Aalto University
School of Science

Lecture 2:
Materials at the atomic scale

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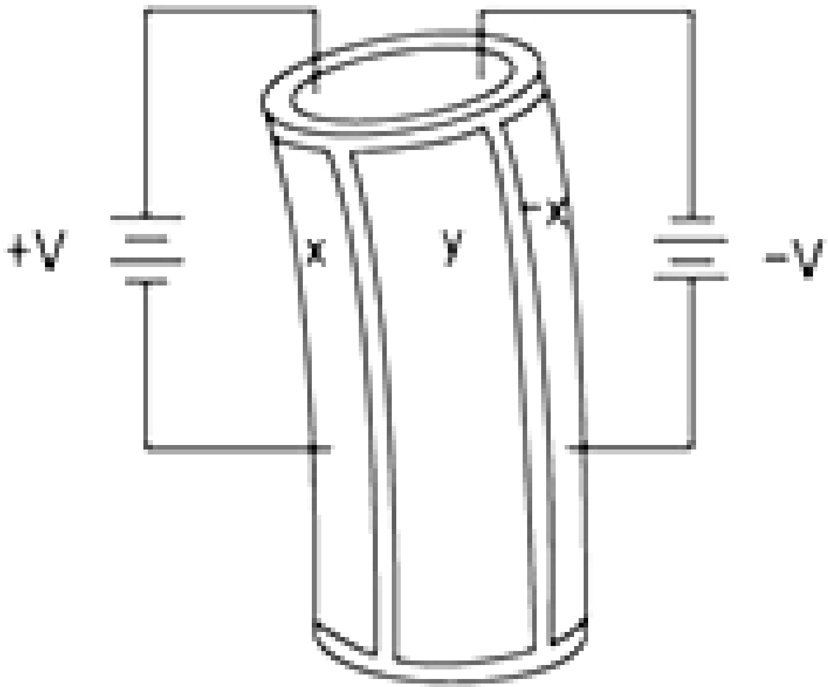
Physical requirements

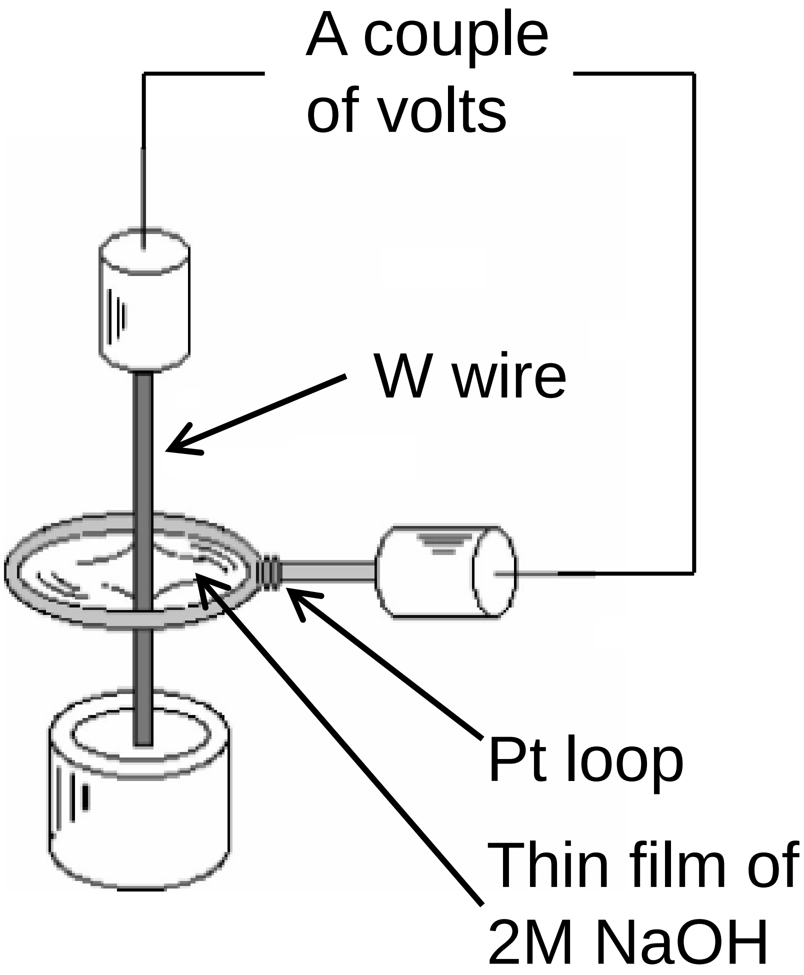
- Precise positioning
  - piezoelectric elements
- Sharp tip
  - STM tip etching or cutting
  - AFM micromachined tips
- Vibration isolation
  - rigid design
  - eddy-current damping
- ambient or UHV

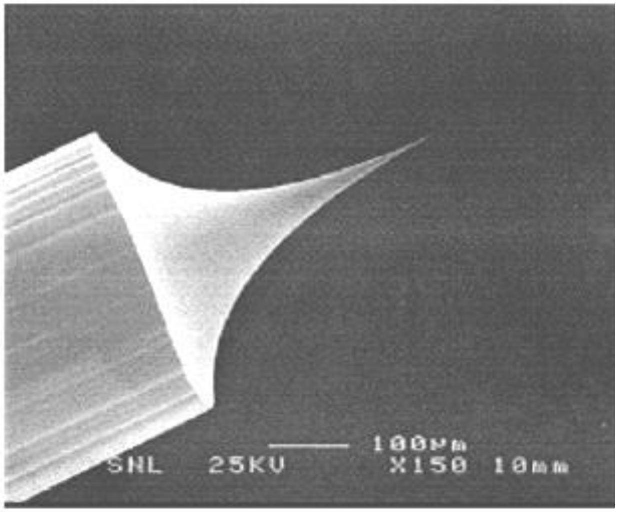
Scanner construction

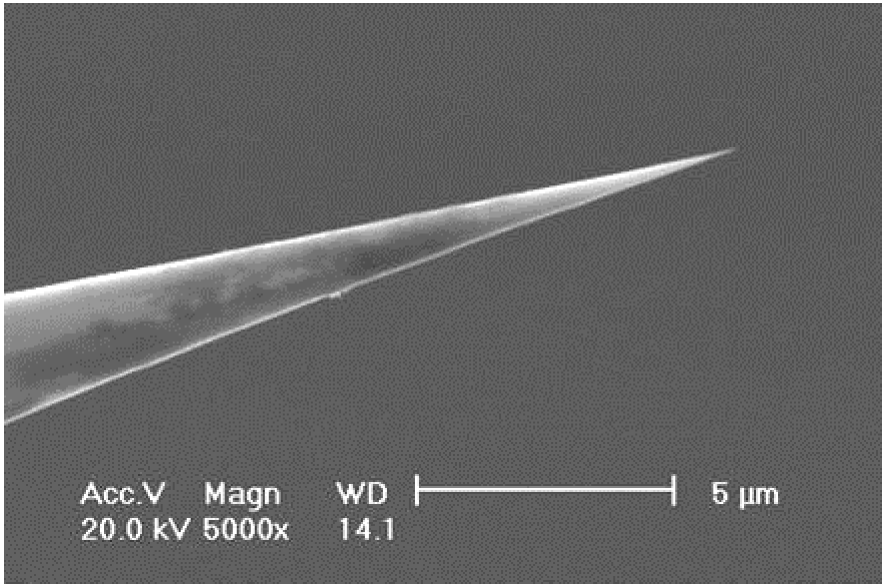
- Piezoelectricity: external voltage will make a crystal expand or contract
- Tube scanner with piezoelectric elements enable positioning with subatomic (picometre) precision
- either tip or sample is scanned



