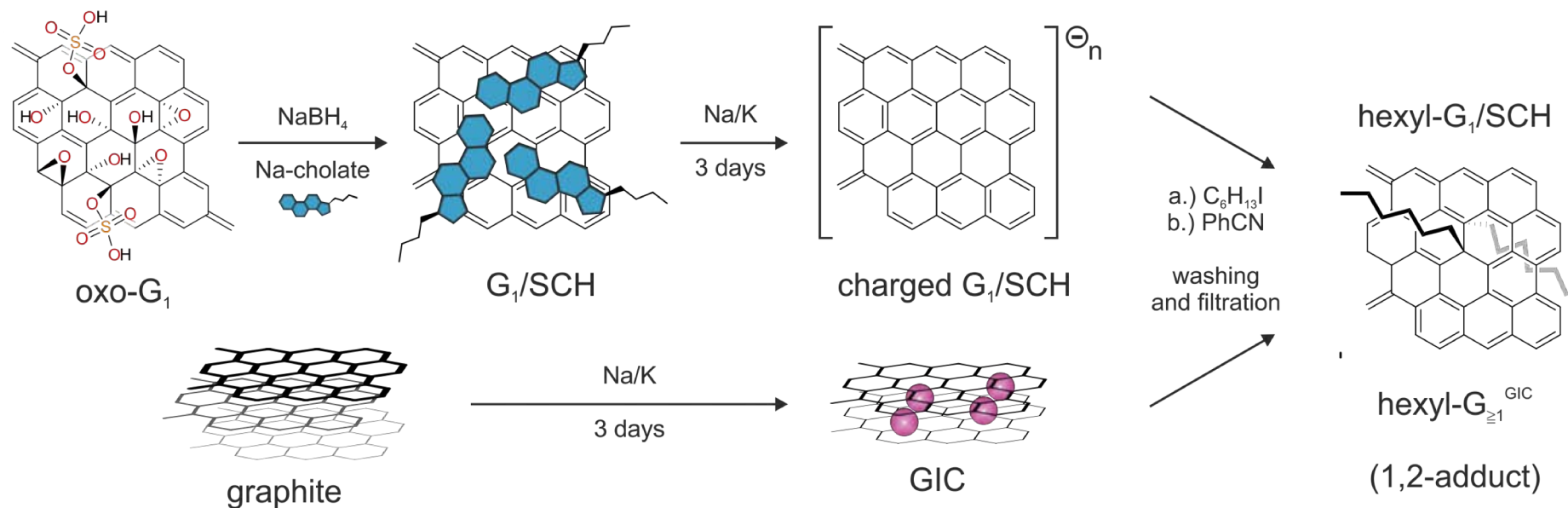


Raman: increment of scanning e.g. 1 micrometer

**Scanning Raman microscope
WiTec alpha 300
EMCCD (10-300 graphene spectra/s,
up to 1300 spectra/s)
laser@532 nm and 488 nm (UHTS300)**





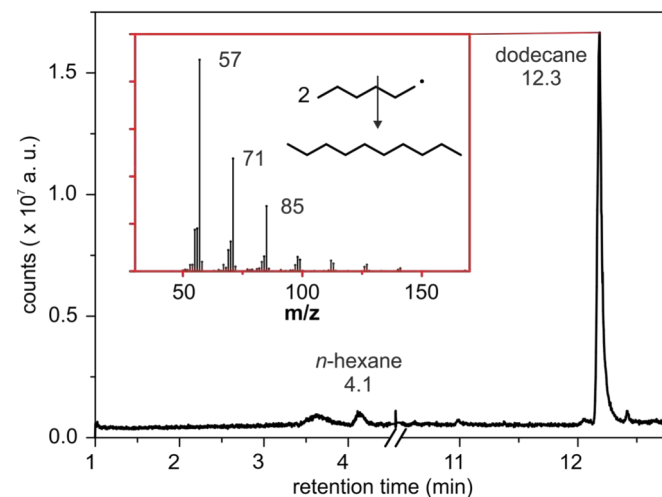


1. Oxo-G: single layers
2. Reduction and stabilization
3. Charging Na/K
4. Hexylation
5. Benzonitrile
(remove excess charge)



Christian E. Halbig

TGA-GC-MS at 250 °C:



Synthesis of oxo-functionalized graphene (oxo-G)

Quality of carbon framework

Certain control over defect formation

Defects as structural motifs

GO

Schafhaeutl

Brodie

Luzi

Hofmann

Staudenmaier

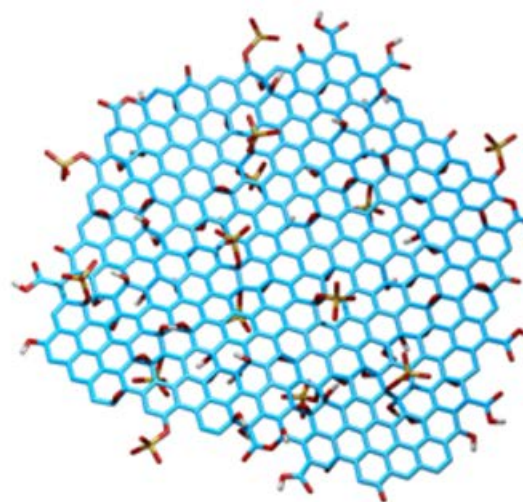
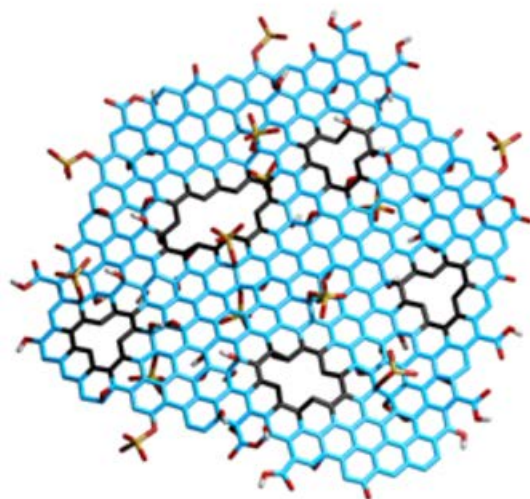
Charpy

Thiele

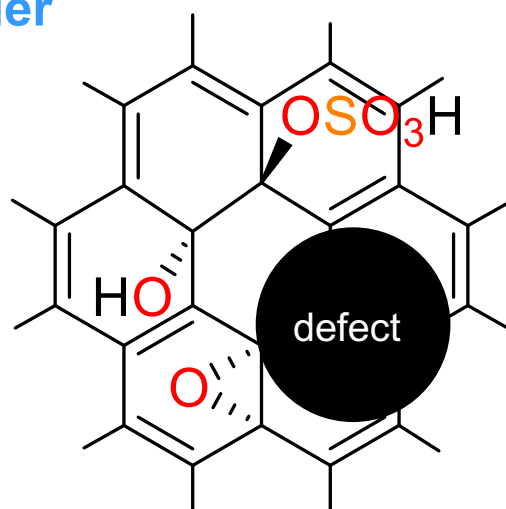
Hummers

Boehm

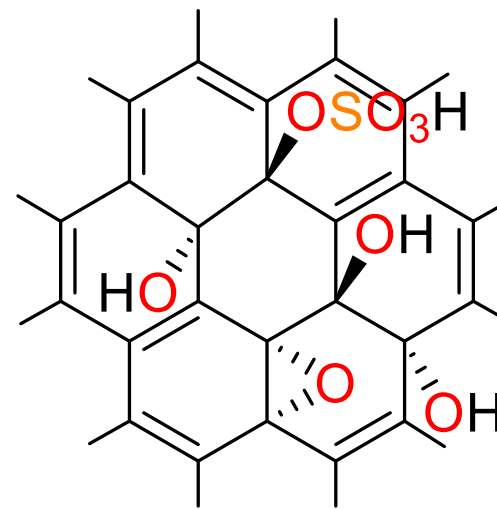
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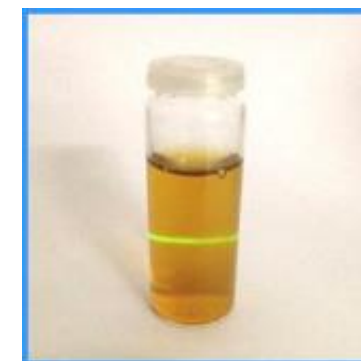
oxo-G₁



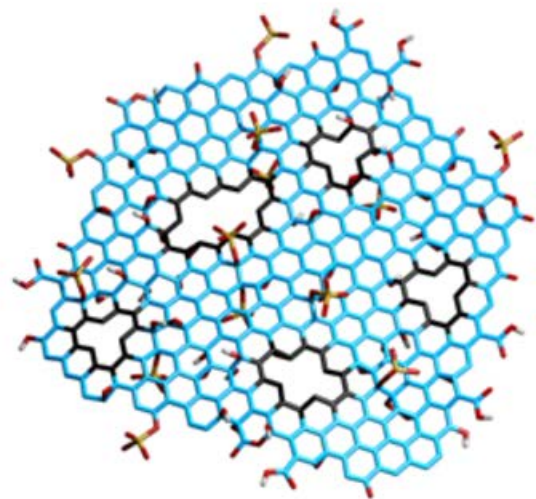
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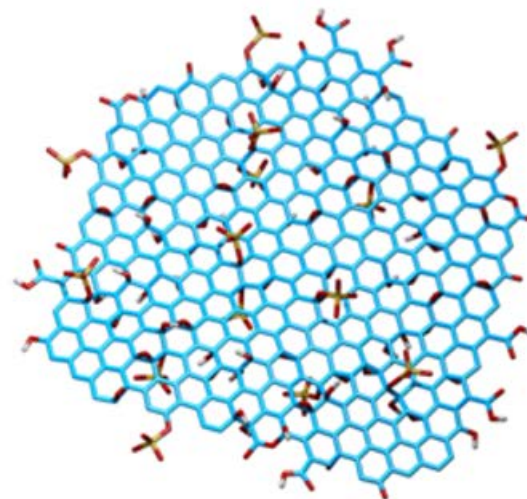
oxo-G₁



