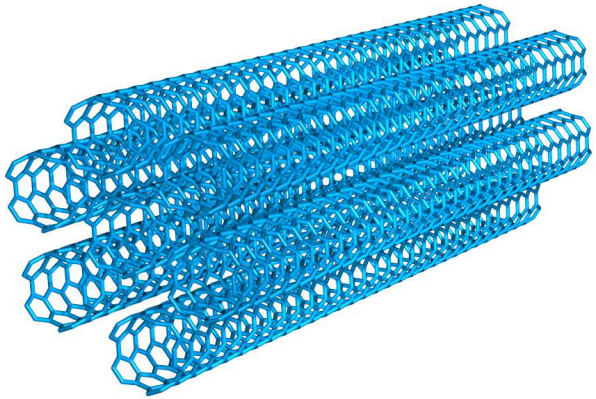
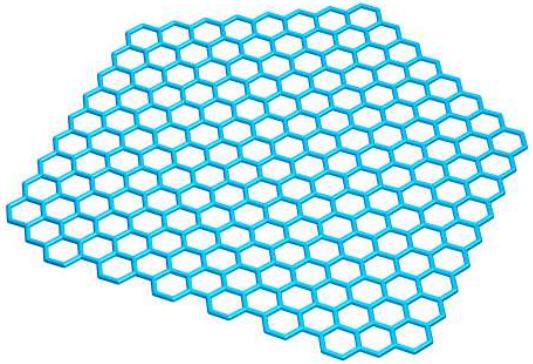
Skalierbare Oxo-Funktionalisierung von sp^2-hybridisierten Kohlenstoffallotropen

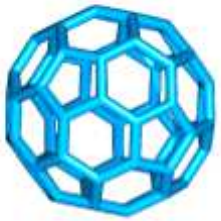




7. 11. 2014
Dr. Siegfried Eigler
Friedrich-Alexander-Universität Erlangen-Nürnberg

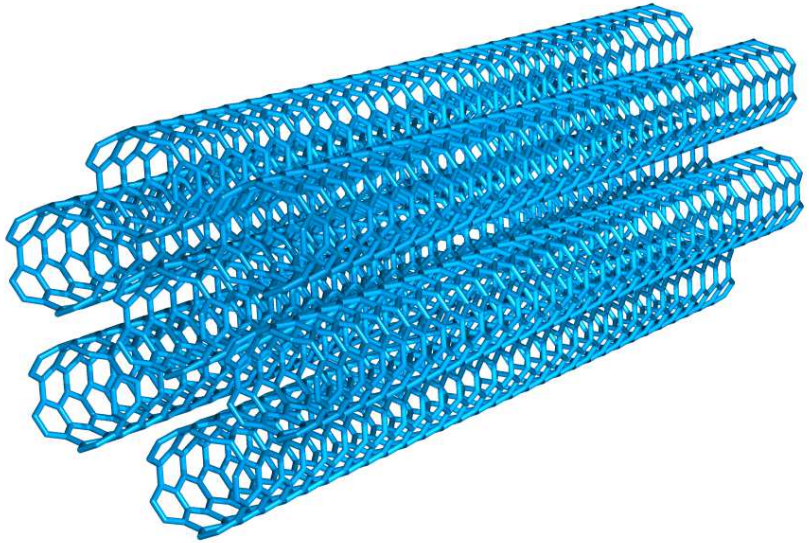
sp^2-Carbon Allotropes - Chemistry

sp^2-Carbon Allotropes:

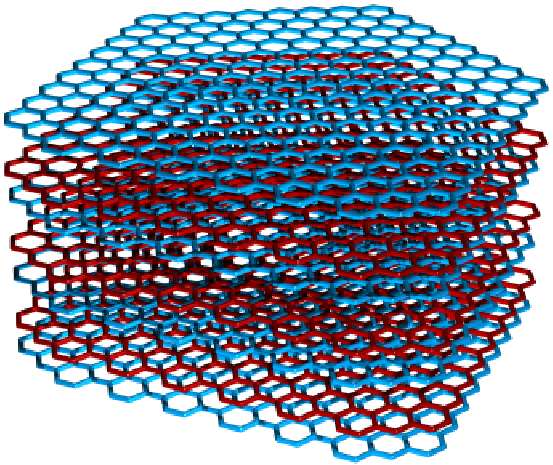


monodisperse

C_{60}



CNT



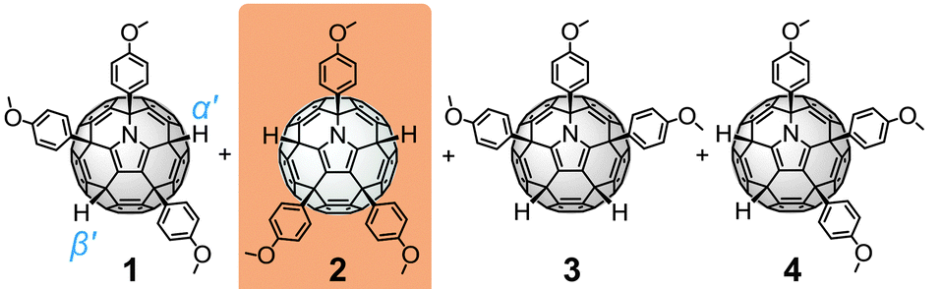
graphite

polydisperse

Monodisperse – $C_{59}N$

$C_{59}N$

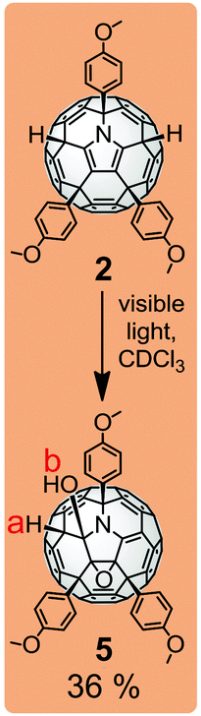
arylation (anisol)



Tris-aryl-di-hydro-aza-fullerene

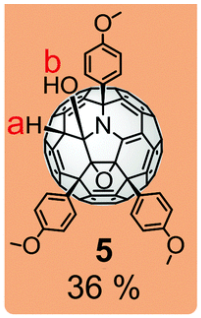
R. Neubauer *et al., Angew. Chem. Int. Ed.* **2012**, *51*, 11722; *Angew. Chem.* **2012**, *124*, 11892;
R. Eigler *et al.*, *Chem. Commun.* **2014**, *50*, 2021.

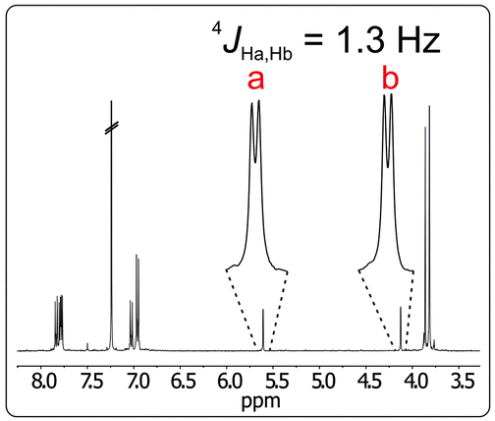
Monodisperse – $C_{59}N$



Oxidation: epoxy / hydroxyl

Exact regiochemistry evaluated

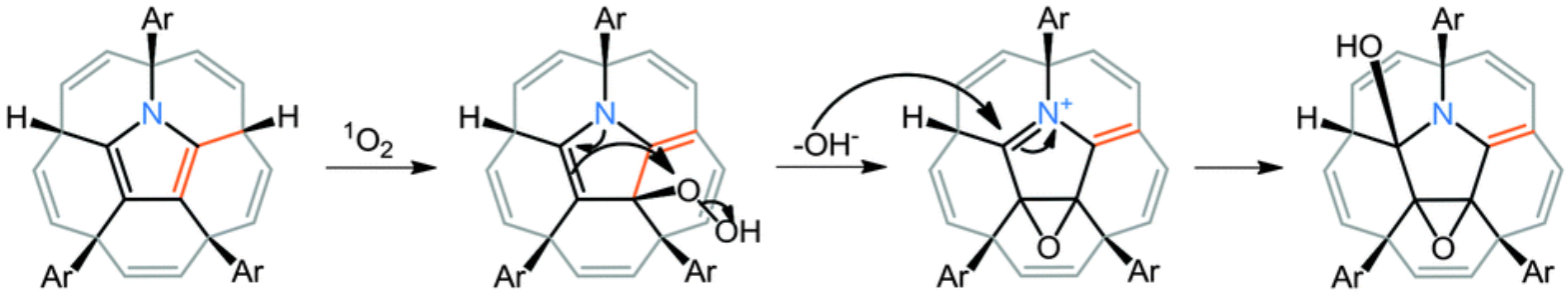




R. Neubauer *et al.*, *Angew. Chem. Int. Ed.* **2012**, *51*, 11722; *Angew. Chem.* **2012**, *124*, 11892;
R. Eigler *et al.*, *Chem. Commun.* **2014**, *50*, 2021.