Tip preparation for STM

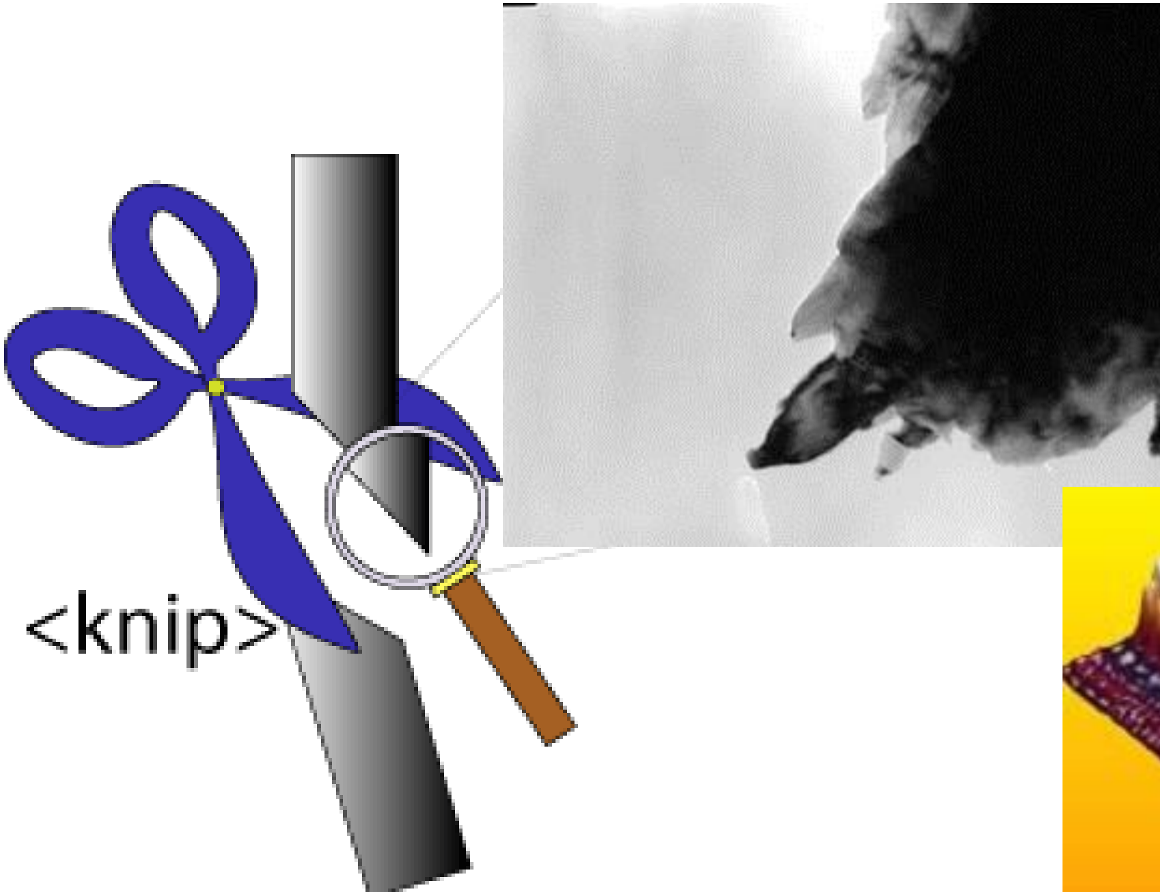


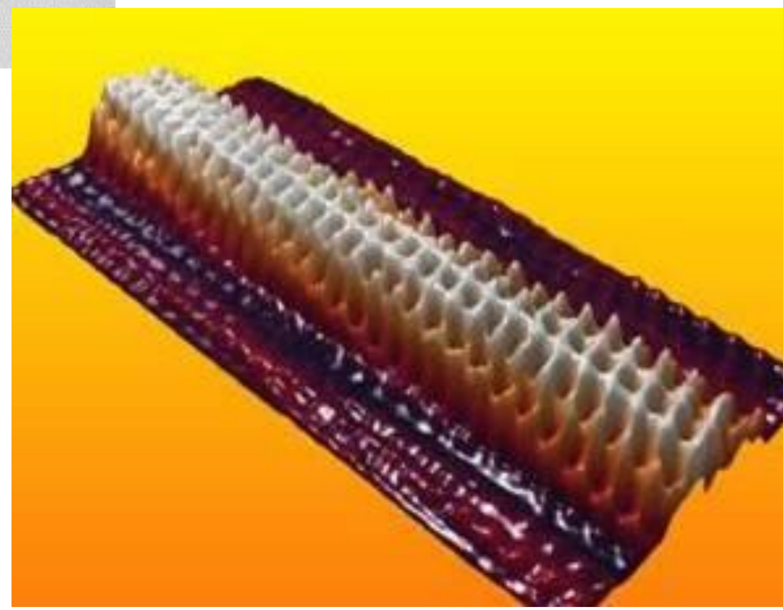




Tungsten not suitable for ambient due to oxidation

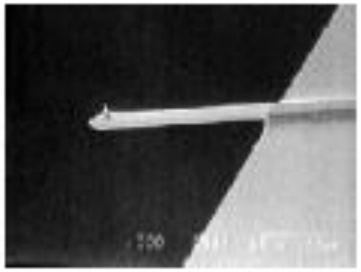
Alternatively; cut Pt/Ir tips

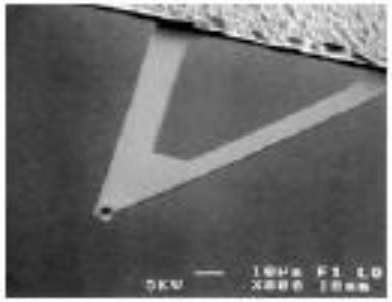


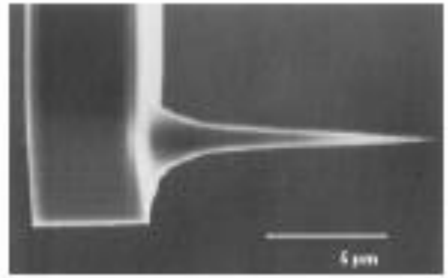


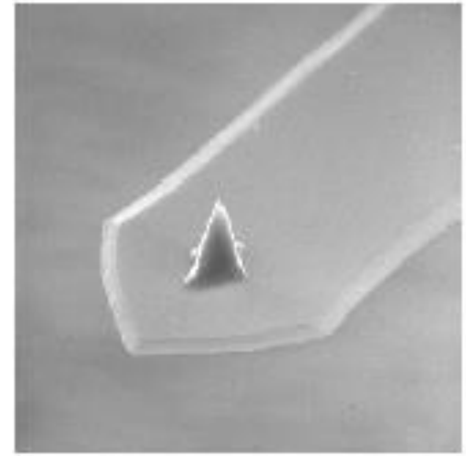
Two-dimensional imaging of electronic wavefunctions in carbon nanotubes, *Nature*, **2001**