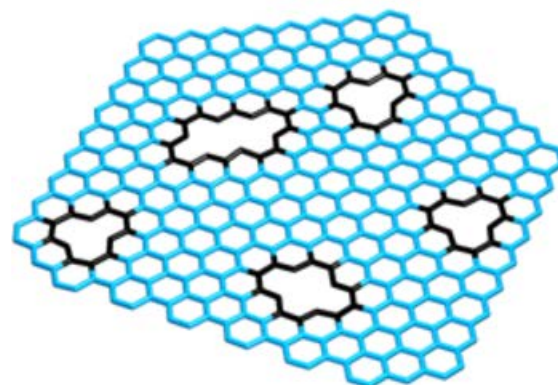
GO



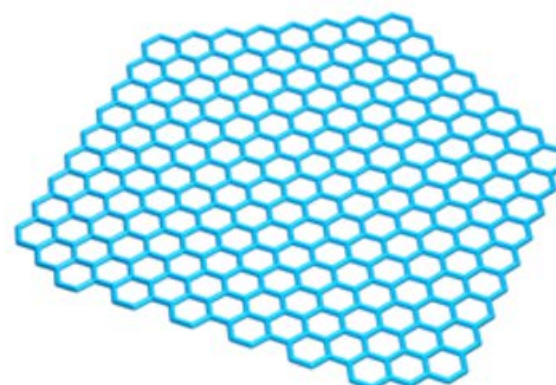
oxo-G₁



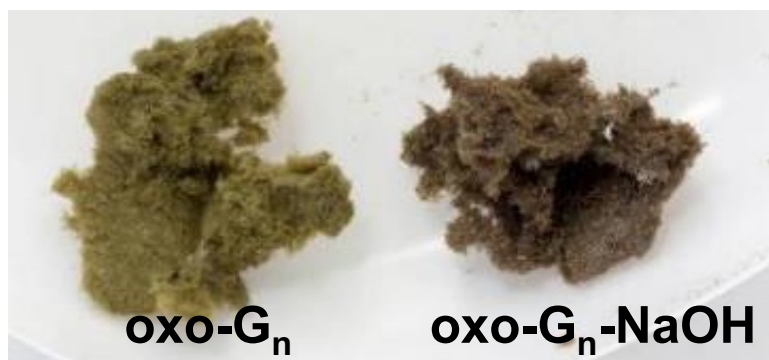
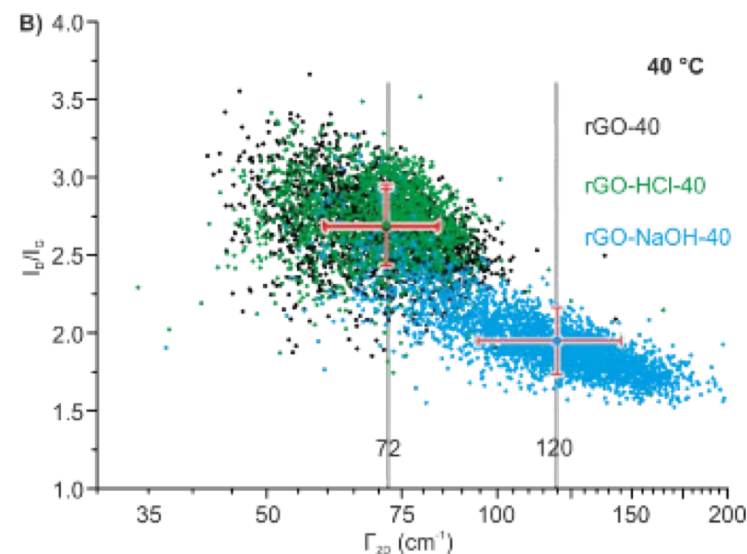
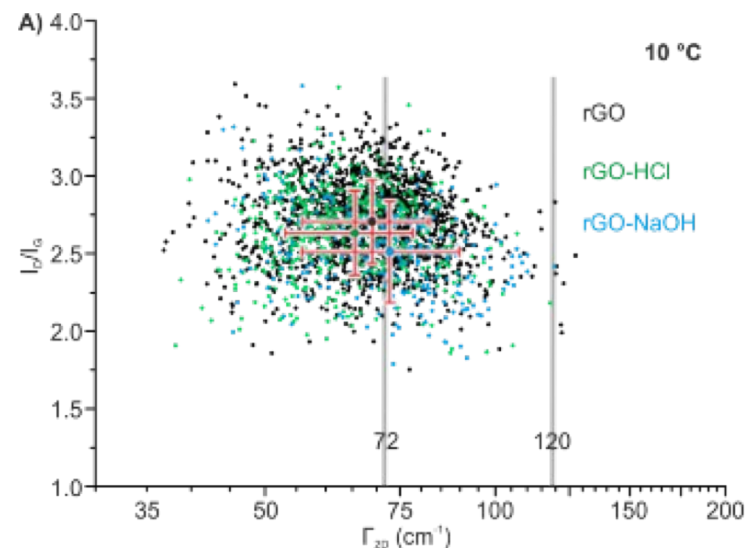
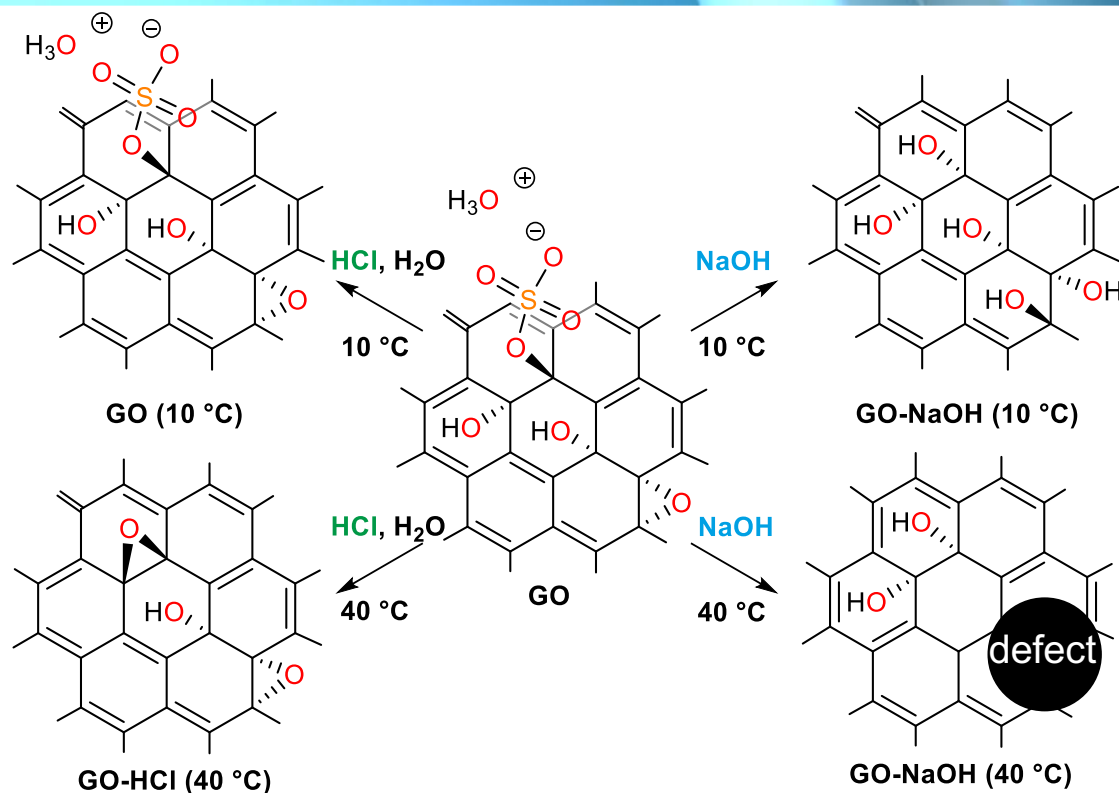
reduction



graphene with defects

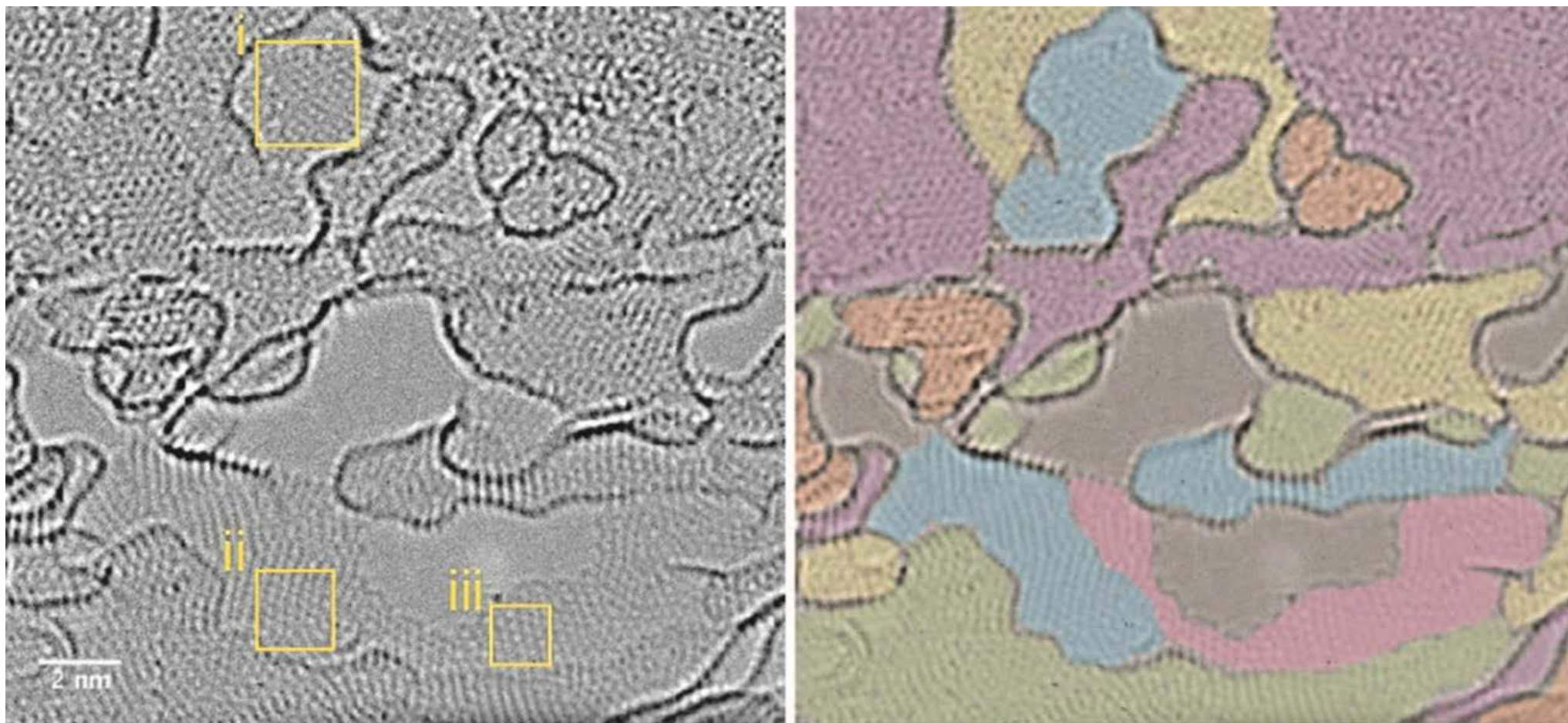


graphene without defects

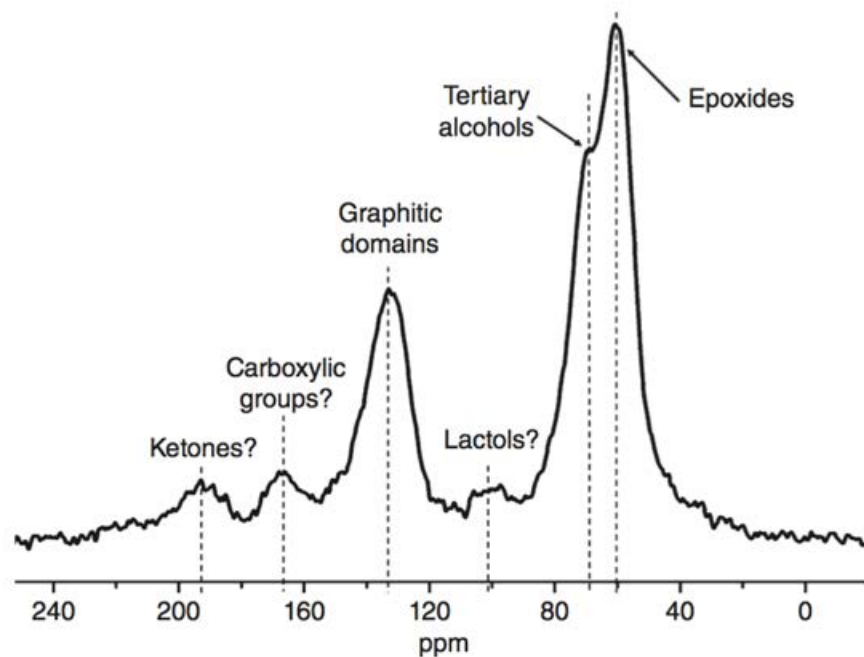
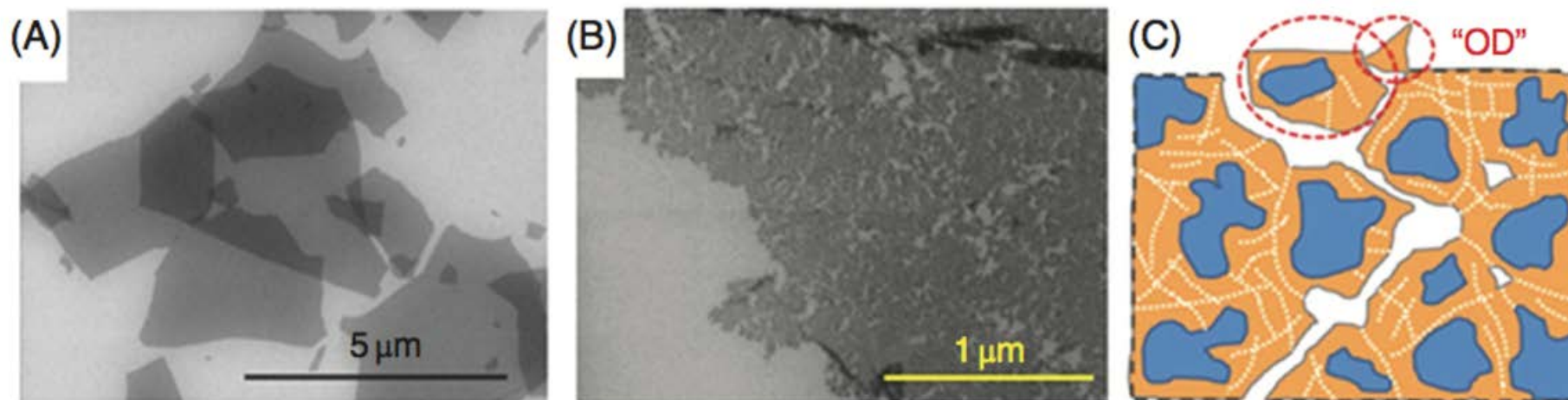