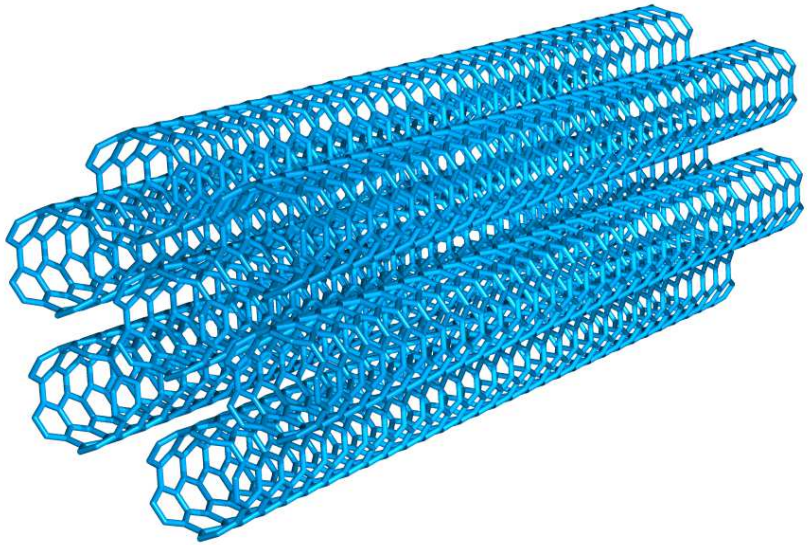
Monodisperse – $C_{59}N$

Proposed reaction mechanism:



R. Neubauer *et al.*, *Angew. Chem. Int. Ed.* **2012**, *51*, 11722; *Angew. Chem.* **2012**, *124*, 11892;
R. Eigler *et al.*, *Chem. Commun.* **2014**, *50*, 2021.

Novel Reaction Principle – SWCNTs

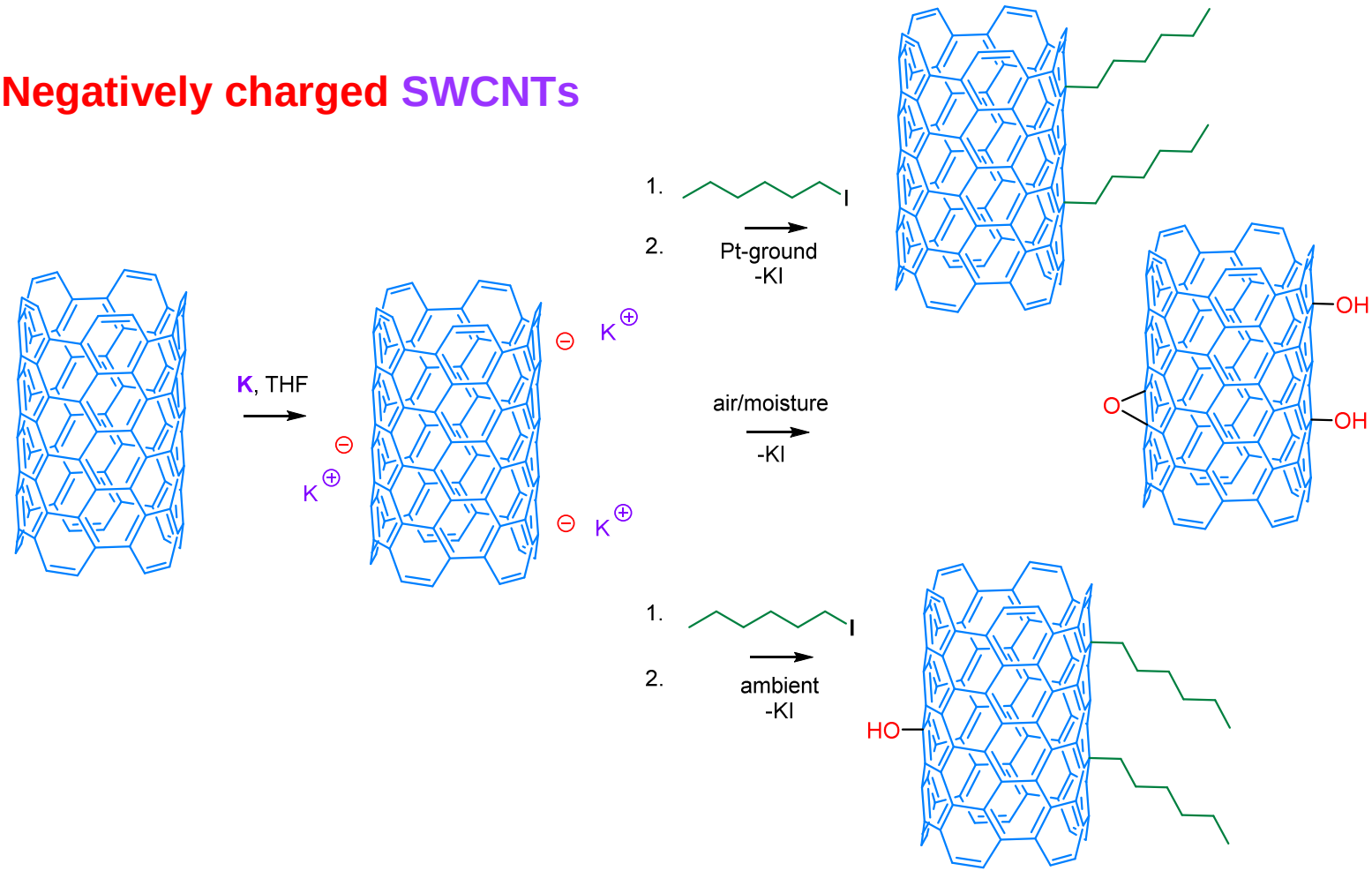


SWCNTs **polydisperse**

F. Hof, S. Bosch, S. Eigler, F. Hauke, A. Hirsch, *J. Am. Chem. Soc.* **2013**, *135*, 18385.

Novel Reaction Principle – SWCNTs

Negatively charged SWCNTs



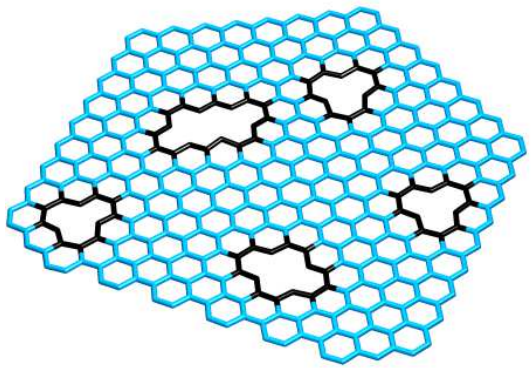
C/K:
degree of functionalization

Tunable: Properties of SWCNTs

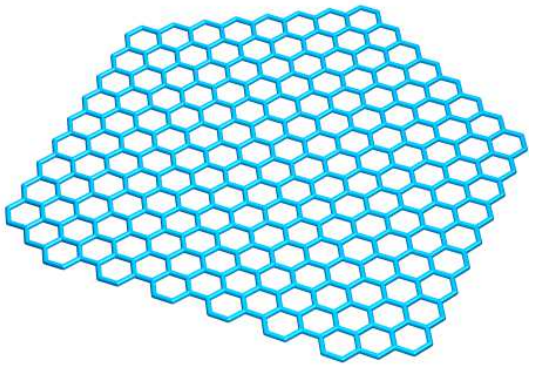
F. Hof, S. Bosch, S. Eigler, F. Hauke, A. Hirsch, *J. Am. Chem. Soc.* **2013**, *135*, 18385.