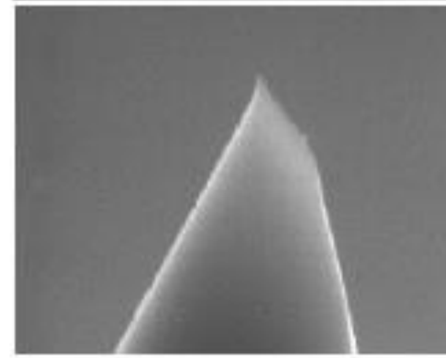
AFM tips



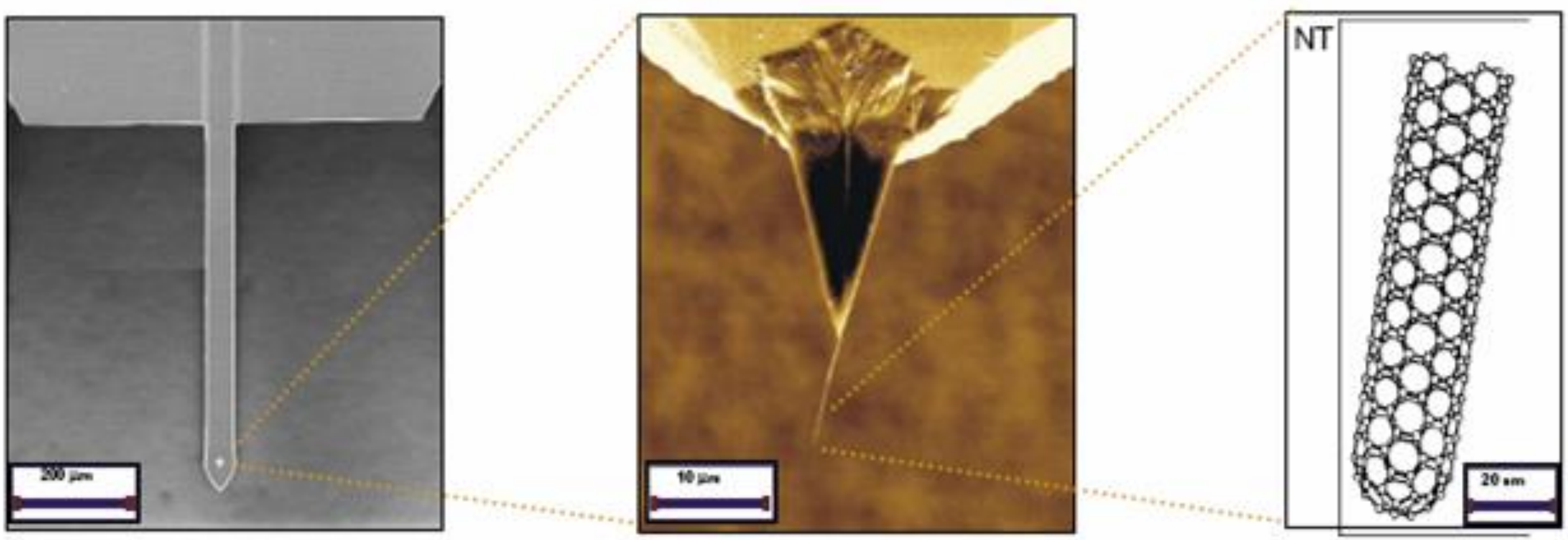




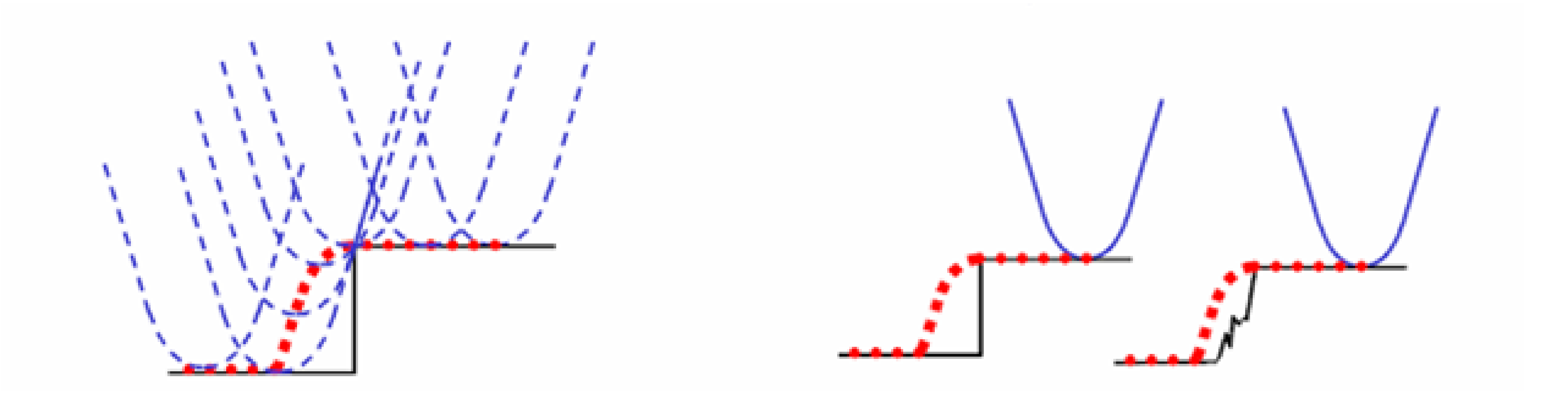


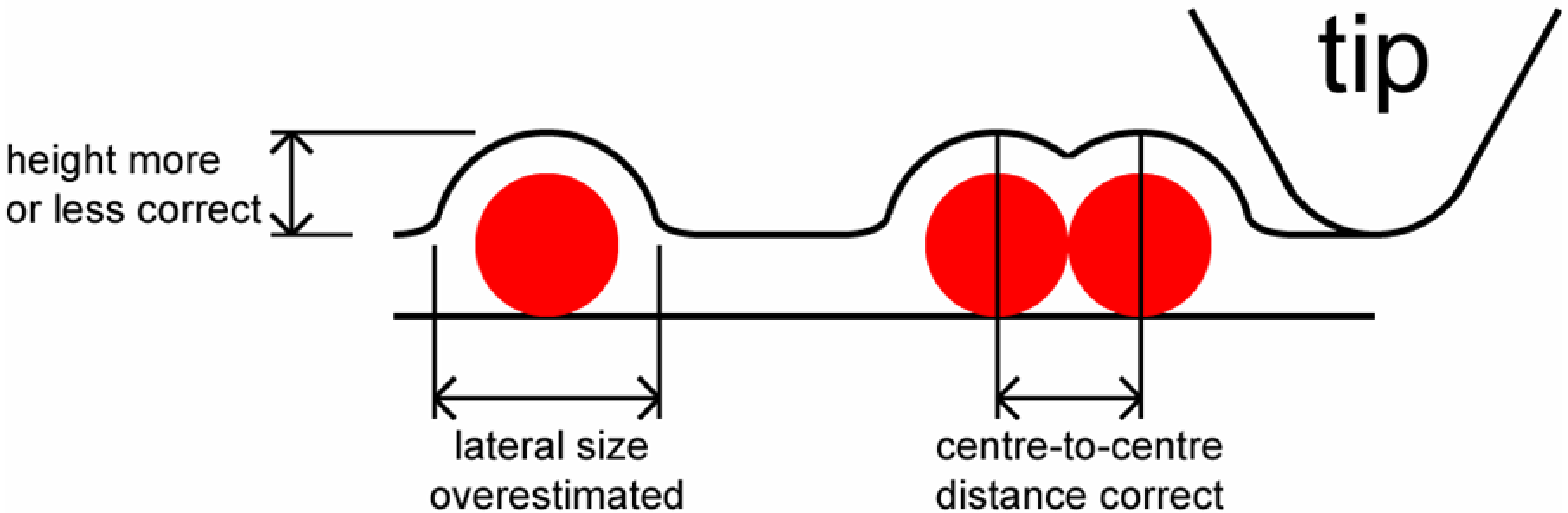


R > 2 nm
Q: 100s to 100s of thousands
k: 0.01 – 1000 N/m
f_0: 10-100s kHz



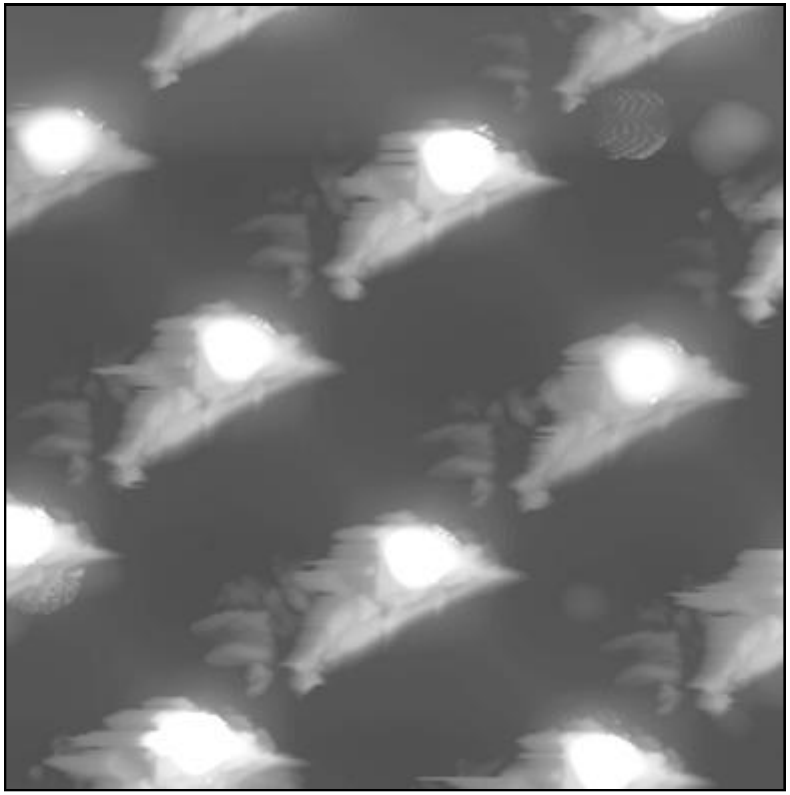
tip-size effects: convolution



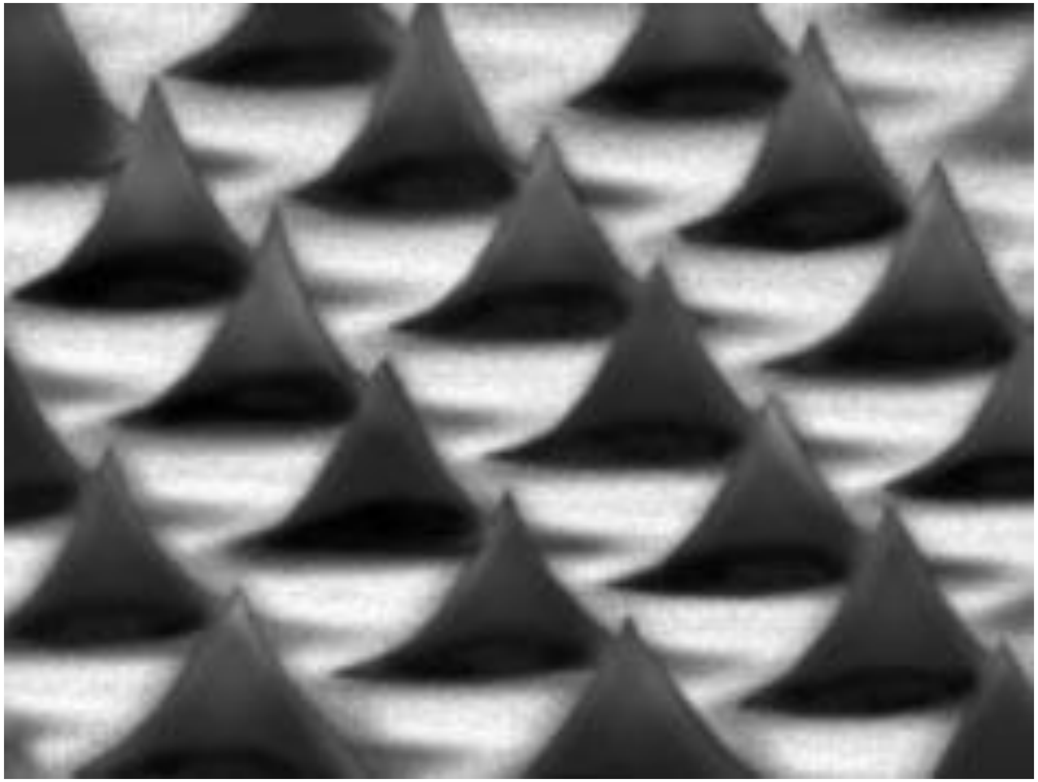