Structure changes: carbon framework stable under controlled reaction conditions

HRTEM micrograph of **commercial source of Graphene oxide**
Direct Imaging:

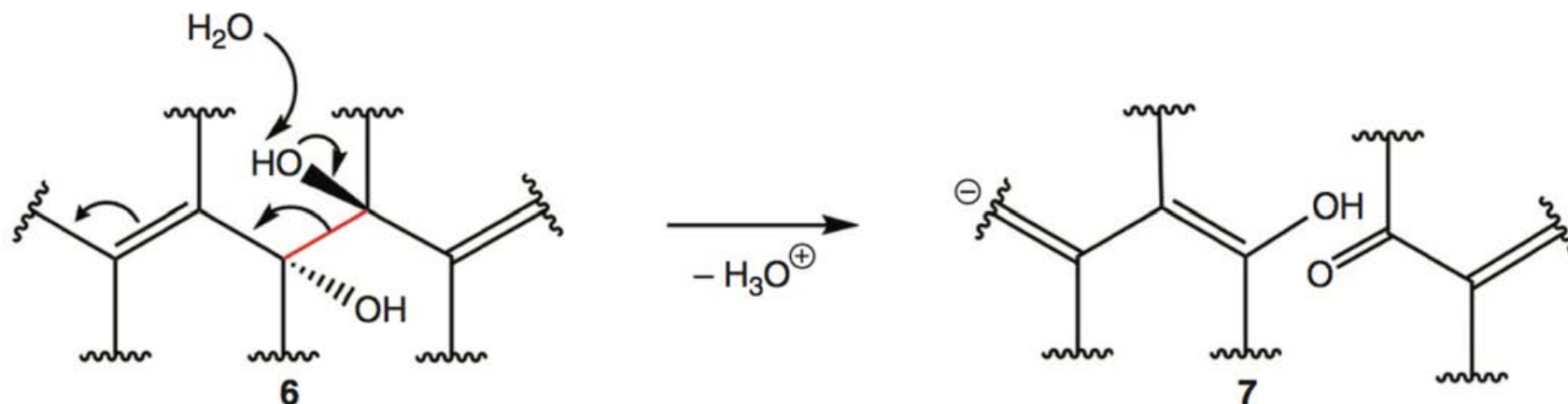


Carbon Framework of Graphene Oxide: amorphous, no long-range order, many distorted domains: Strong influence on physical properties.

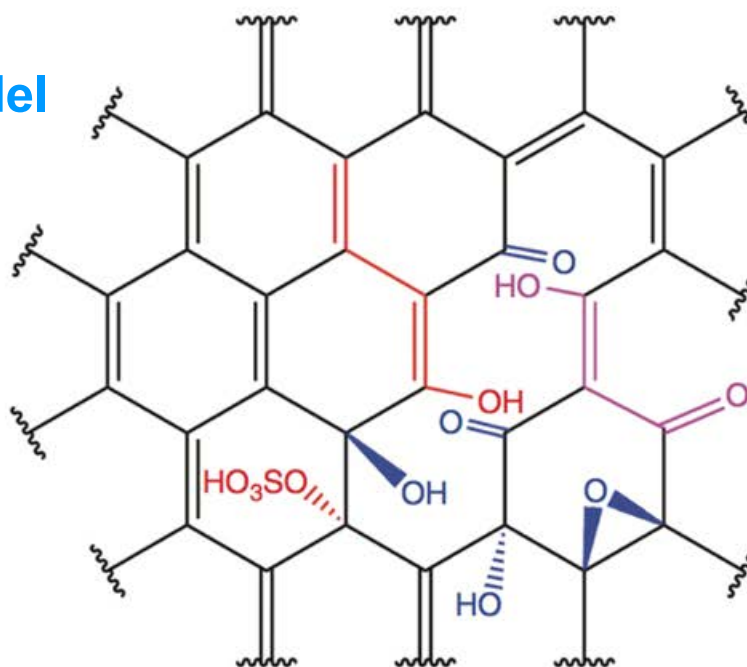


NMR: Evidence for oxo-species requiring C-C bond breakage

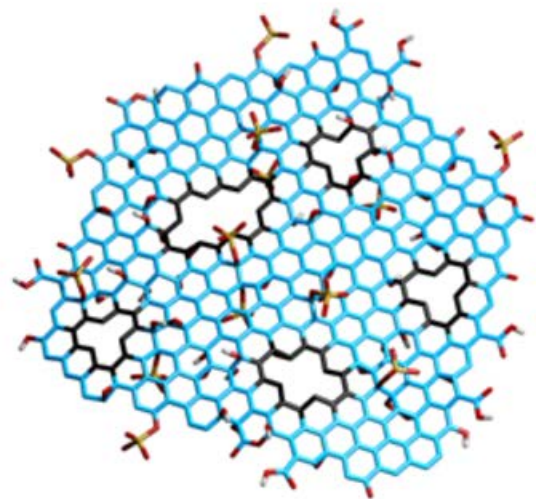
Origin of the Acidity of Graphene Oxide



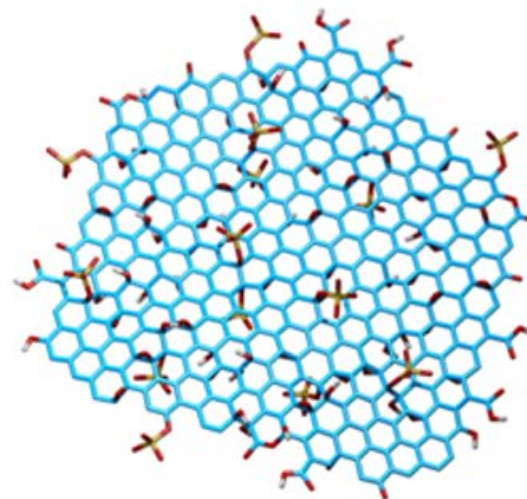
Simplified Dynamic Structure Model of Graphene Oxide



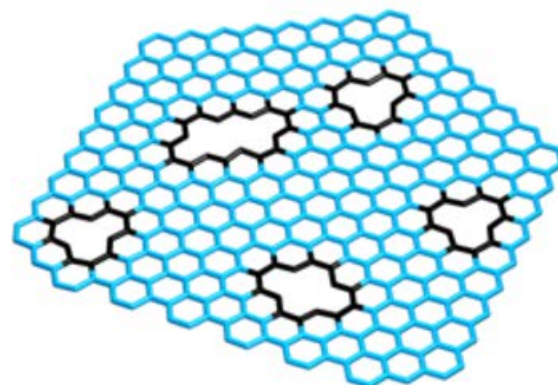
GO



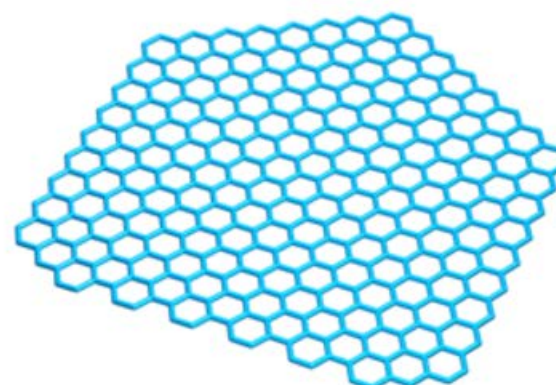
oxo-G₁



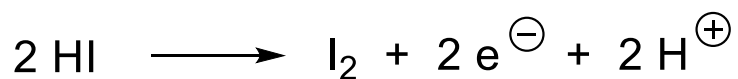
reduction



graphene with defects

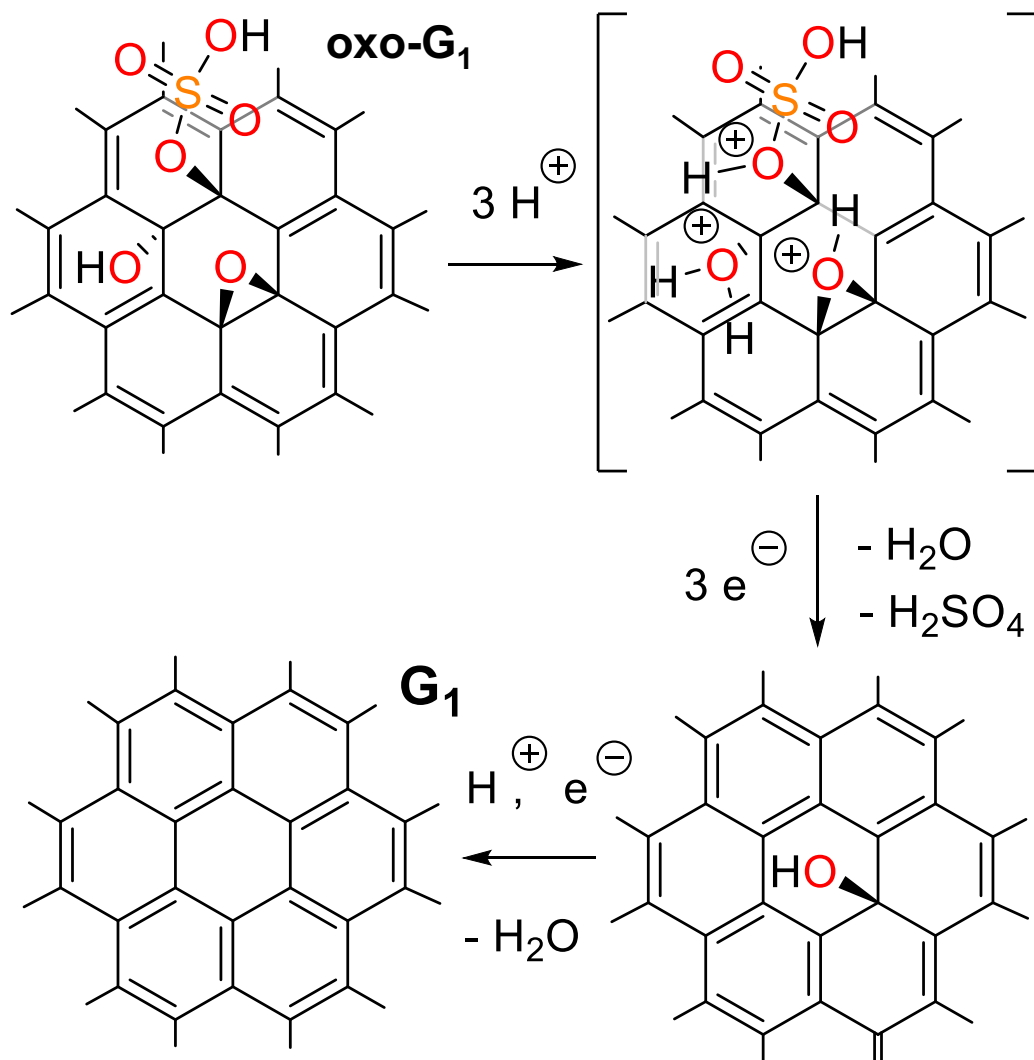


graphene without defects

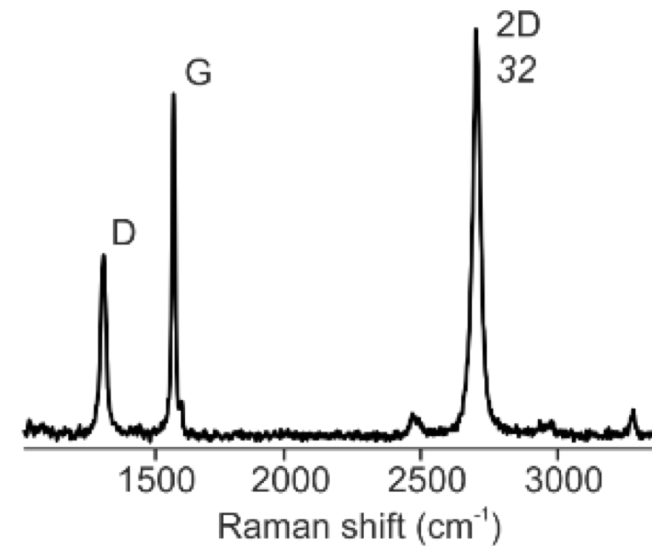
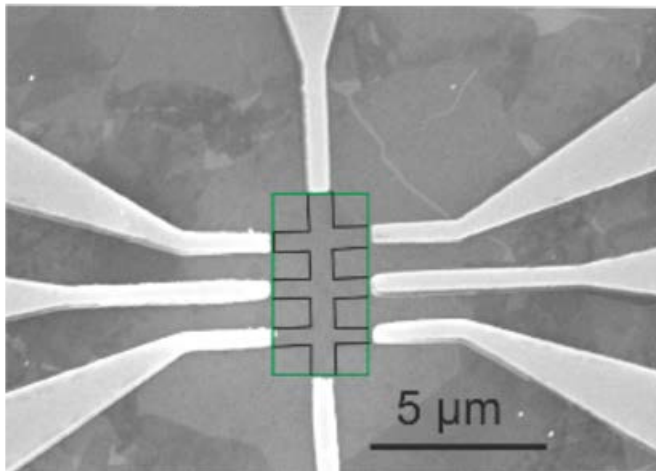


Reduction –
defunctionalization is
complete using HI / TFA

reduction by e-beam
generated radicals possible



- S. Eigler *et al.*, *Chem. Commun.* **2013**, 49, 7391;
J. Phys. Chem. C **2014**, 118, 7698;
Phys. Chem. Chem. Phys. **2014**, 118, 19832;
 R. Flynt, A. Kahnt, S. Eigler, B. Abel *et al.*
Am. J. Nano Res. Appl. **2014**, 2, 9-18;
Nanoscale, **2015**, 7, 19432.
RSC Adv. **2016**, 6, 68835-68845.