Defects

Carbon Framework in Graphene



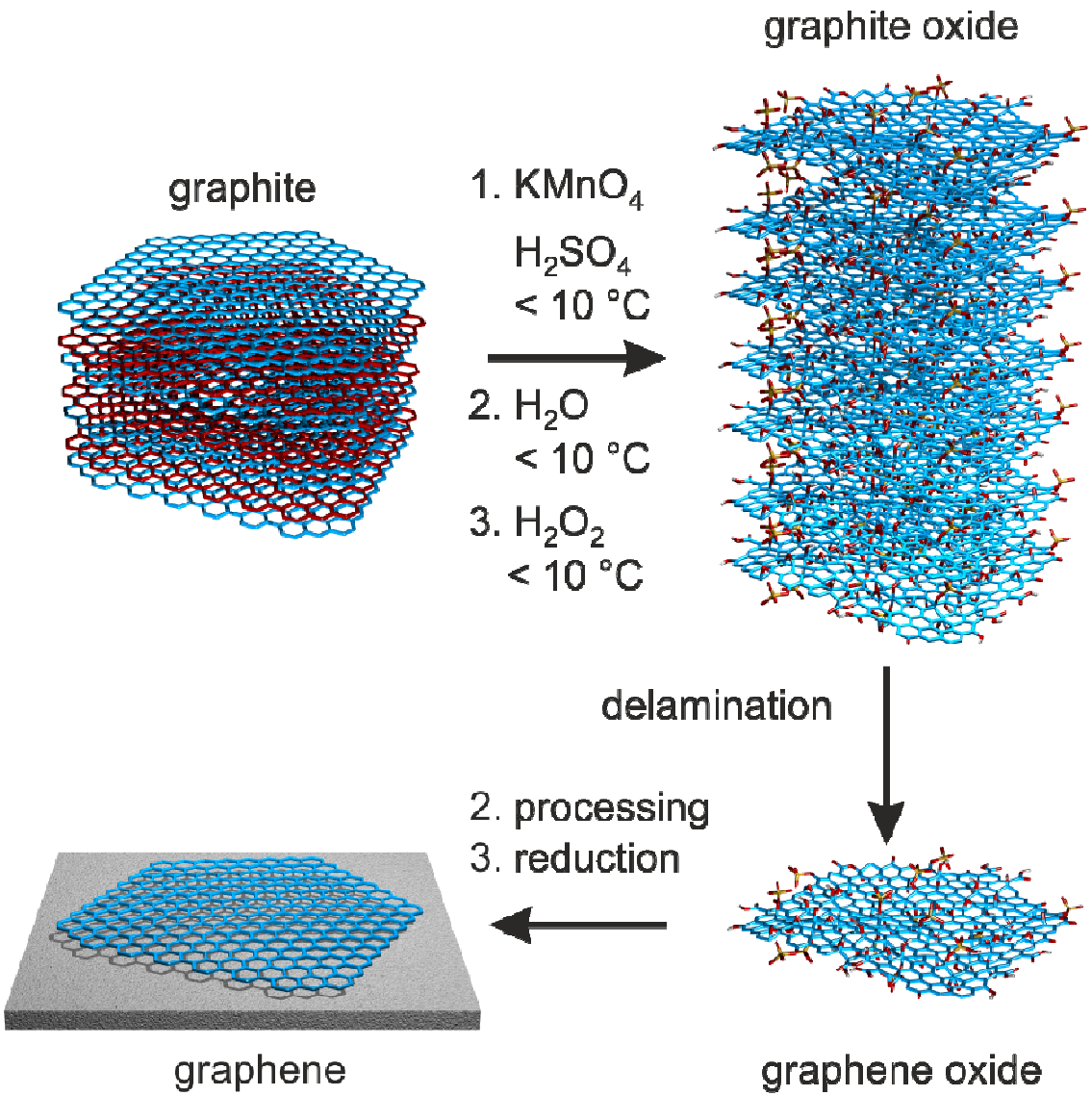
graphene with defects

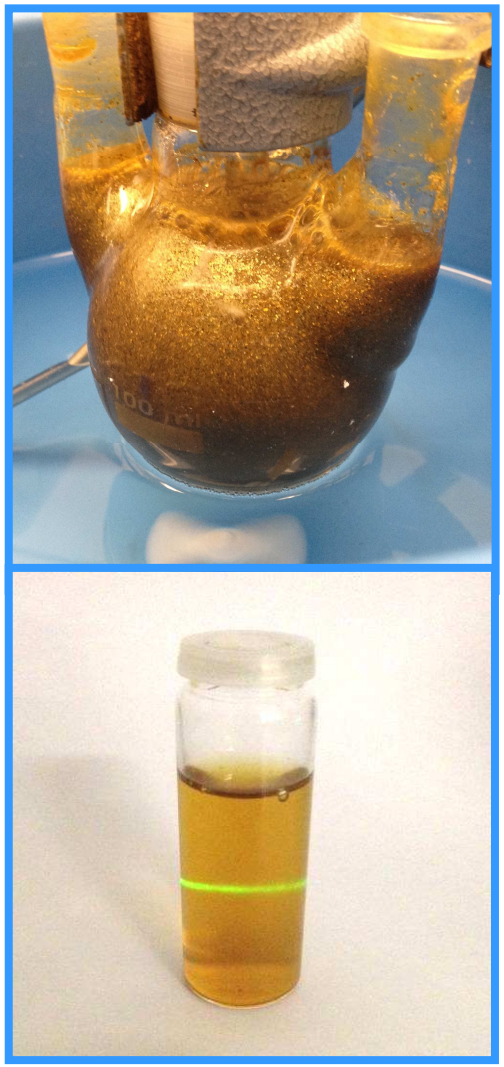


graphene without defects

S. Eigler *et al.*, *Adv. Mater.* **2013**, *25*, 3583; S. Eigler, A. Hirsch *Angew. Chem. Int. Ed.* **2014**, *43*, 7720.

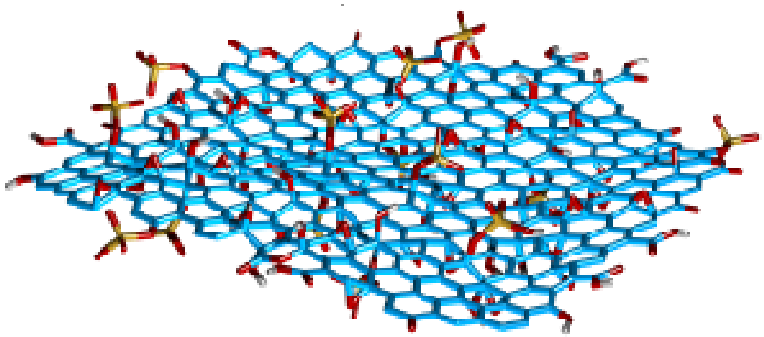
Synthesis of ai-GO: preventing CO_2 formation



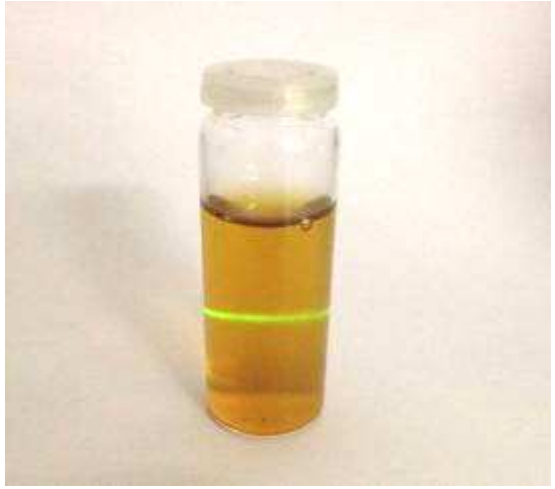


S. Eigler *et al.*, *Adv. Mater.* **2013**, *25*, 3583; S. Eigler, A. Hirsch *Angew. Chem. Int. Ed.* **2014**, *43*, 7720.