tip artefacts

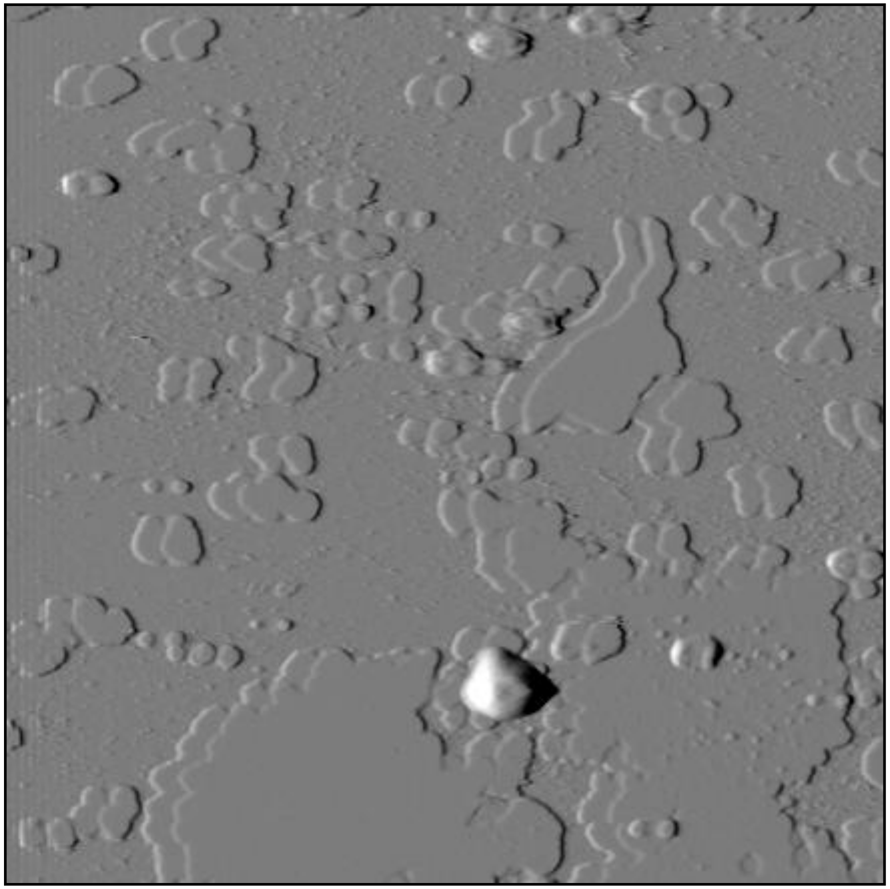
AFM image

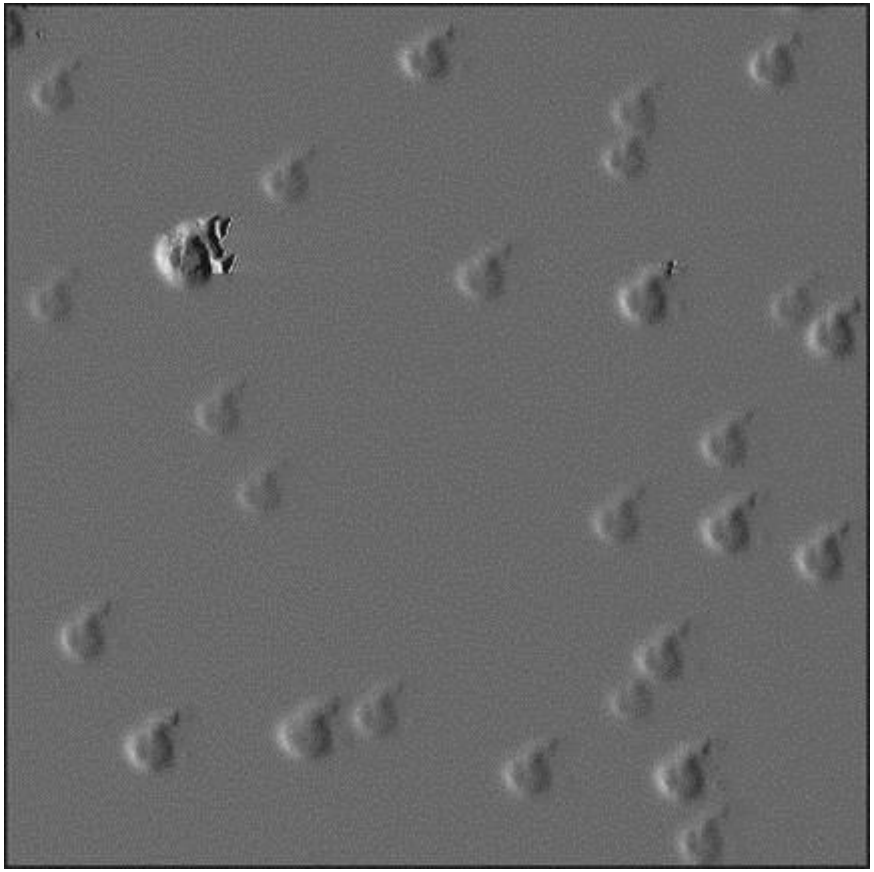


SEM image



More AFM images with a shapy tip

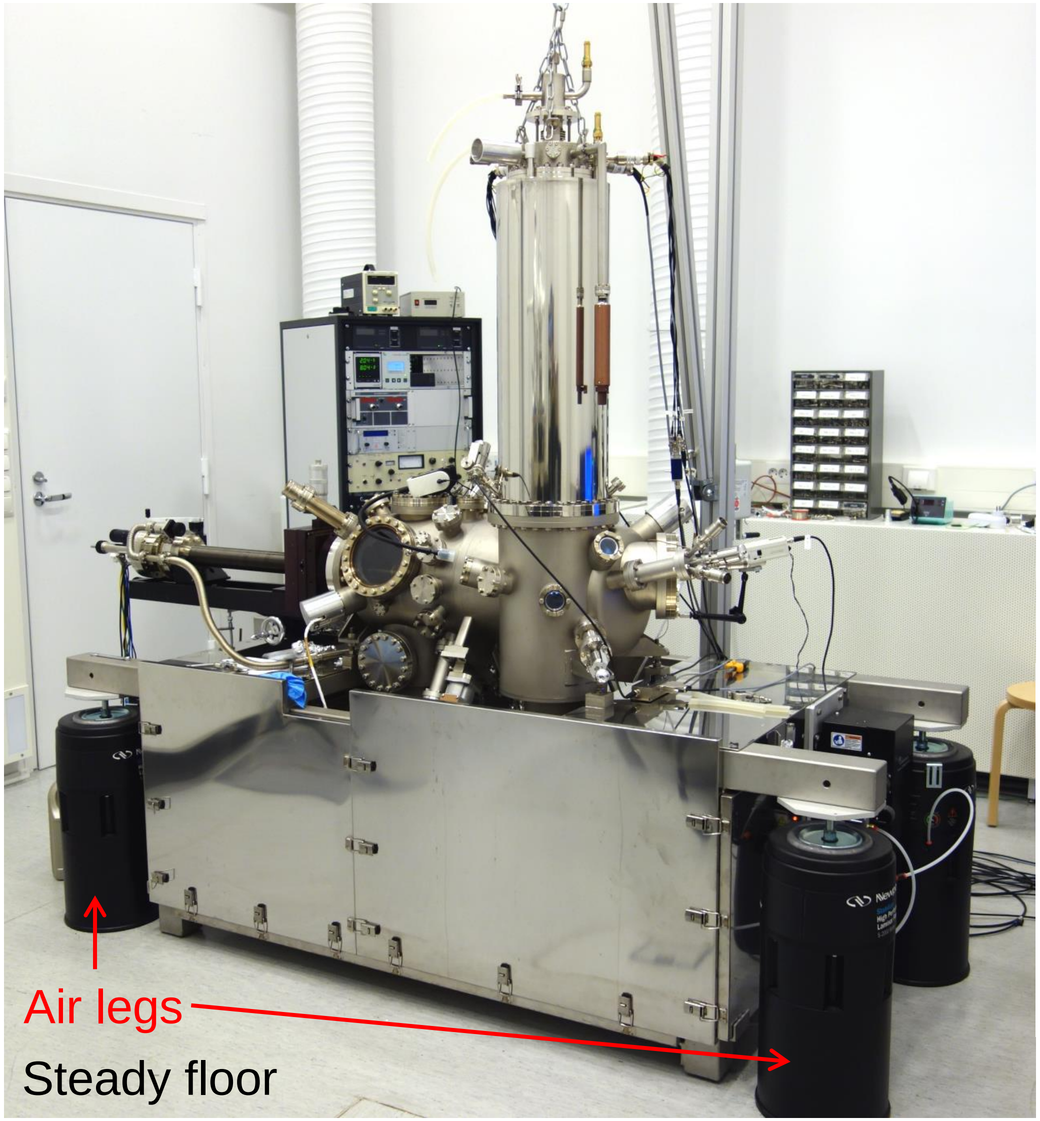


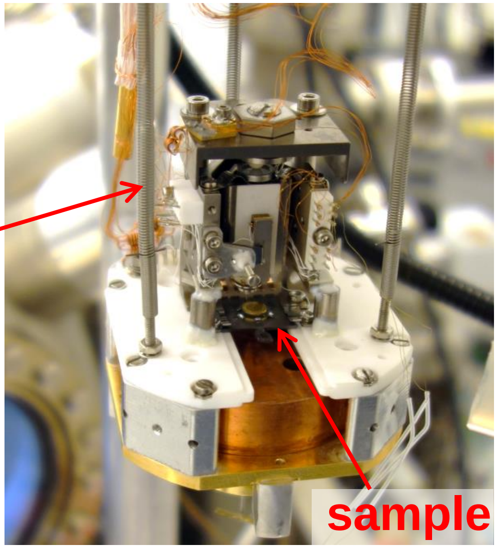


Reminder:

- All experiments carried out in ultra-high vacuum (10^{-10} mbar) and low-temperatures (T = 5K).
- UHV: Need clean surfaces