Devices: (Prof. Müller / Dr. Enzelberger-Heim)

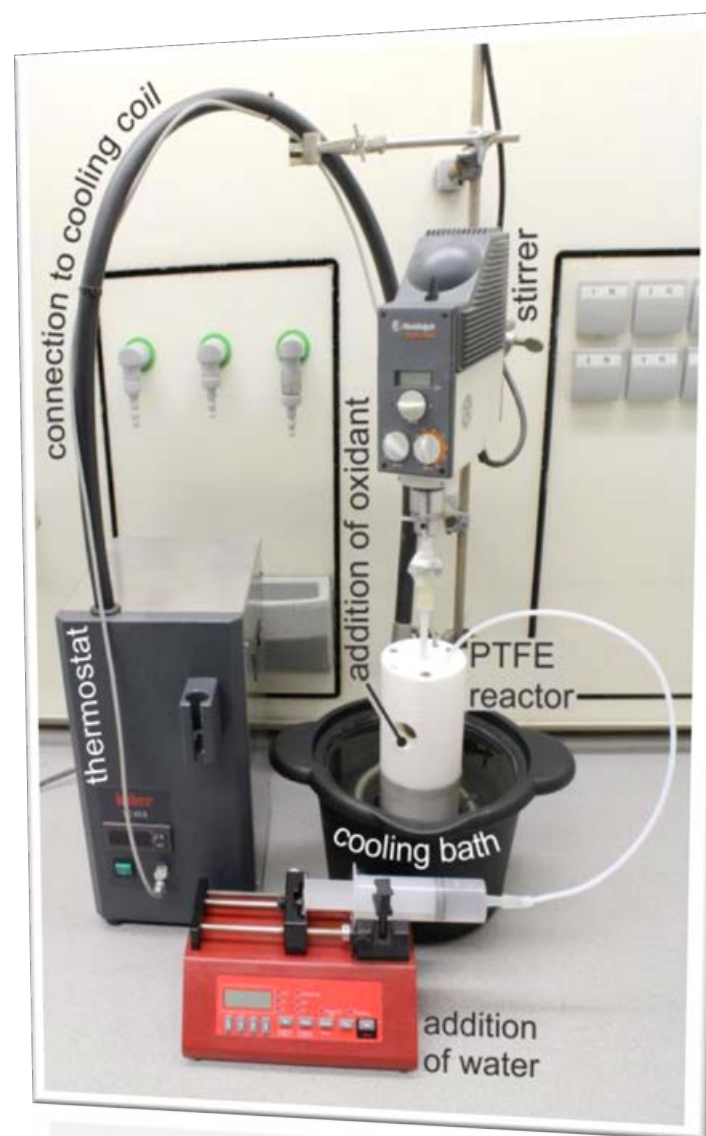
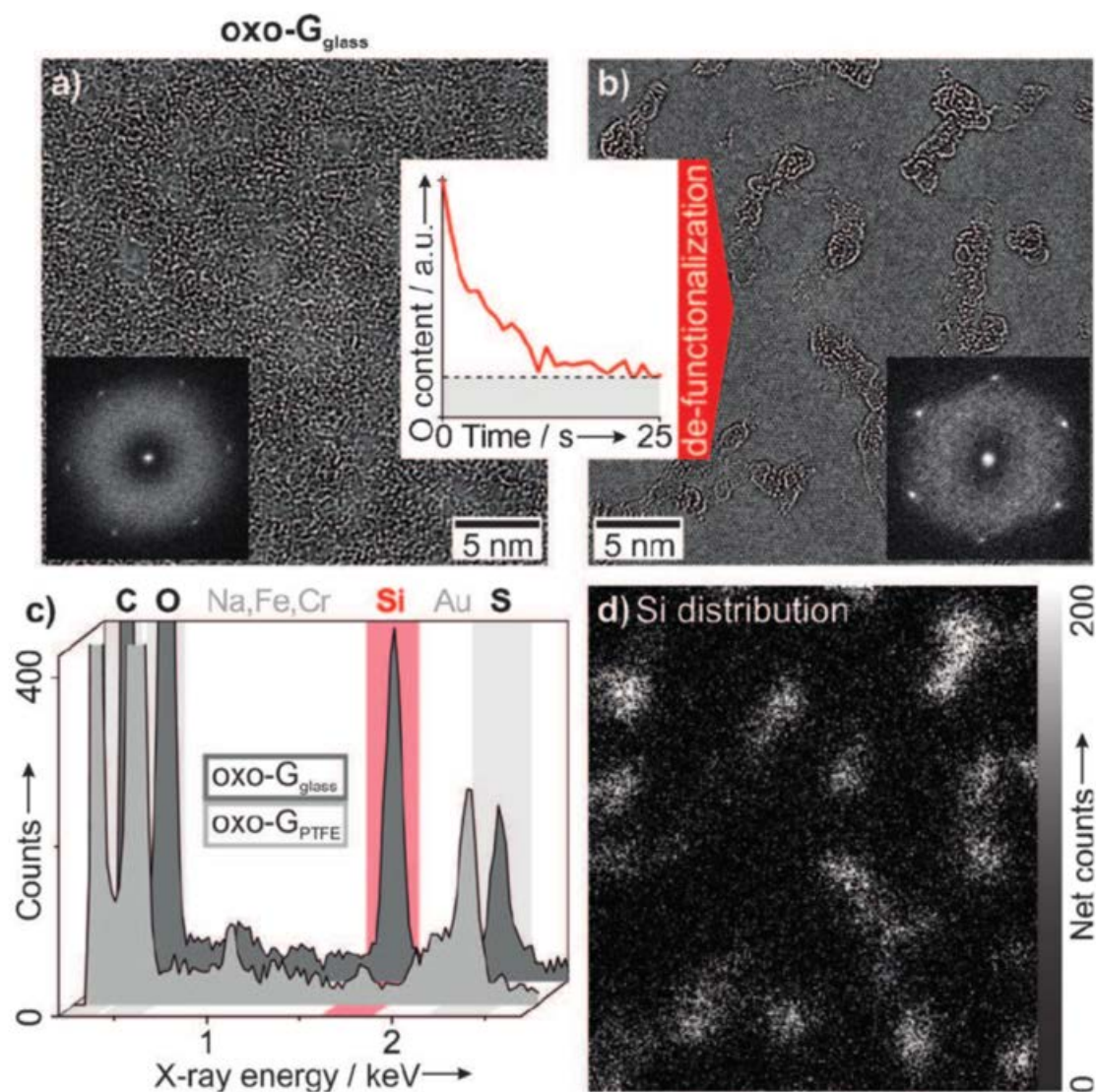
Physical measurements confirm 2D nature of graphene (and HRTEM)

defect density of about 0.01%: $\mu = 2000 \text{ cm}^2/\text{Vs}$

defect density about 0.3%: $\mu = 250 \text{ cm}^2/\text{Vs}$

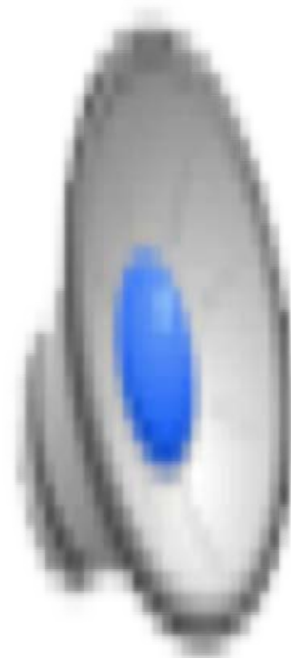
Reference from literature (defect density several %): $\mu = 0.1-10 \text{ cm}^2/\text{Vs}$

Pure and simple: HRTEM



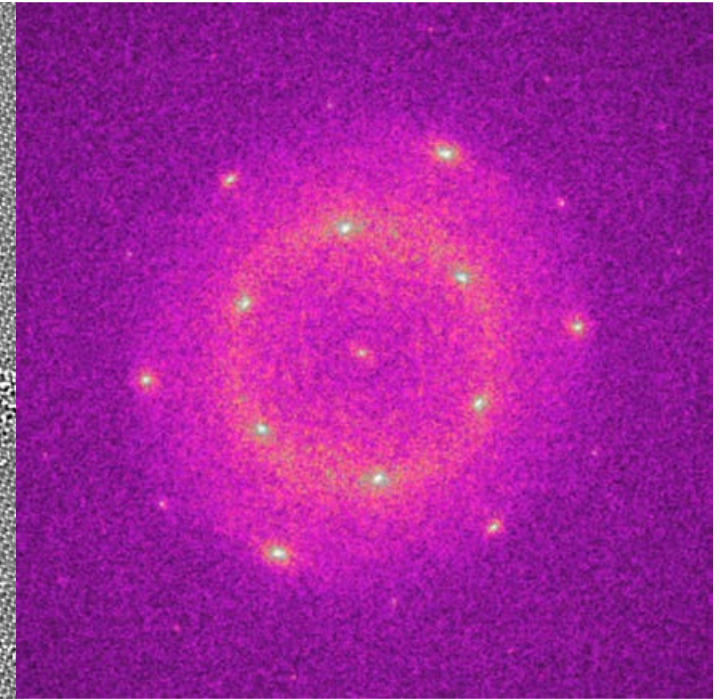
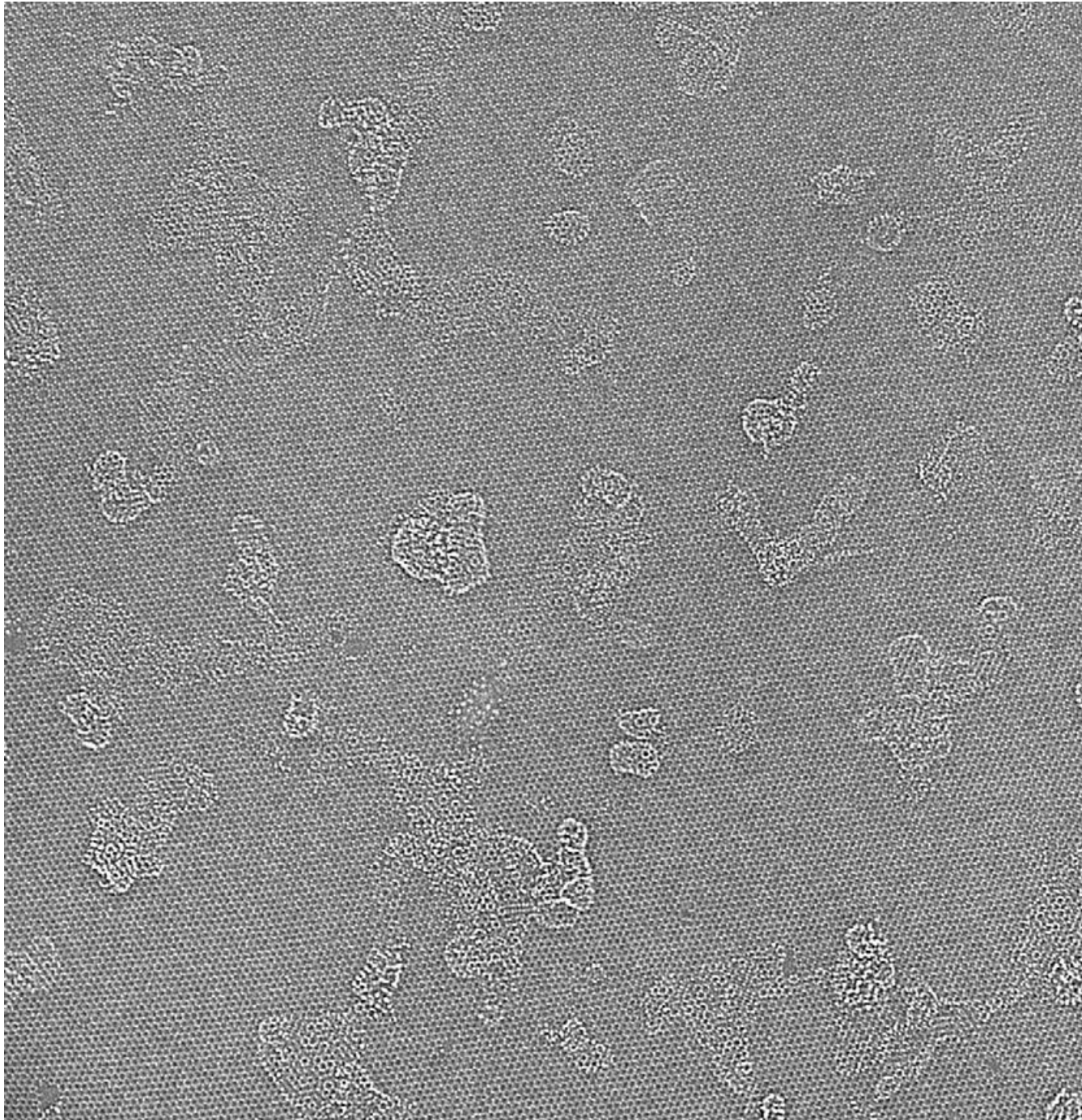
Collaboration: Dr. Butz / Prof. Spiecker
(Erlangen)