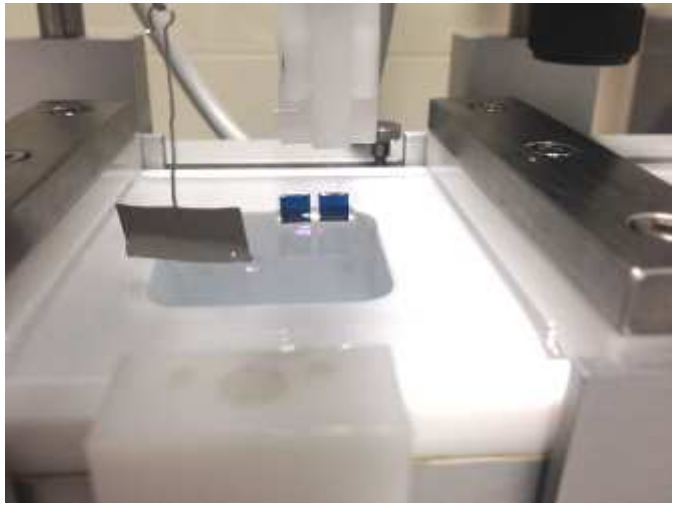
Ai-GO



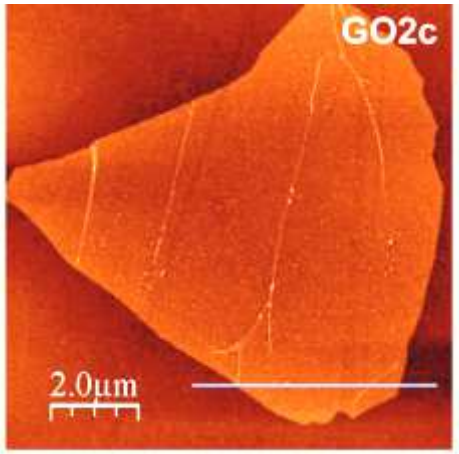
ai-GO dispersion:



Langmuir-Blodgett:



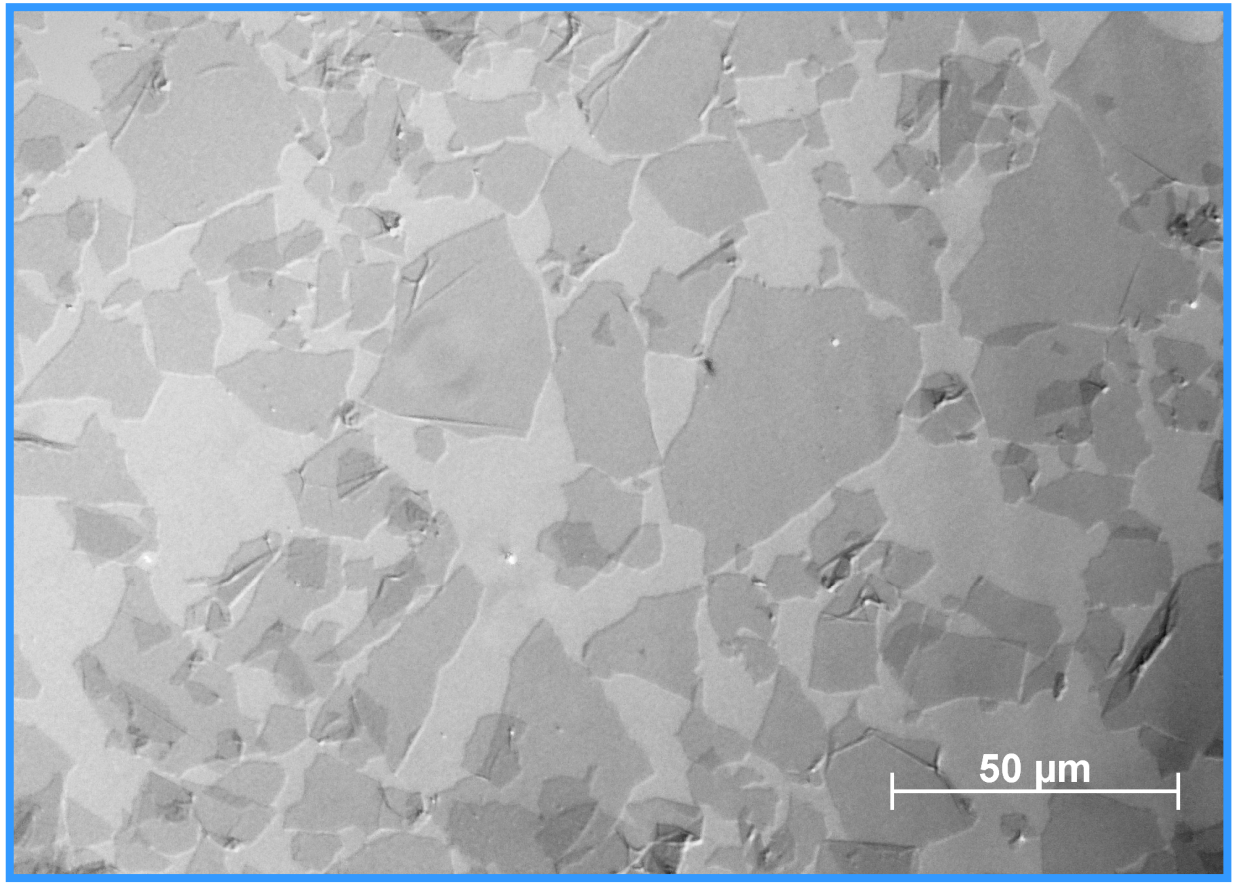
AFM



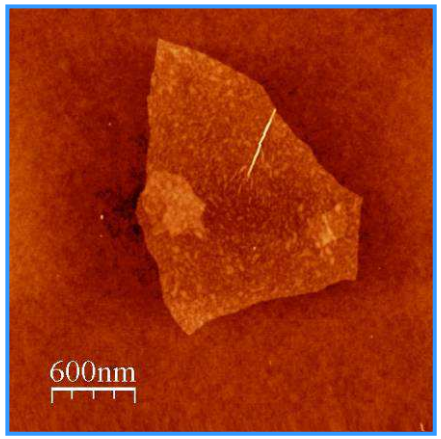
S. Eigler *et al.*, *Carbon* **2012**, *50*, 3666.

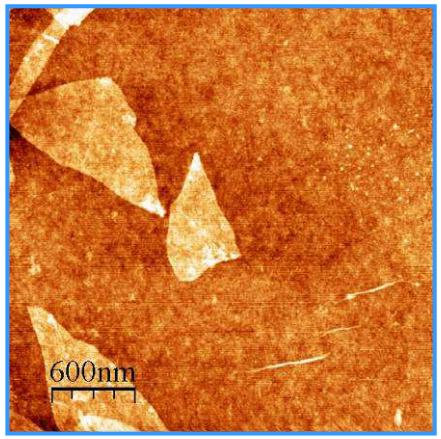
Size of flakes of ai-GO

Optical microscope image:



AFM images:

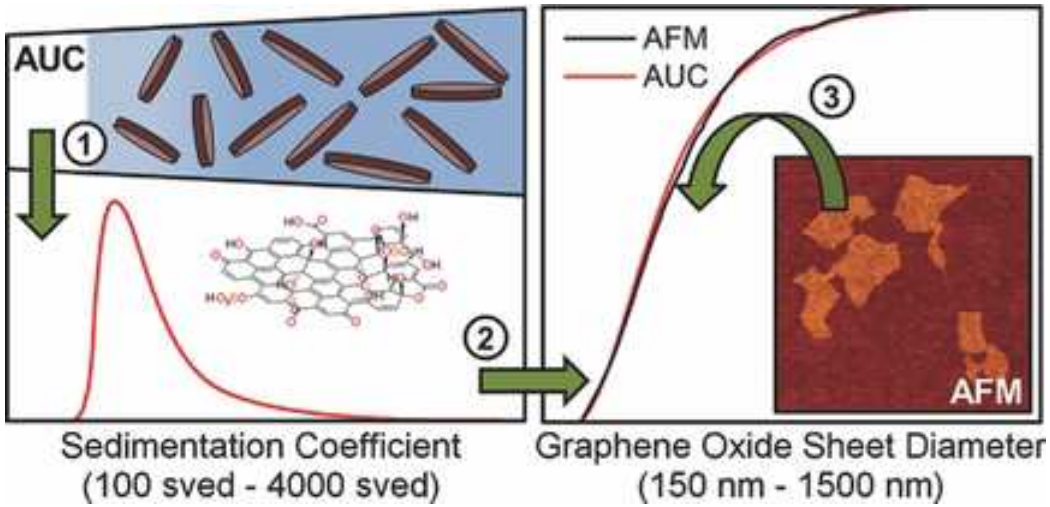


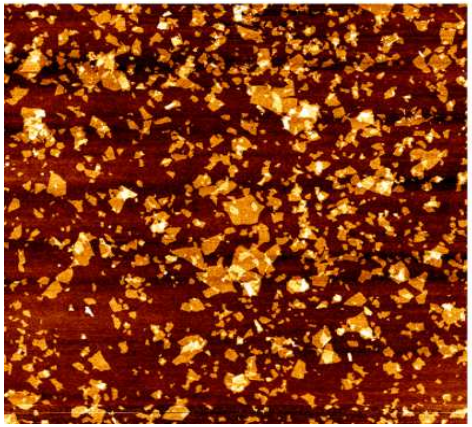


Particle Size – Processing Parameter

Collaboration: Prof. Peukert, Johannes Walter, Thomas J. Nacken

Model: relation – lateral dimension and gravity field





20 µm

Example: (15 min at 10 °C) average size of flakes: **10-30 µm**

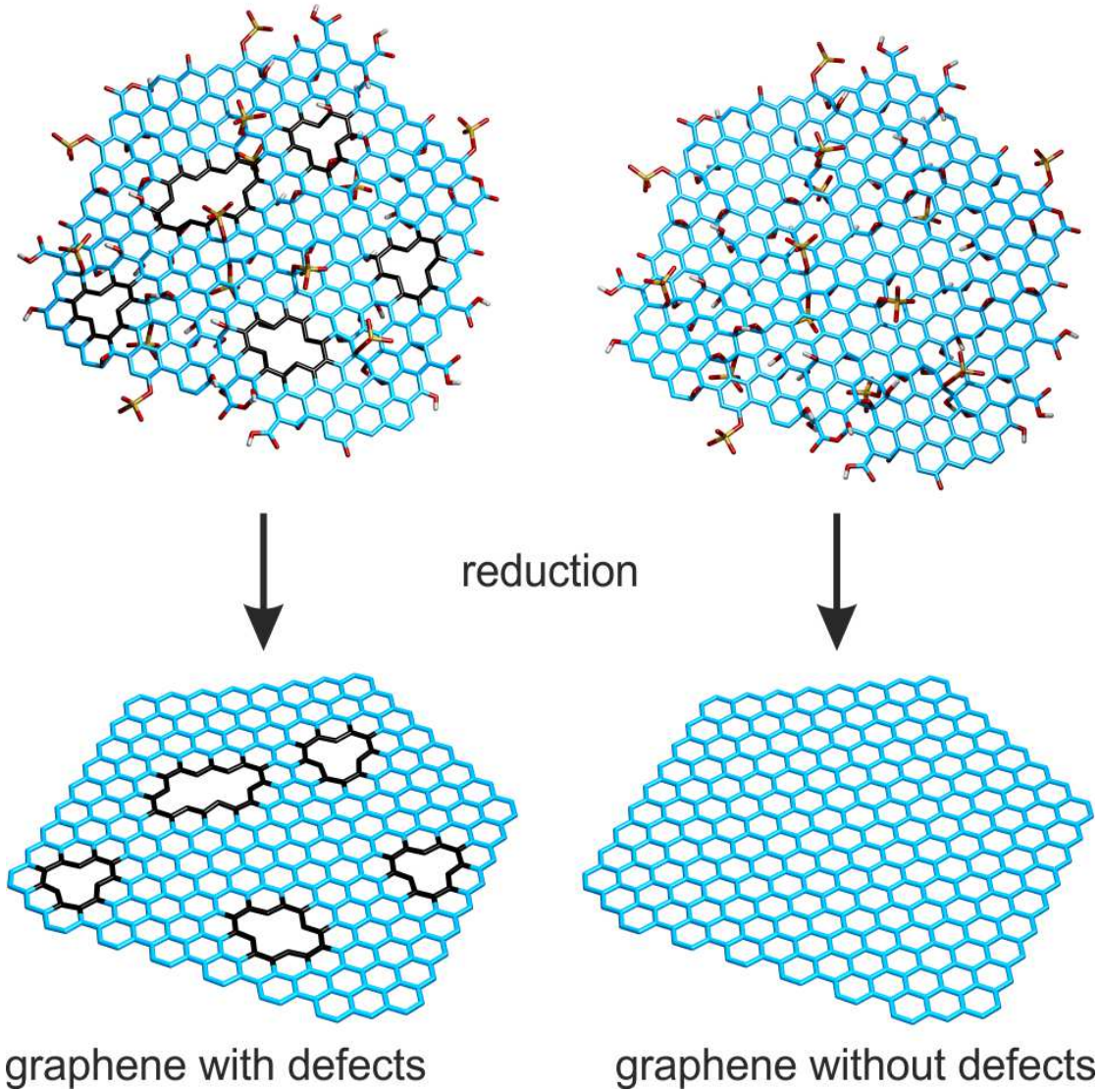
1. 7700 U/min
(removal of small flakes)

2. 4600 U/min
(removal of large particles)

Sorting flakes by size

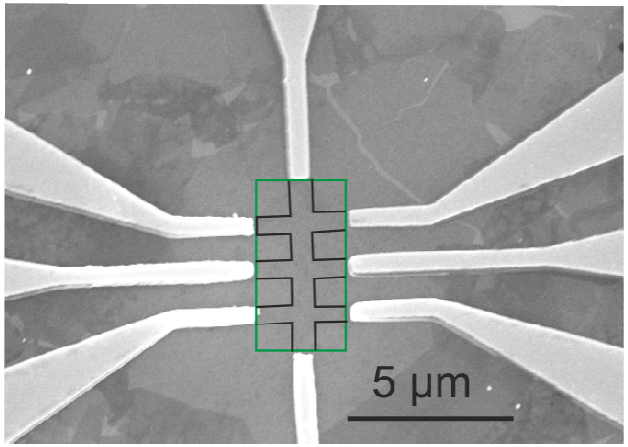
J. Walter *et al.*, *Small* **2014**, DOI:10.1002/smll.201401940.

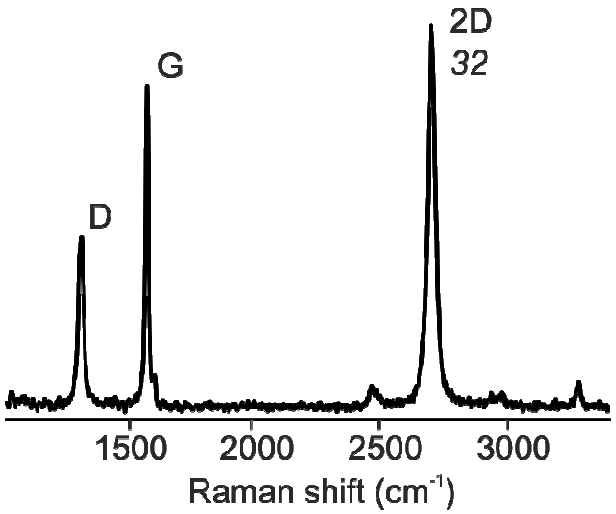
Graphene Oxide with Defects and Without Defects



S. Eigler *et al.*, *Adv. Mater.* **2013**, *25*, 3583; S. Eigler, A. Hirsch *Angew. Chem. Int. Ed.* **2014**, *43*, 7720;
S. Eigler, *Phys. Chem. Chem. Phys.* **2014**, *16*, 19832.