- Usually well-defined surfaces (e.g. single crystals)
- Low-T: stability of the atoms/molecules (no diffusion) and stability of the microscope
  - noise level ~1 pm
  - drift < 1nm / day (1 nm ~ 3 atoms)

In the lab...



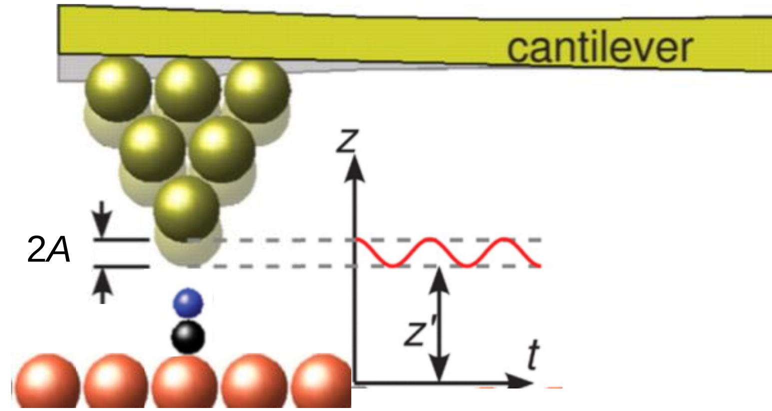


Spring suspension + eddy-current damping

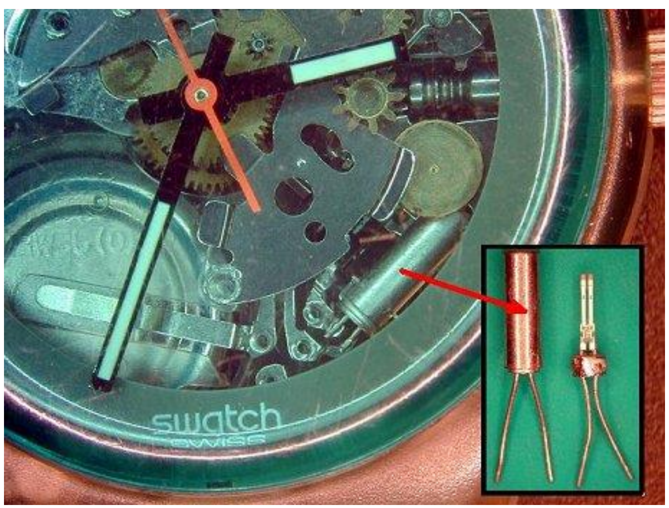
- STM and AFM
- quartz tuning fork force sensor