Pure and simple:



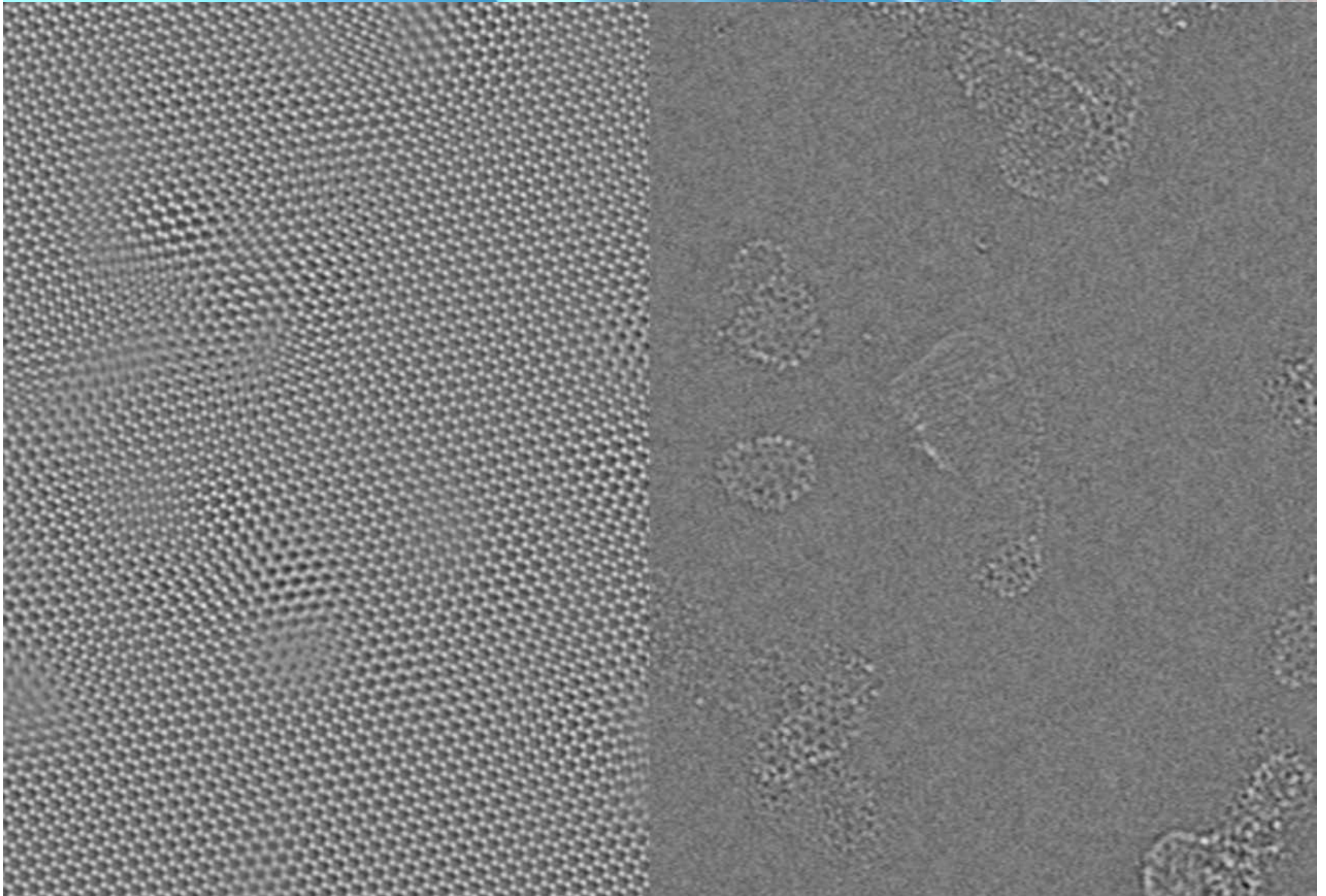
Collaboration: Dr. Butz / Prof. Spiecker
(Erlangen)

Angew. Chem. Int. Ed. **2016**, 55, 115771–15774.



diffractogram

Collaboration:
Prof. Ute Kaiser,
Dr. Felix Börrnert
(Ulm)



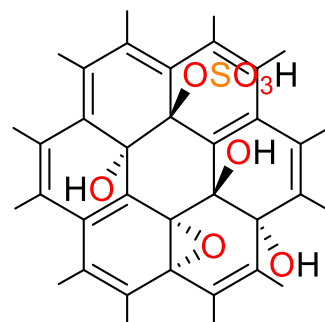
Synthesis of oxo-functionalized graphene (oxo-G)

Quality of carbon framework

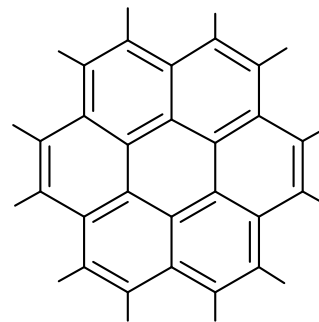
Certain control over defect formation

Defects as structural motifs

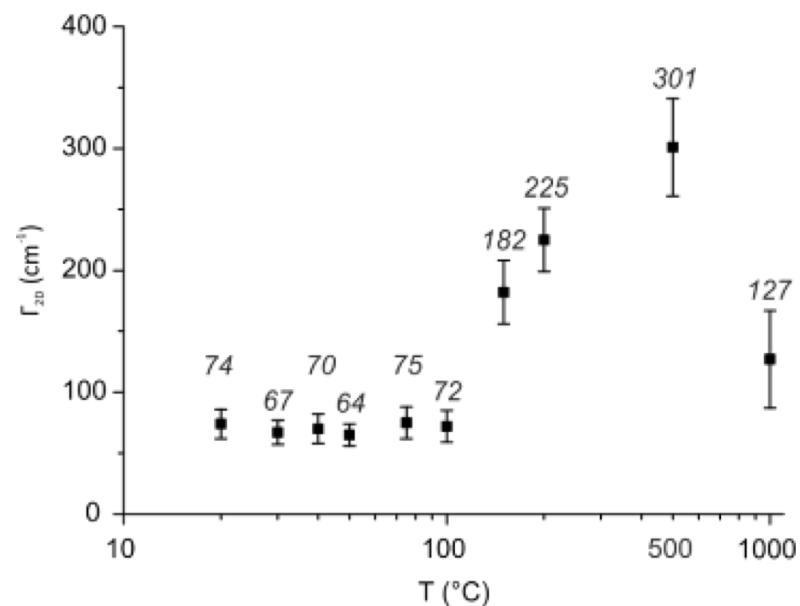
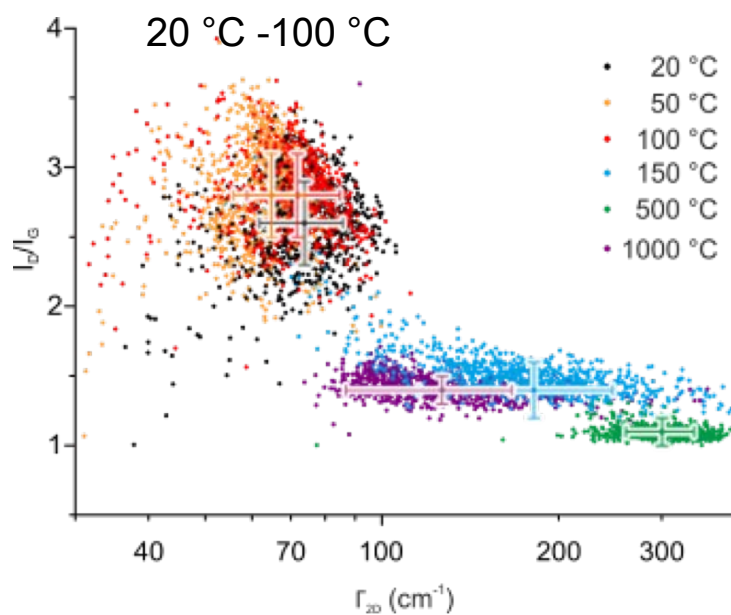
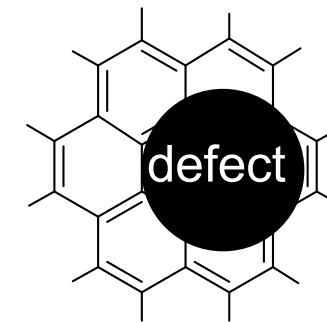
Stability of Carbon-Framework: oxo-G₁ stable up to 100 °C