Electrical Properties of graphene from ai-GO





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

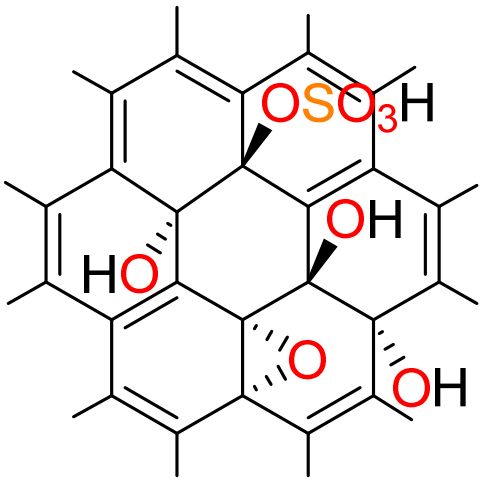
Physical measurements confirm 2D nature of graphene

Flakes defect density of about **0.01%:** **μ = 2000 cm²/Vs**
defect density **about 0.3%:** **μ = 250 cm²/Vs**

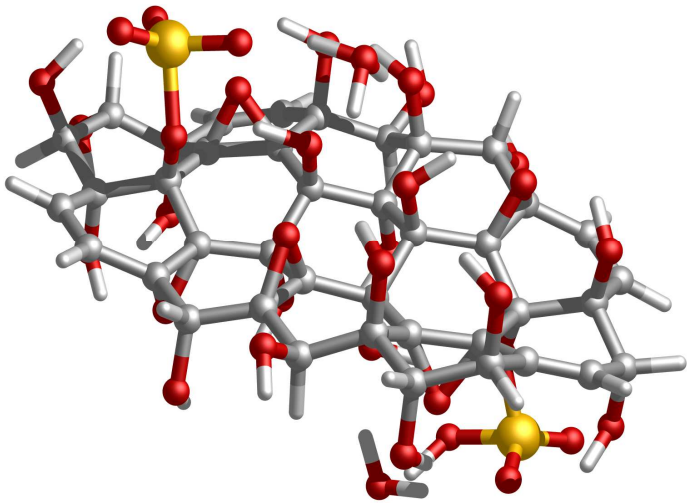
Reference from literature (defect density several %): **μ = 0.1-10 cm²/Vs**

S. Eigler *et al.*, *Adv. Mater.* **2013**, *25*, 3583.

Structure of ai-GO



ai-GO



Regiochemistry not known to date

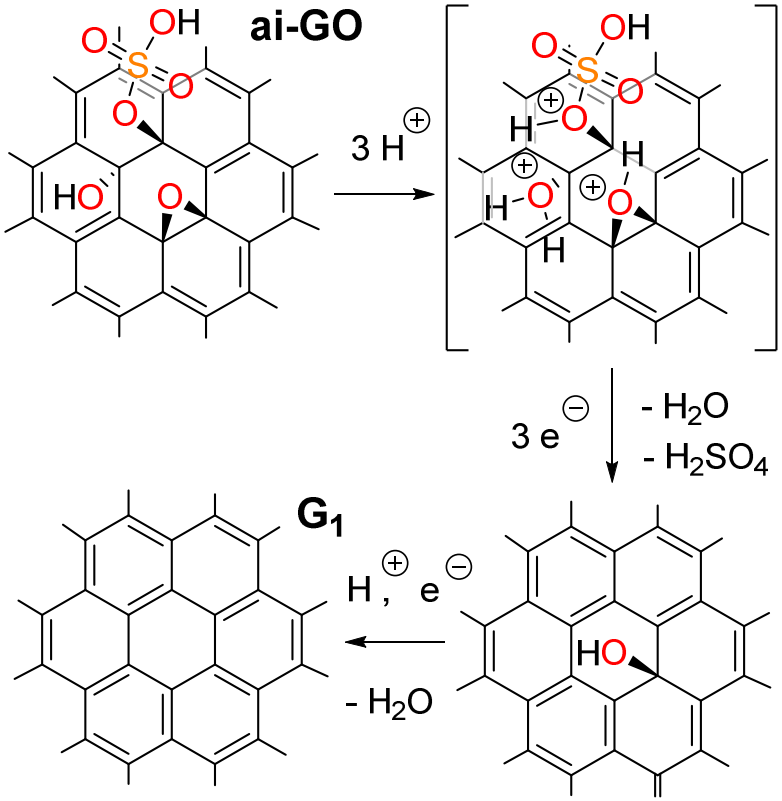
Both sides of basal plane:

Hydroxyl groups
Epoxy groups
Organosulfate groups

S. Eigler *et al.*, *Chem. Eur. J.* **2013**, *19*, 9490.

Reduction of Film of Flakes of ai-GO

$$2\,HI \longrightarrow I_2 + 2\,e^{\ominus} + 2\,H^{\oplus}$$

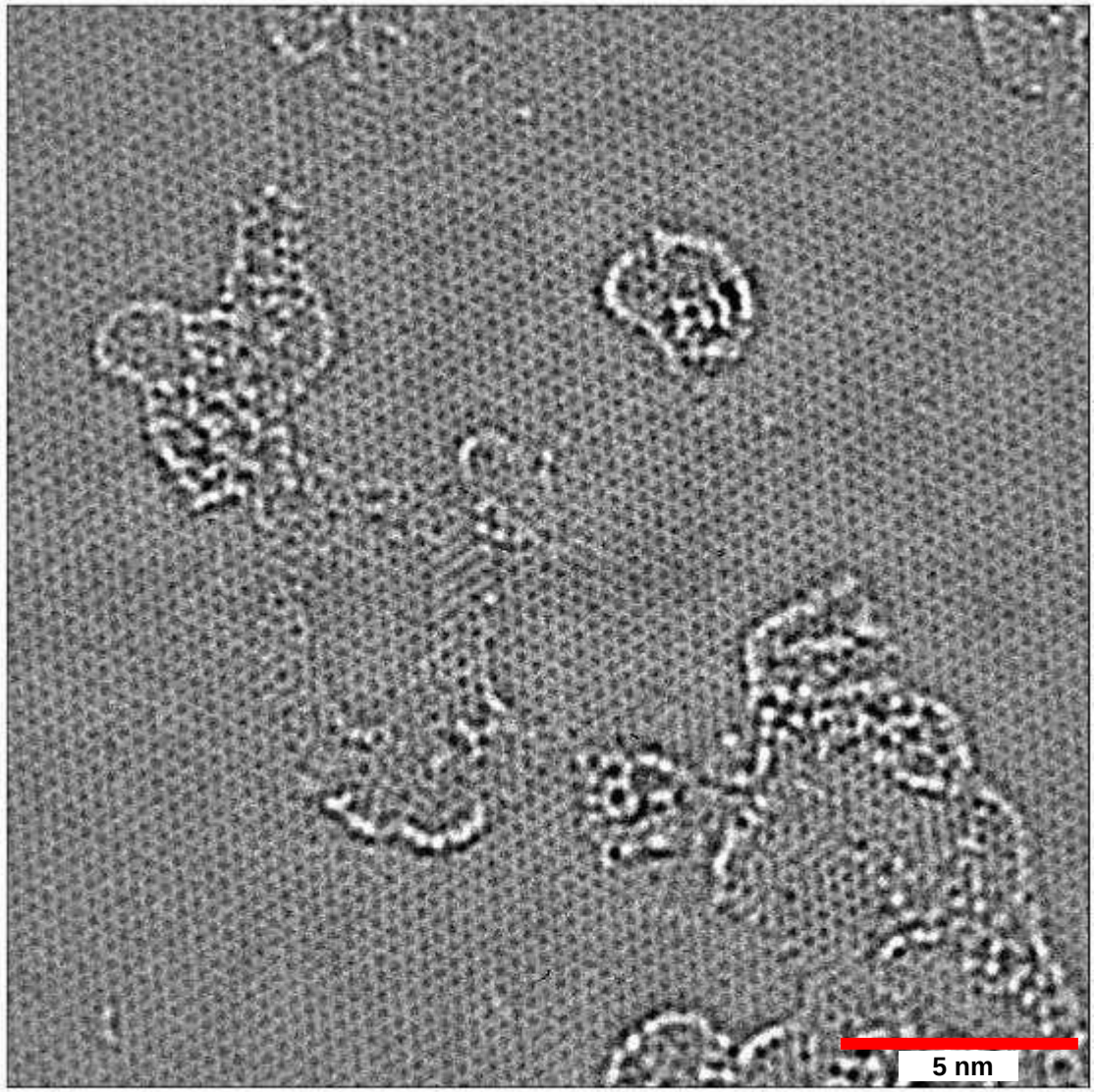


Current process: average density of defects: 0.3% and 10-30 µm flakes

S. Eigler *et al.*, *Chem. Commun.* **2013**, *49*, 7391; S. Eigler *et al.*, *J. Phys. Chem. C* **2014**, *118*, 7698; S. Eigler, *Phys. Chem. Chem. Phys.* **2014**, *118*, 19832.