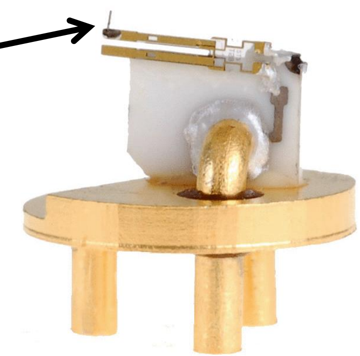
Simultaneous STM and AFM

- Frequency modulation non-contact AFM (nc-AFM)
- Very stiff cantilever
  - k = 1800 N/m
  - f_0 ~ 30 kHz
  - small oscillation amplitudes << 1 Å
  - All electrical detection



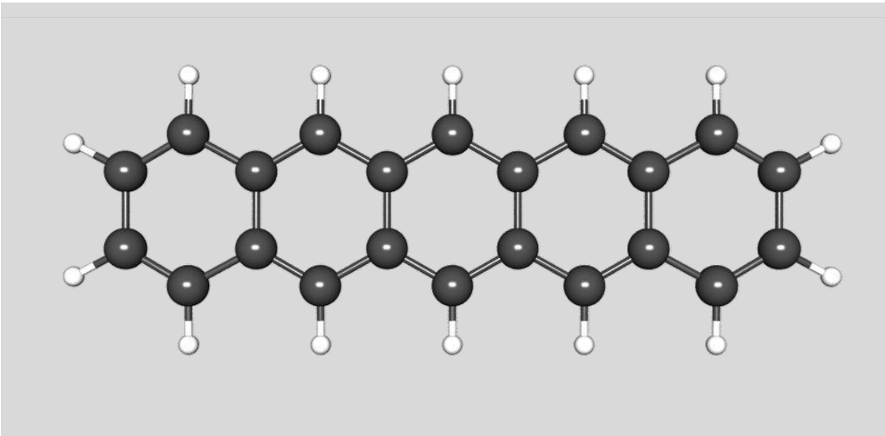
- **STM with an additional data channel giving the short-range tip-sample interaction**