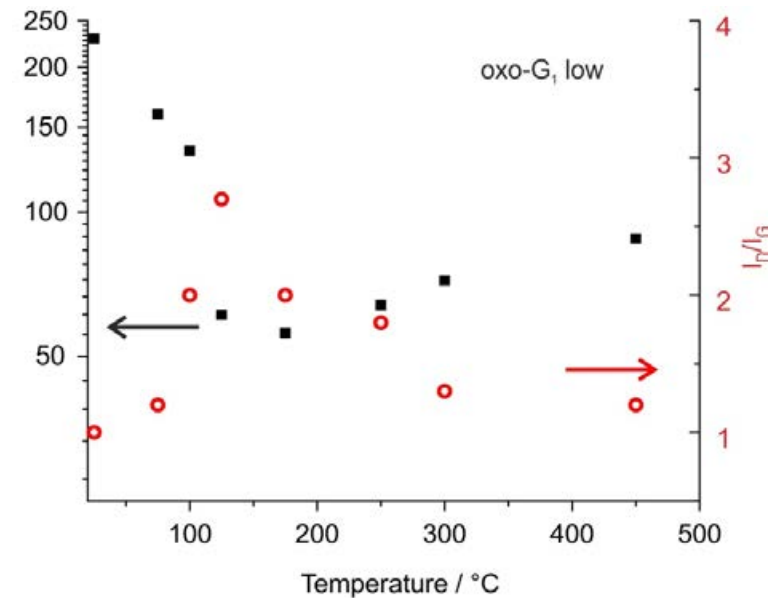
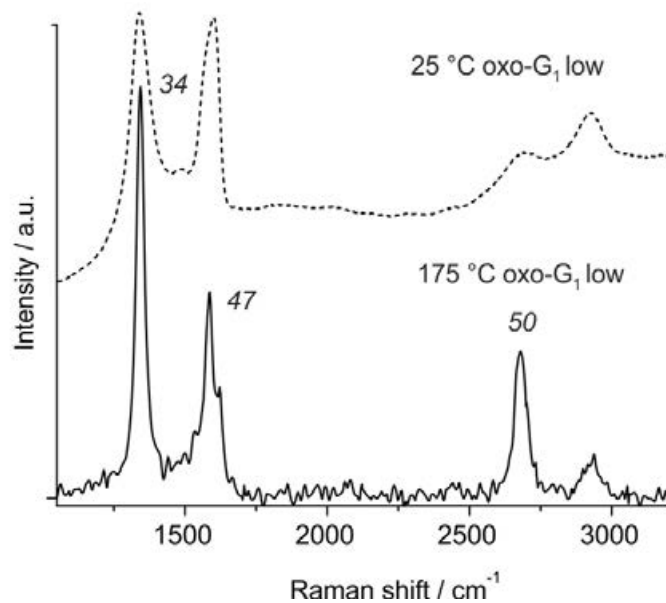
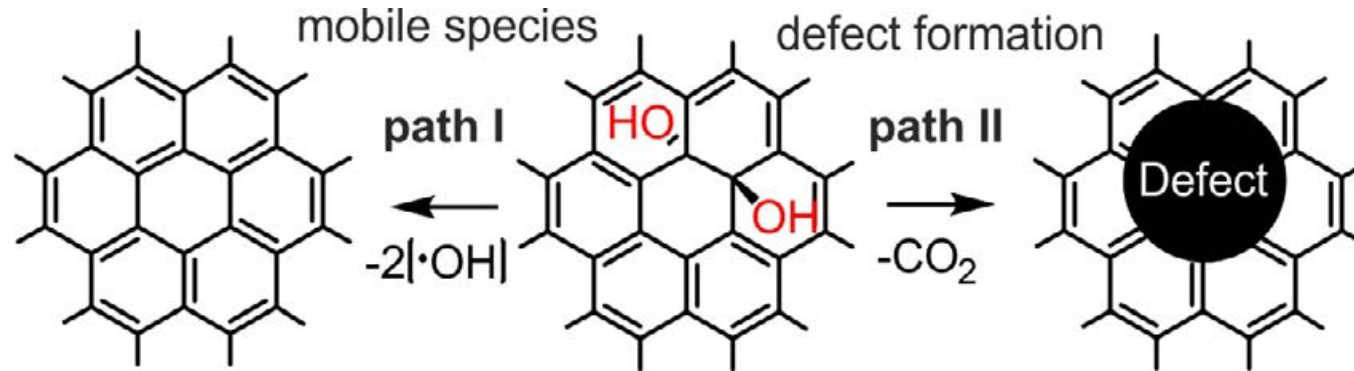


1. Δ (20 °C – 1000 °C)
2. HI/TFA (reduction)

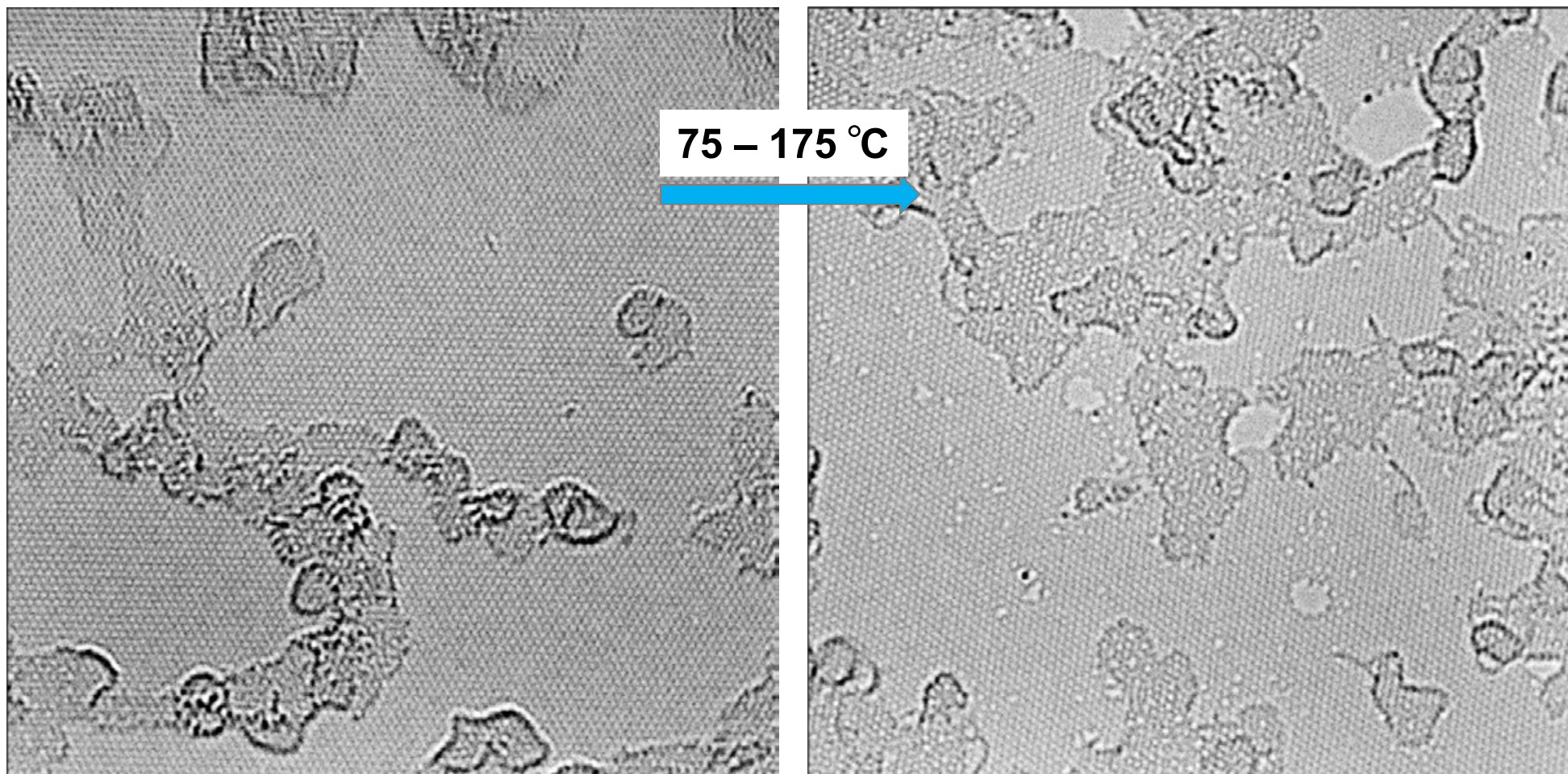


+





HRTEM image of oxo-G₁, *thermal treatment*: (Prof. Ute Kaiser, Dr. Boerrnert, Ulm)



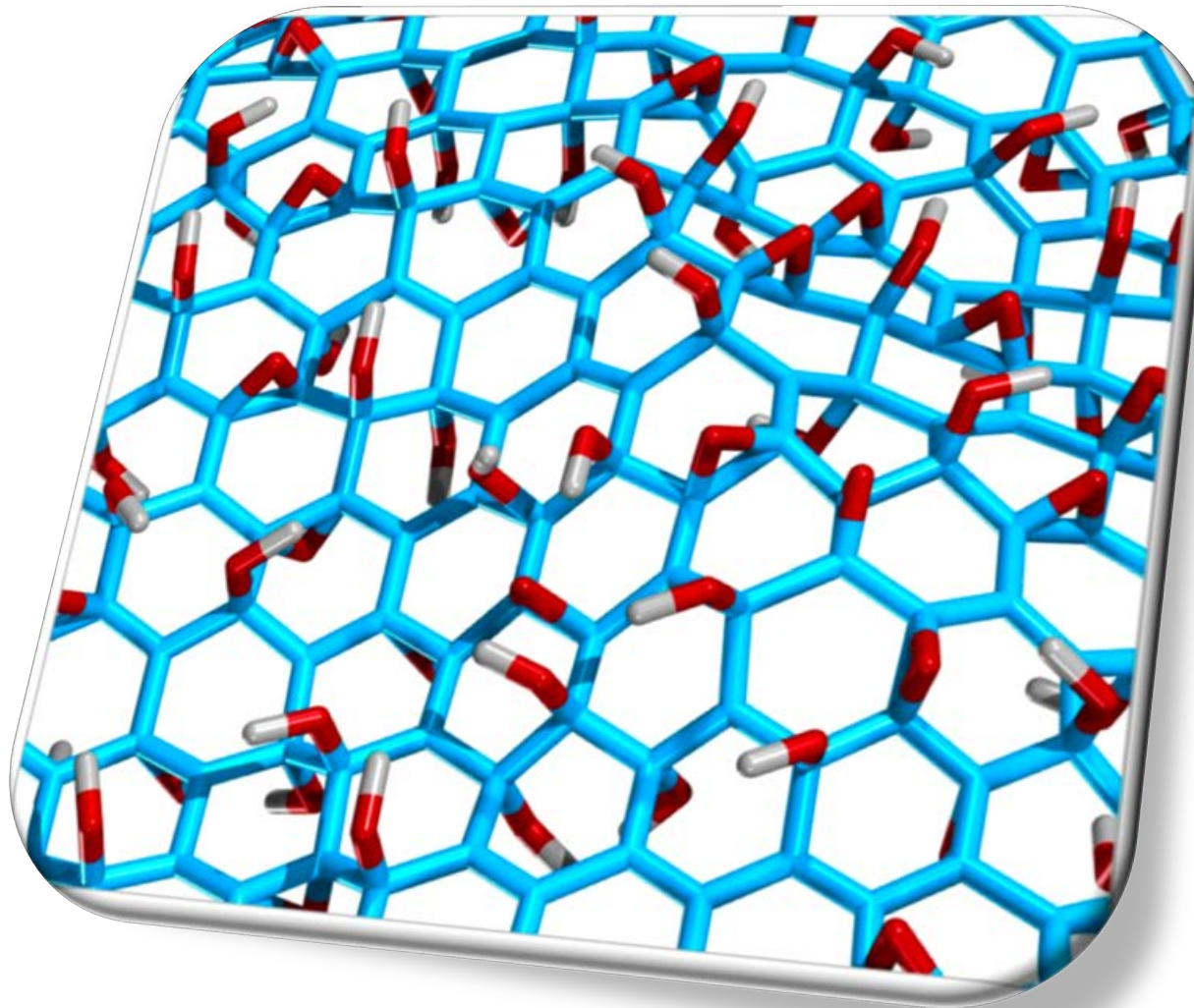
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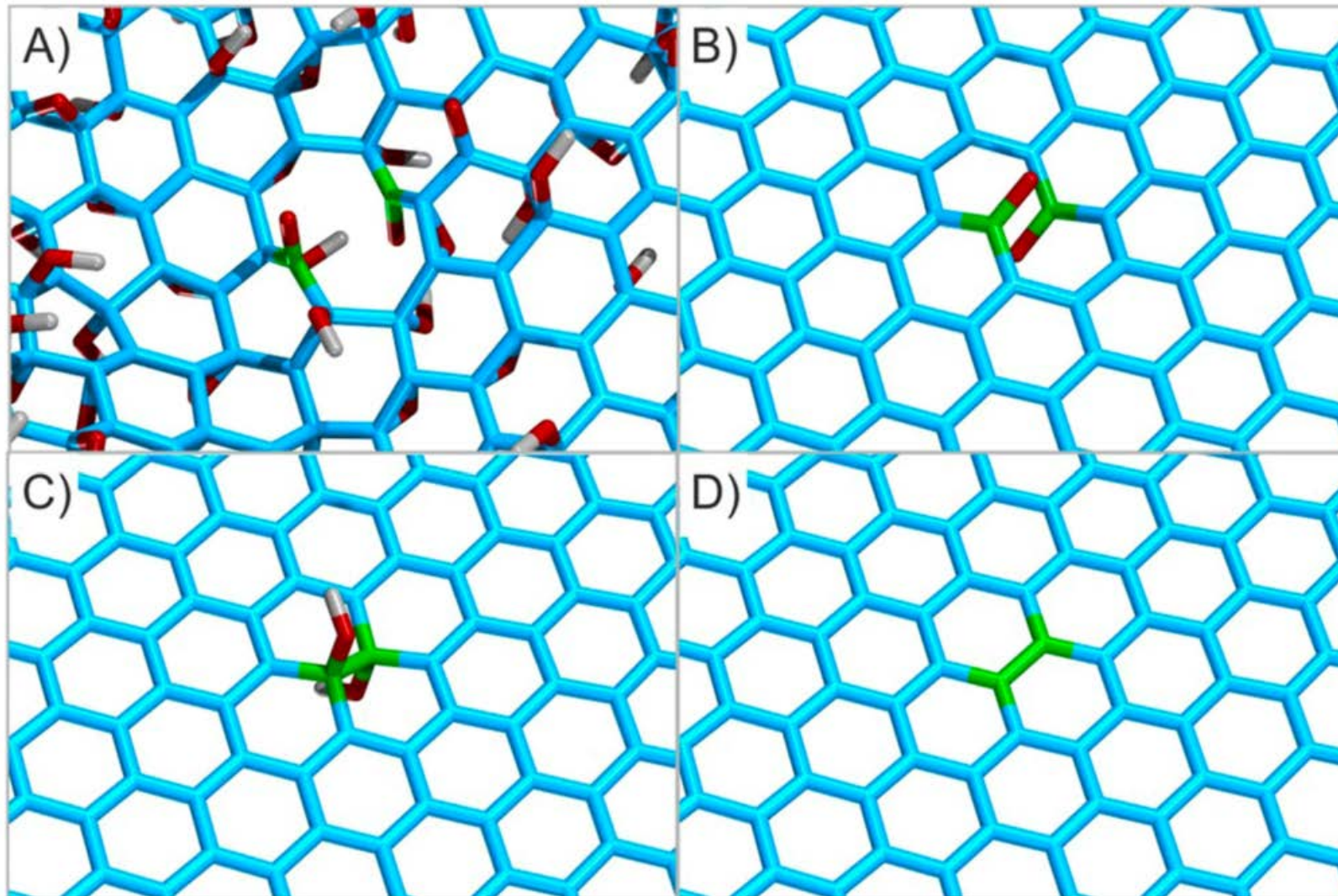
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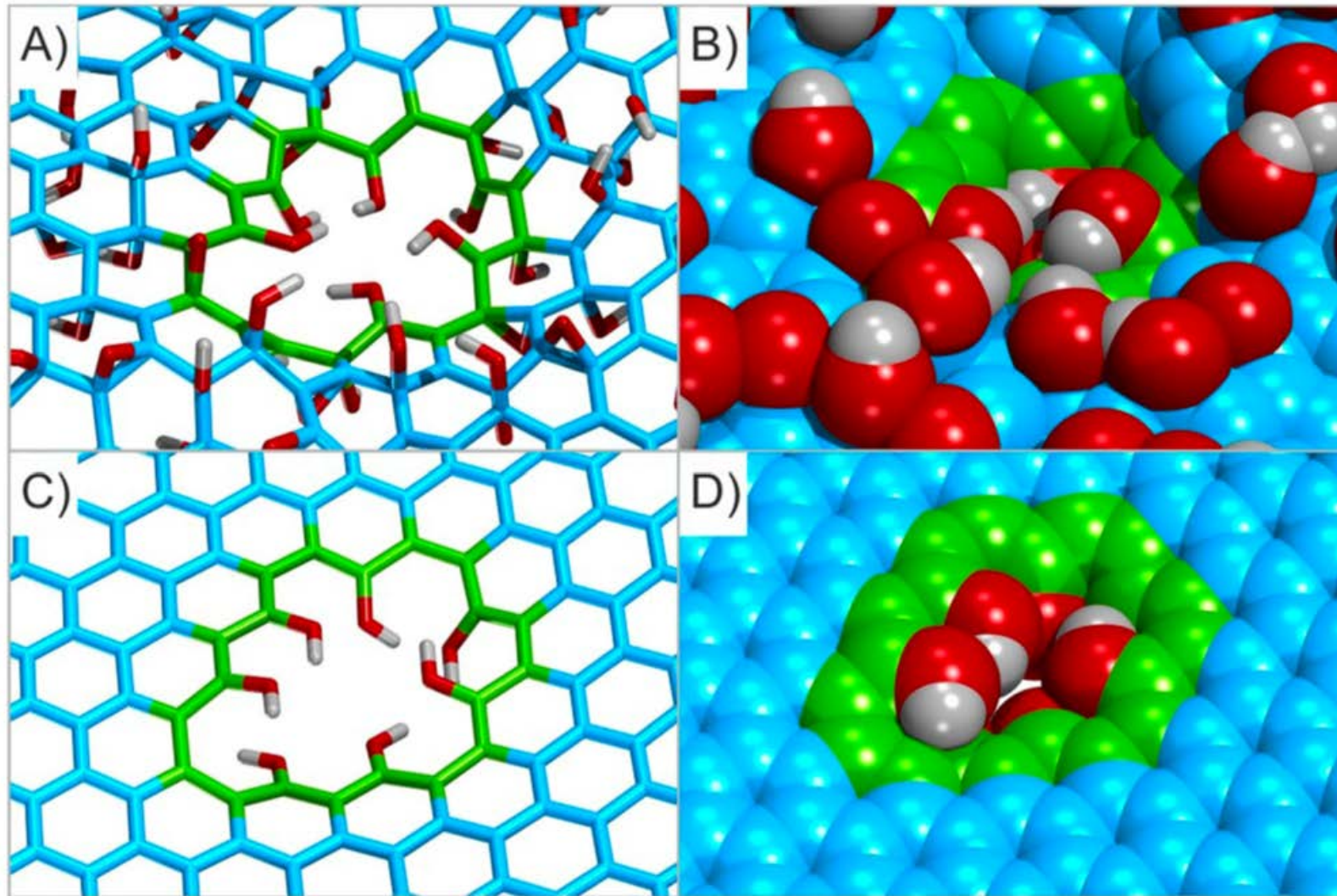
Model of oxo-G: functionalization defects