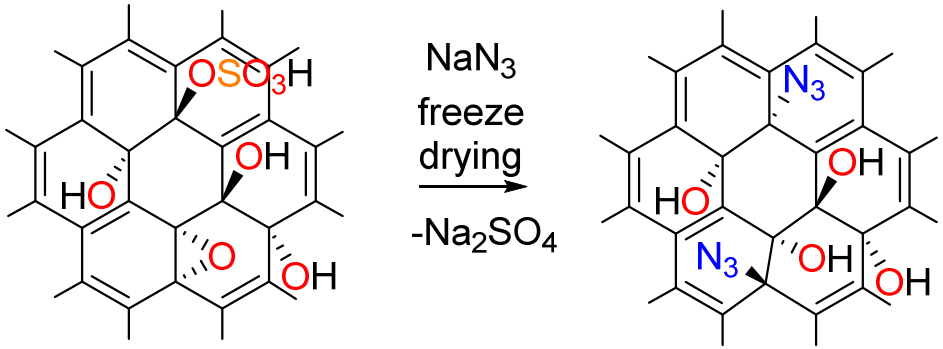
Graphene from ai-GO

HRTEM image of GO, *in situ* reduced: (Prof. Spiecker / Dr. Butz, Erlangen)

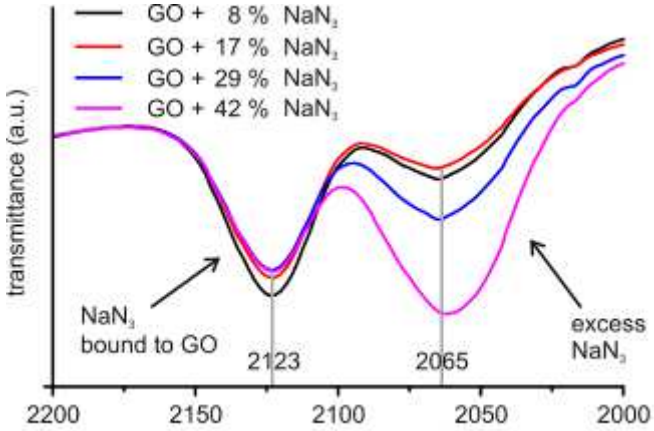


www.fei.com (TITAN-HRTEM)

Functionalization of ai-GO with NaN_3



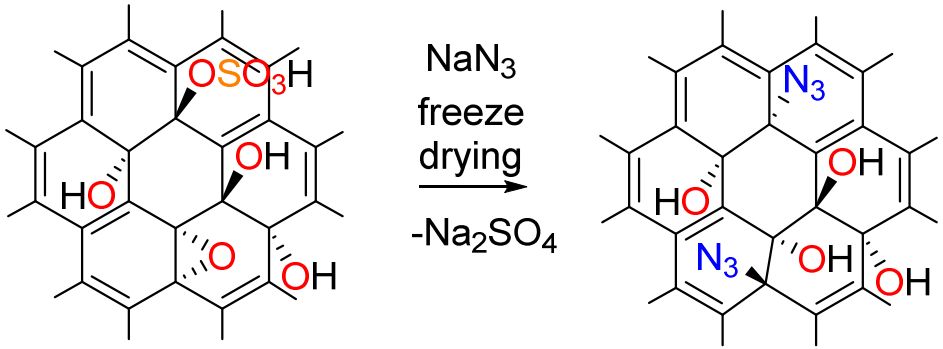
ZnSe-window:



Reaction occurs in solids

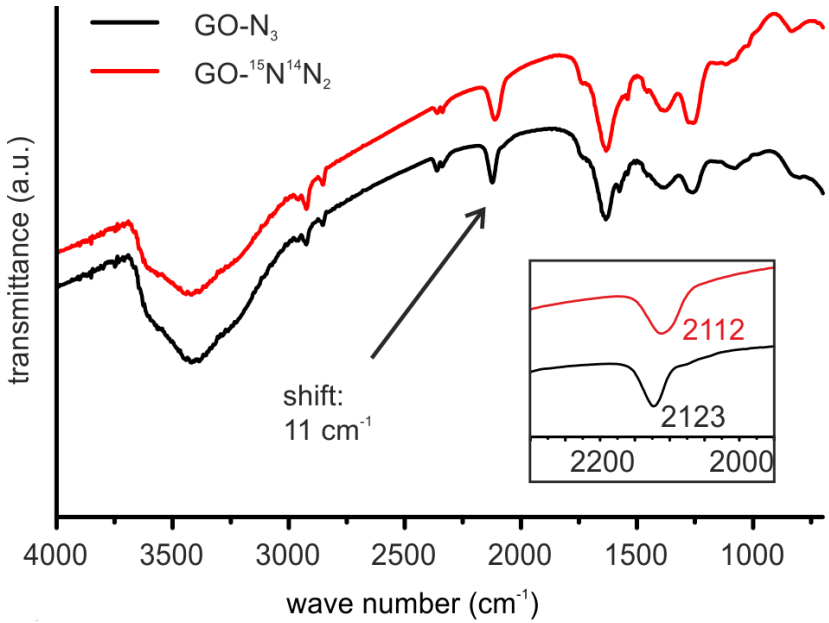
S. Eigler *et al.*, *Nanoscale* **2013**, *5*, 12136.

Functionalization of ai-GO with NaN_3

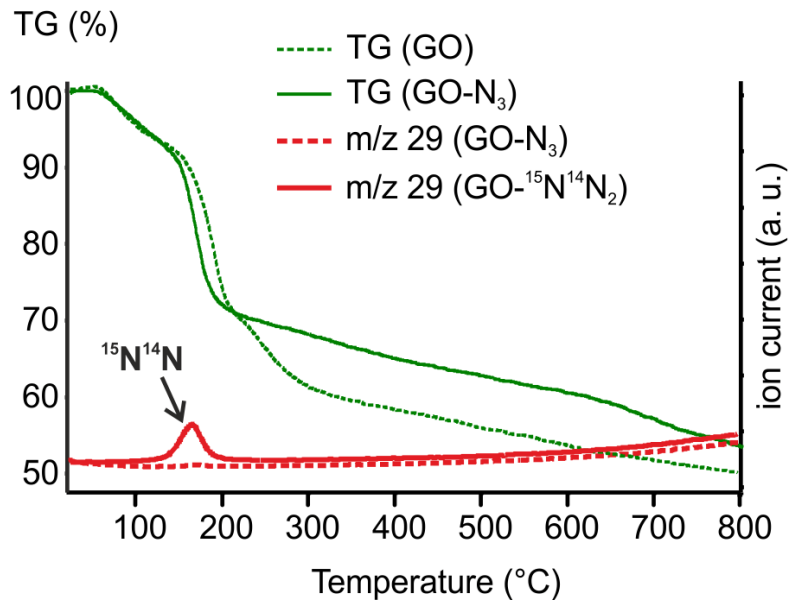


Analysis with ^{15}N labeled azide:

FTIR:

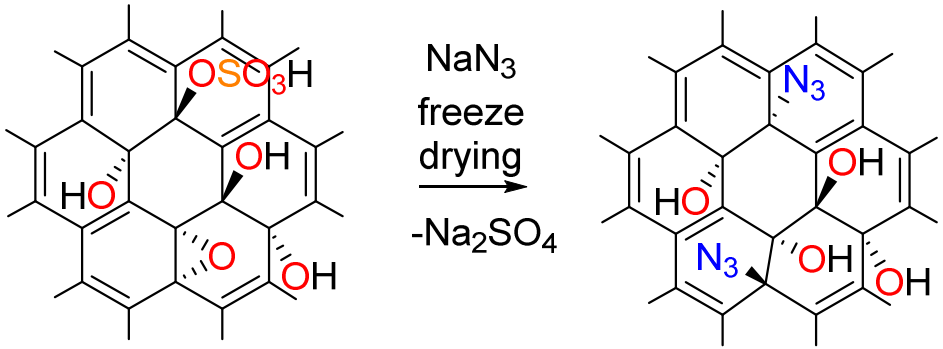


TGA - MS:



S. Eigler *et al.*, *Nanoscale* **2013**, *5*, 12136.

Functionalization of ai-GO with NaN_3



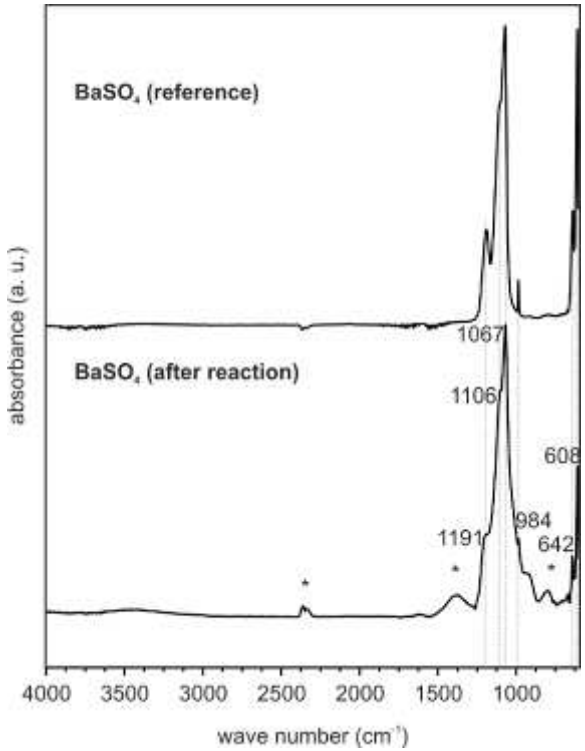
Analysis of supernatant after centrifugation:

$$Ba^{2+} + SO_4^{2-} \xrightarrow{HCl} BaSO_4 \downarrow$$

Purified ai-GO: no sulfate found in supernatant

Re-dispersed ai-GO-N_3: $BaSO_4$ precipitate found

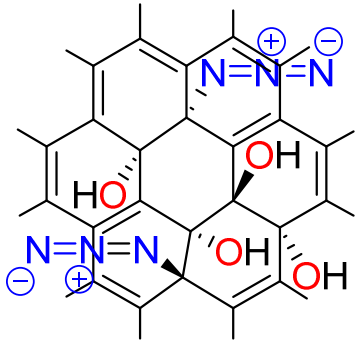
Organosulfate acts as leaving group



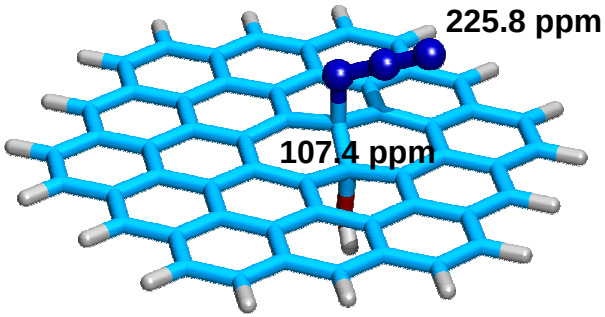
S. Eigler *et al.*, *Nanoscale* **2013**, *5*, 12136.

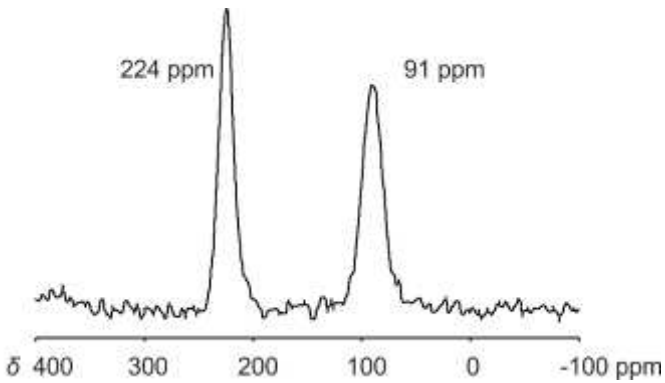
Functionalization of ai-GO with NaN_3

Evaluation of the chemical structure:

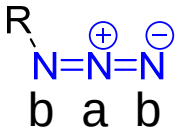


solid state ^{15}N NMR: (Prof. Ishii, Chicago)

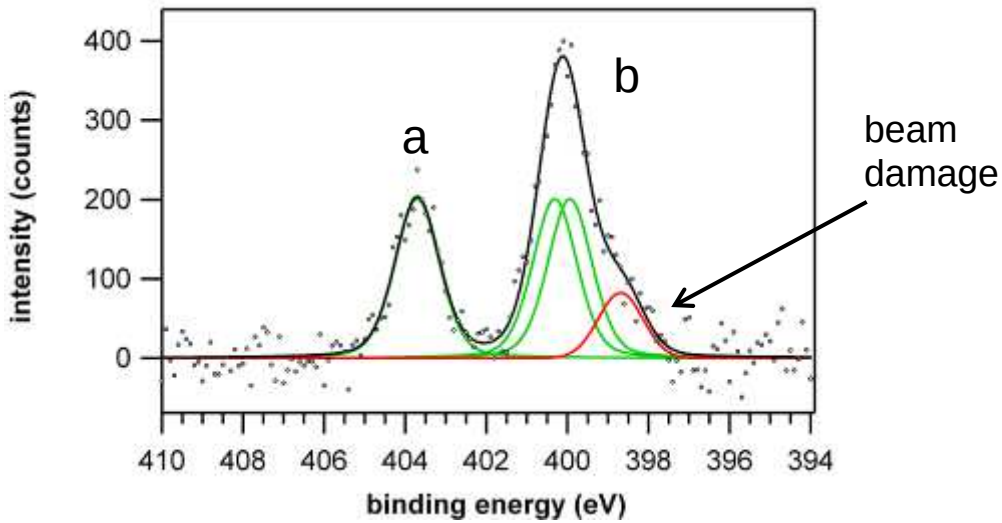




XPS: (Prof. Steinrück / Dr. Papp, Erlangen)



Shifts comparable to other organic azides:
J. Am. Chem. Soc. **1994**, *116*, 4395.



Geometry: B3LYP/6-31G(d)
Chemical shielding tensors: GIAO with BPW91/6-311+G(d) (calibrated method)

S. Eigler *et al.*, *Nanoscale* **2013**, *5*, 12136.

Oxo-functionalized Graphene

Basis for controlled synthesis of graphene architectures

- ai-GO with few defects (average 0.3%)
- *Carbon framework stable up to 100 °C*
- *Carbon framework stable for functionalization*
- Organosulfate groups used for functionalization

Graphene oxide: Collective term for various oxo-functionalized graphene derivatives with a variable density of defects

Acknowledgement

Financial support: since 2014: DFG (EI-938);
Mentors: Prof. Hirsch, Prof. Steinrück, Prof. Halik

Co-workers:
Stefan Grimm, Philipp Rietsch, Christian Halbig
Prof. Hirsch group member: Regina Eigler, Ferdinand Hof

Devices:
Dr. Michael Enzelberger-Heim
Philipp Hofmann
Dr. Wolfgang Kroener
Prof. Paul Müller

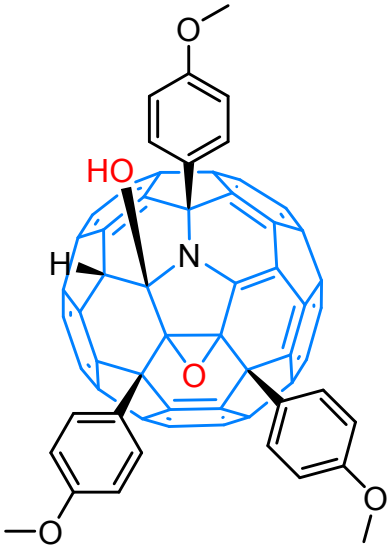
XPS:
Michael Röckert
Dr. Jie Xiao
Dr. Christian Papp
Dr. Ole Lytken
Prof. Hans-Peter Steinrück

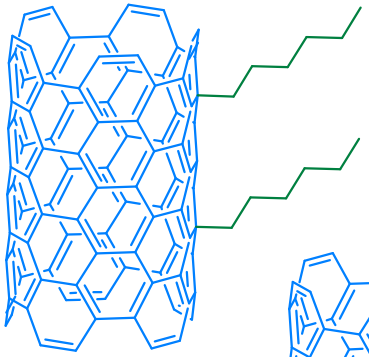
ssNMR:
Yichen Hu
Prof. Ishii
Prof. Walter Bauer

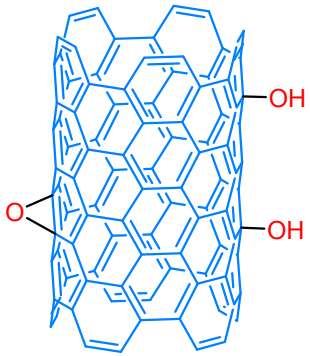
Devices self assambled:
Dr. Zhenxing Wang
Prof. Halik

HRTEM:
Dr. Benjamin Butz
Christian Dolle
Prof. Spiecker

Particle size:
Johannes Walter,
Thomas J. Nacken,
Cornelia Damm,
Thaseem Thajudeen,
Prof. Peukert







Thanks for your kind attention