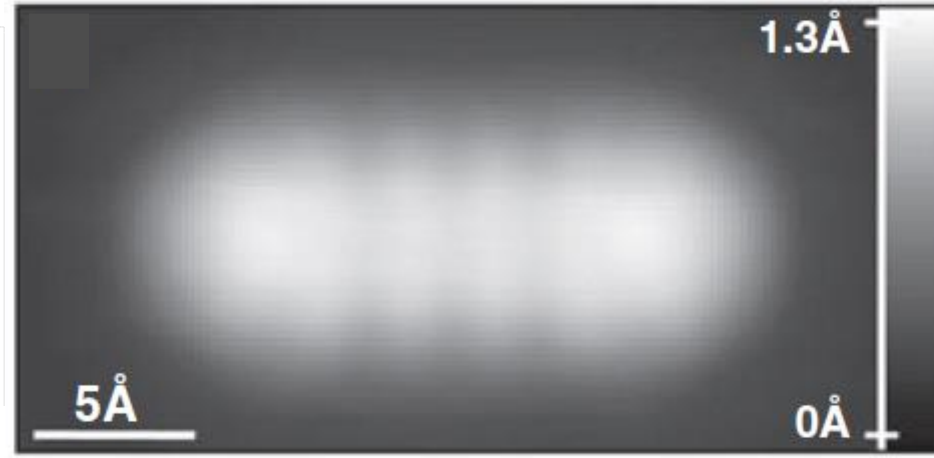




Details: F.J. Giessibl, Rev. Mod. Phys. 75, 949 (2003)

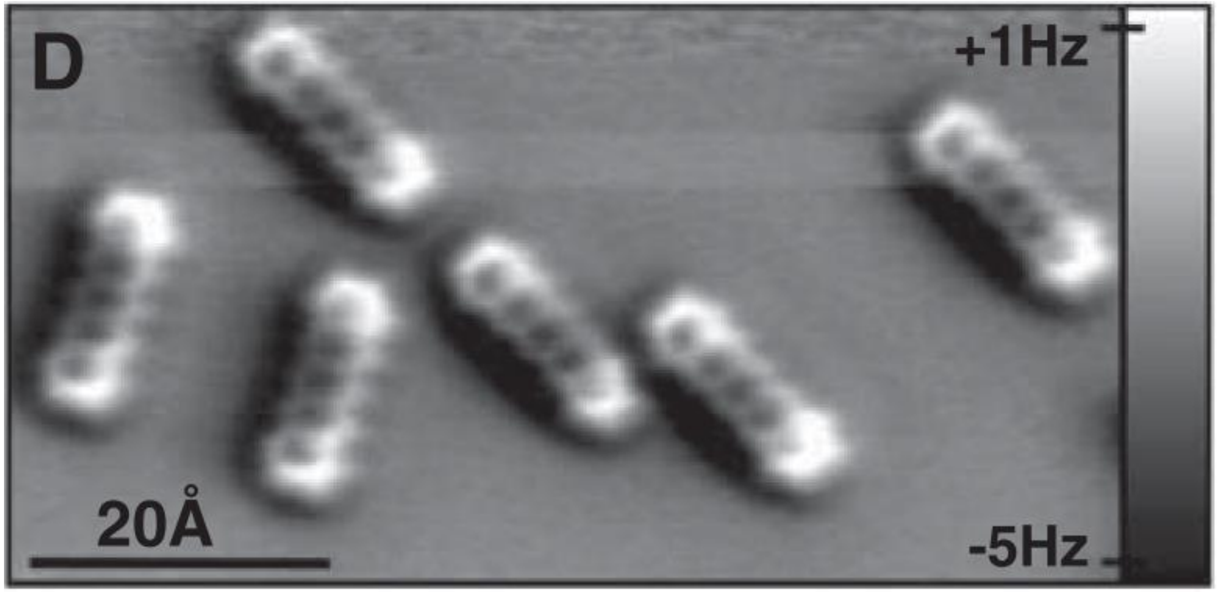
STM of a molecule



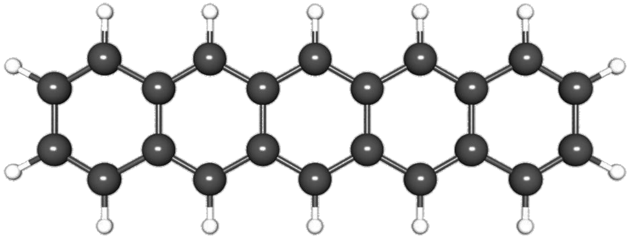


- Where are the atoms?
- Measure current – this is not directly related to the positions of the atoms