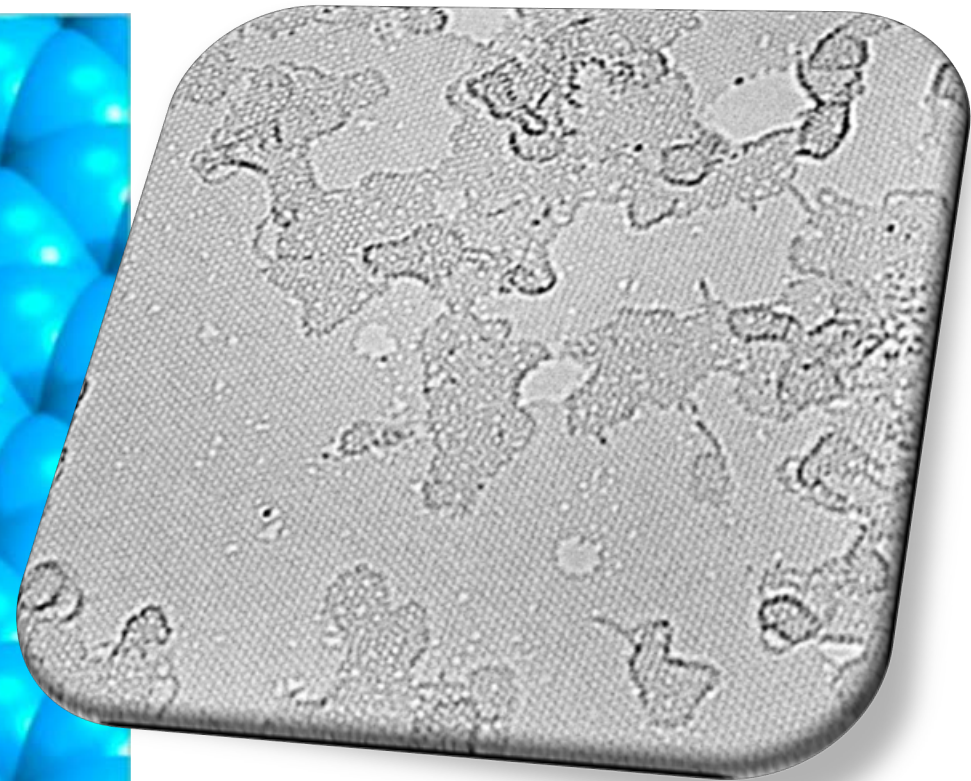
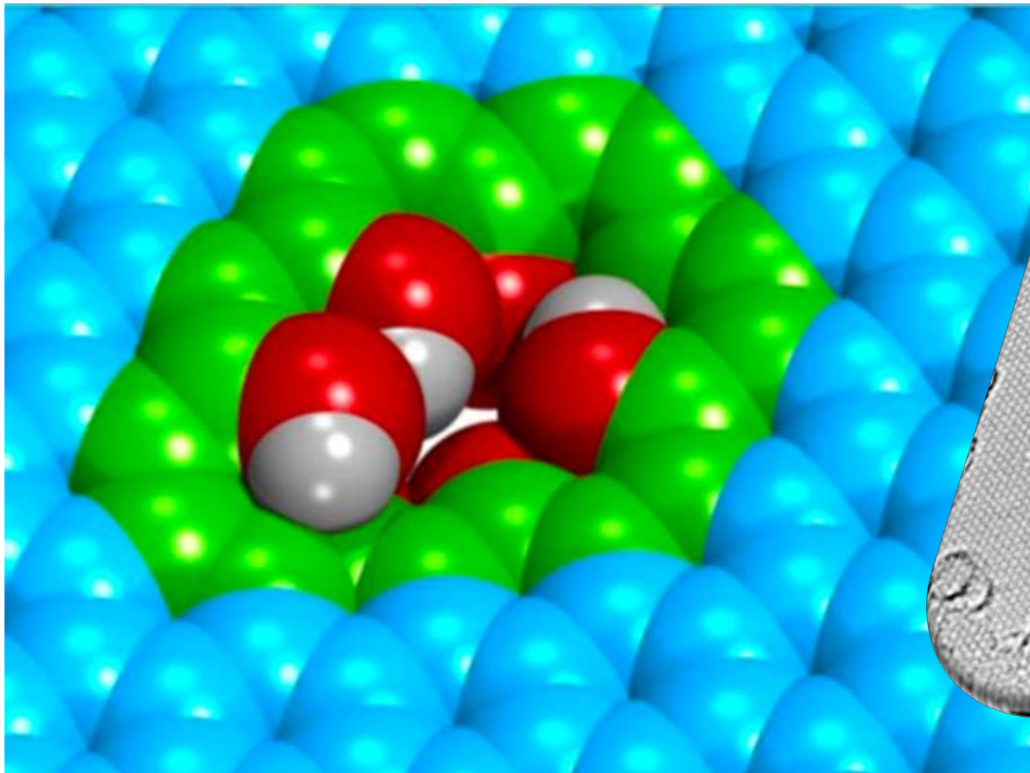
Break of C-C bond: Transient defect



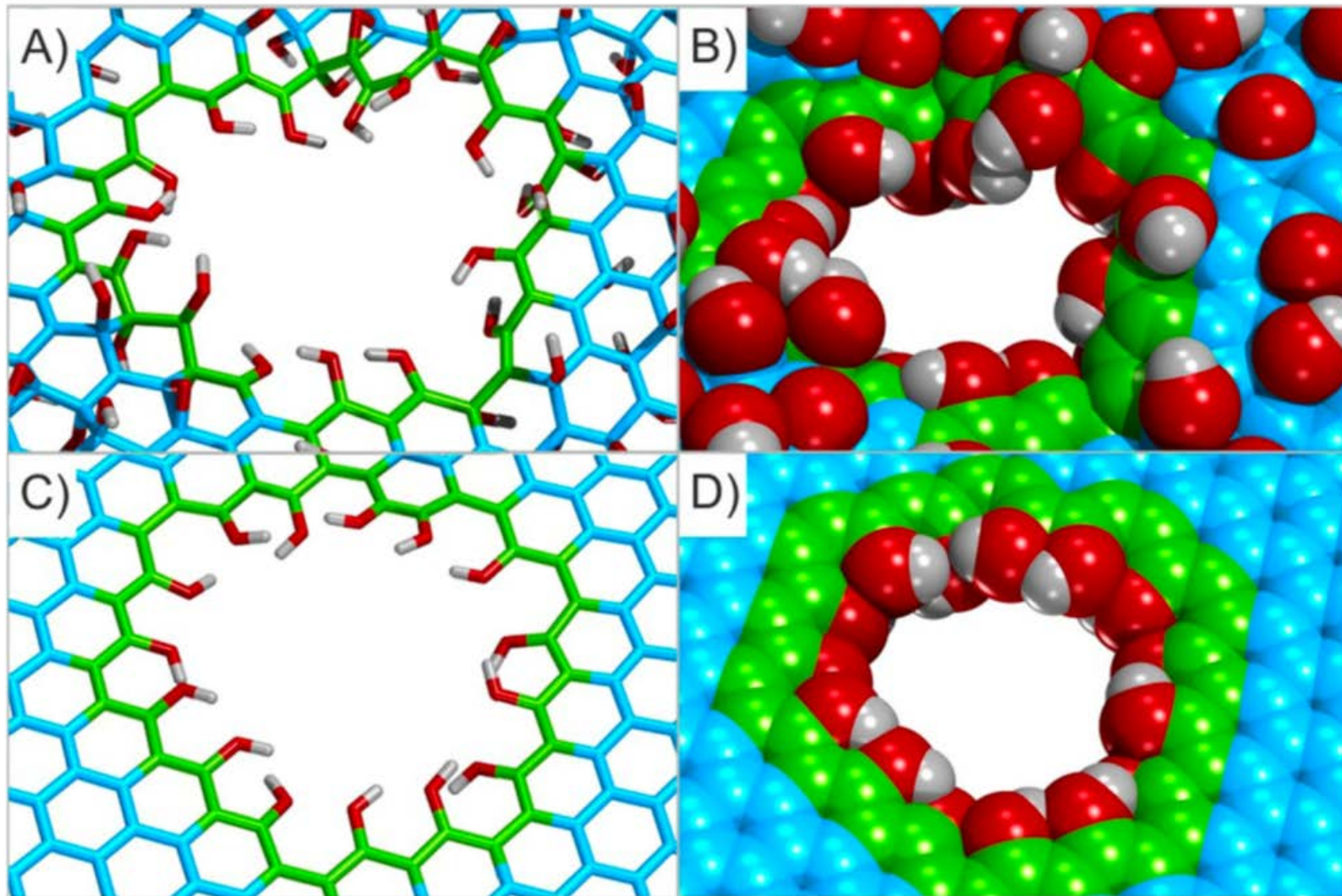
Seven missing C-atoms: Vacancy defect but not a hole



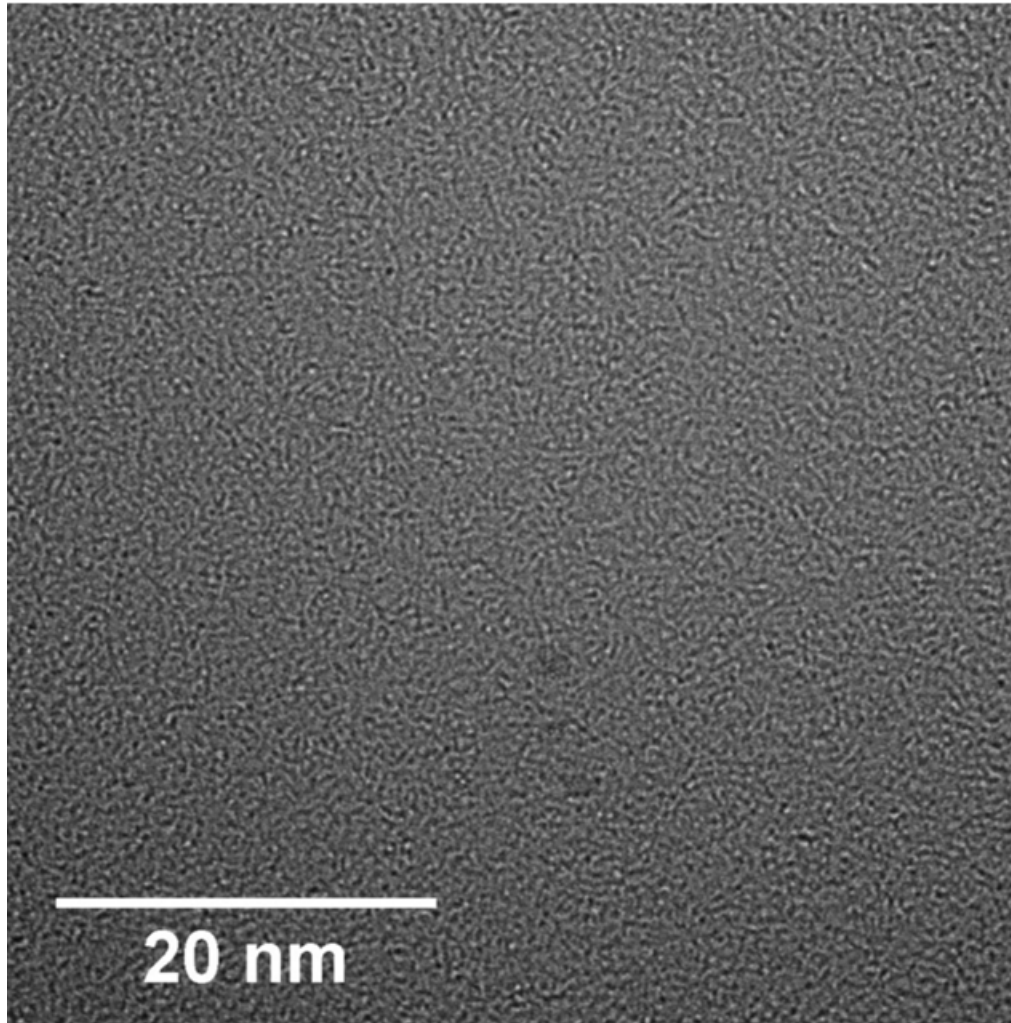
Seven missing C-atoms: Vacancy defect but not a hole



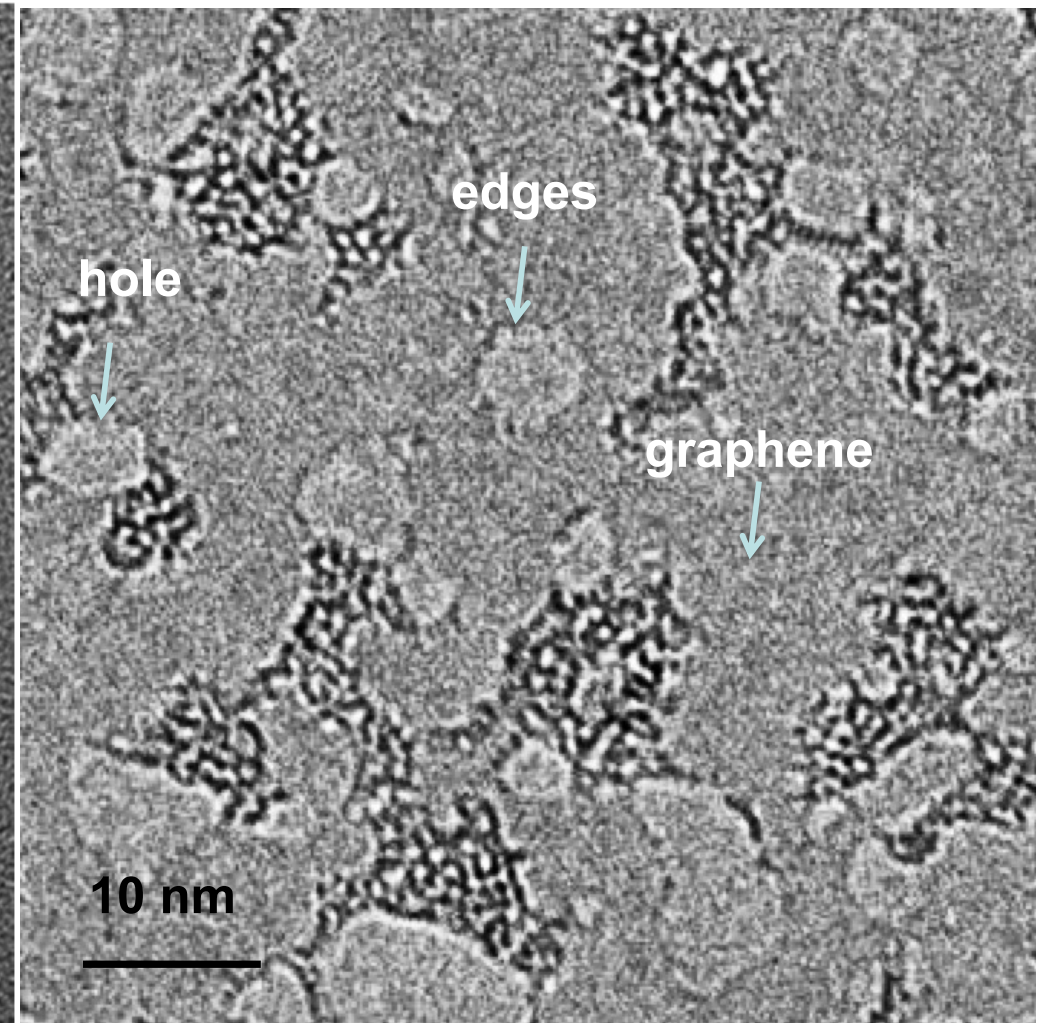
35 missing C-atoms: hole formation



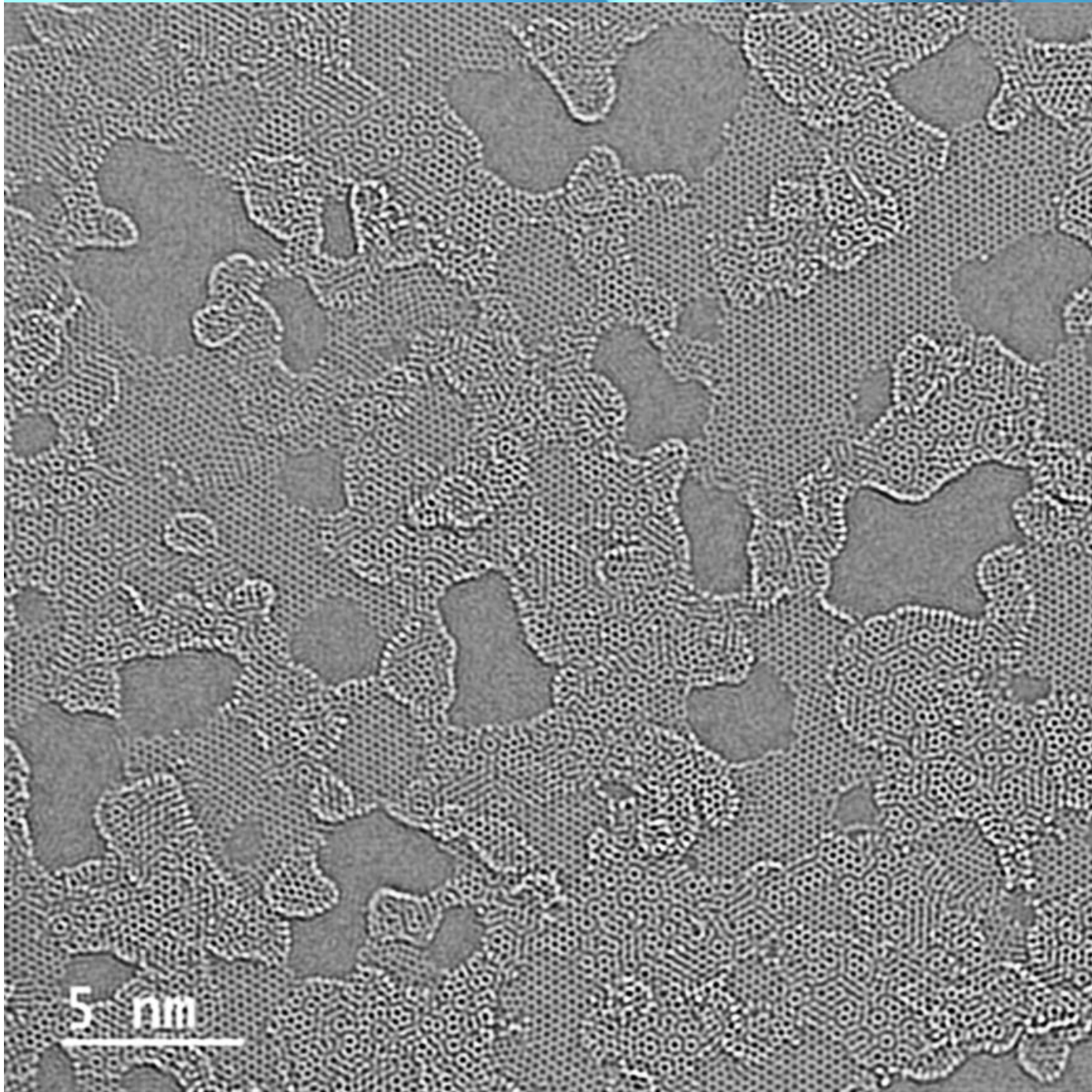
Contaminants on surface



Visible holes in graphene



Oxo-G heated to 300 °C



Thermal treatment
of oxo-G_{50%}
300 °C in vacuum

- Rearrangement
- Holes
- Stable membrane
- Partial double layer structure

Thanks for Your Attention

Dr. Lei Han, Dr. Patrick Feicht, Steffen Brülls, Dr. Severin Schindler, Christian Halbig, Philipp Rietsch, Zhengping Wang, Dengkun Wang