Atomic resolution on molecular systems

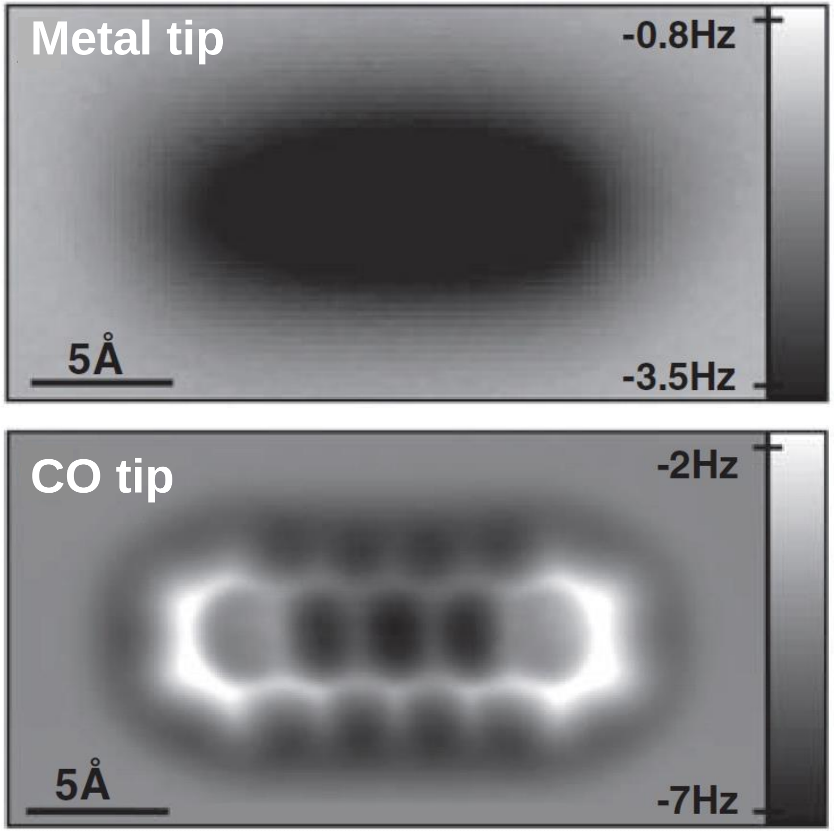


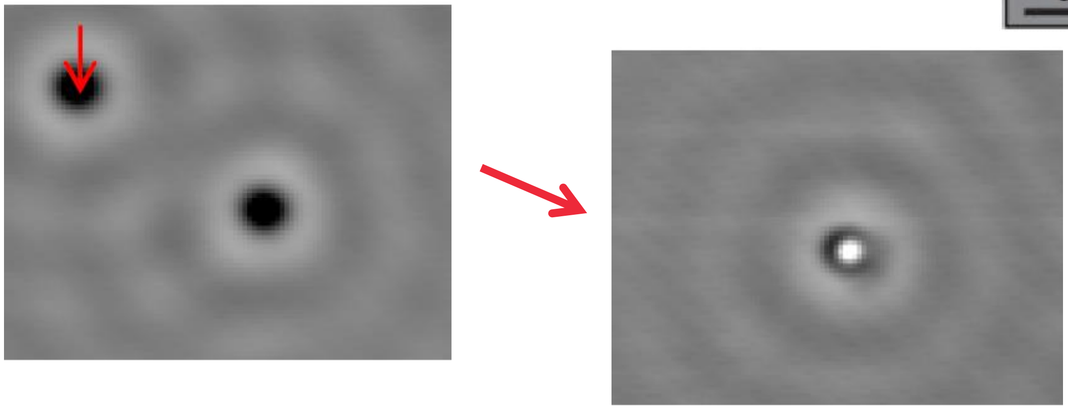
- Best possible STM/AFM with the QPlus sensor
- Where are the atoms?
- Metallic tips are reactive – large attractive forces between the tip and sample causes the molecule to be moved before reaching atomic resolution
- Sudden tip change!



What happened?

- Tip apex was made non-reactive tip by accidental pickup of a CO molecule
- Can be done on-purpose in a controlled way
- Allows atomic resolution imaging under Pauli repulsion

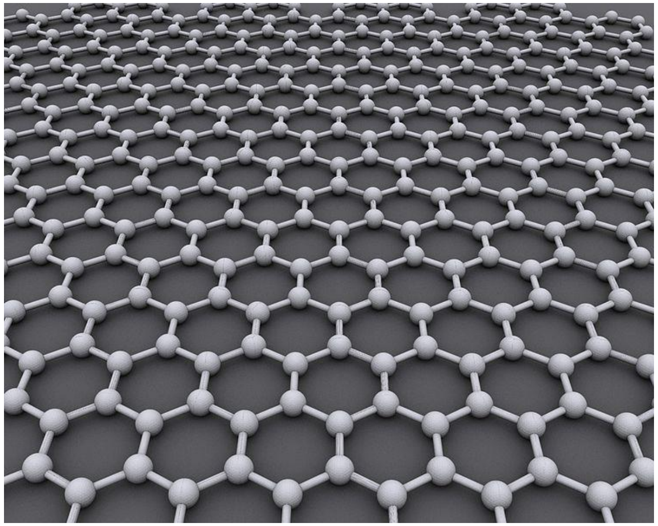


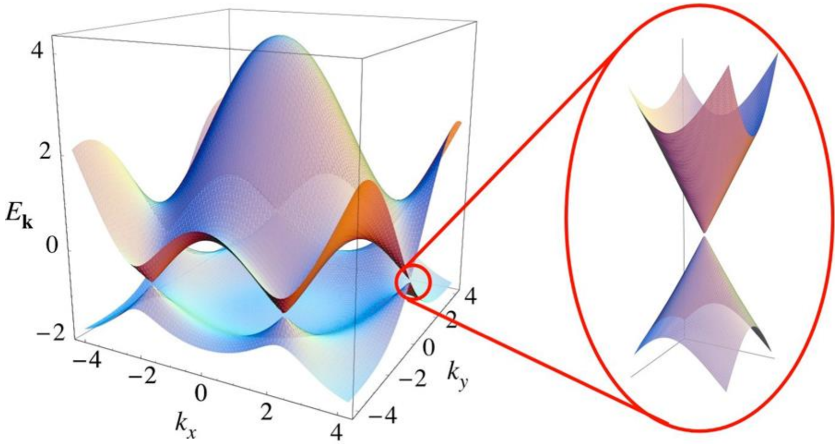


Science 325, 1110 (2009).

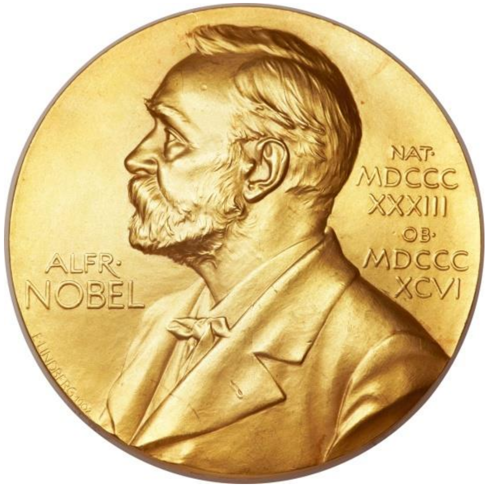
Graphene – what are we doing?

- Single-atom thick network of carbon
  - Several exceptional properties (electronic, mechanical etc.)
- We are interested in electronic properties
  - No gap – how to make a transistor?
  - Post-CMOS: Something completely different?





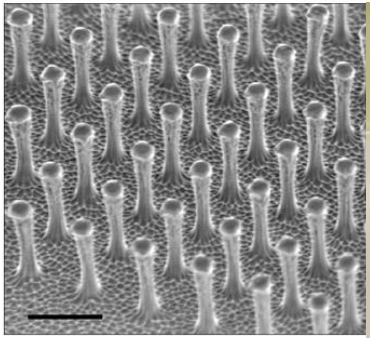
Nobel prize



- Physics Nobel-prize to Andre Geim and Konstantin Novoselov in 2010 for “*for groundbreaking experiments regarding the two-dimensional material graphene*”.

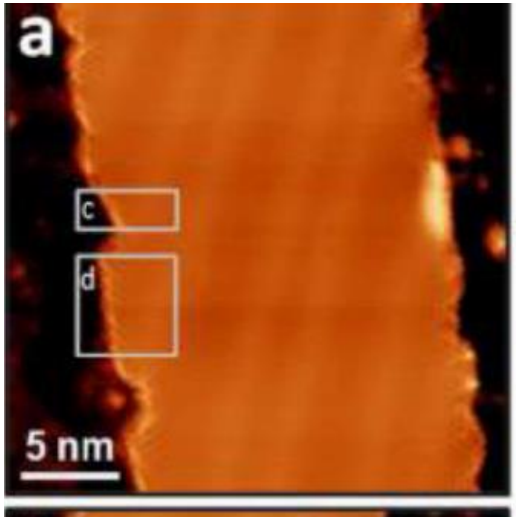
Other less-known facts on Andre Geim:

- Inventor of the Gecko tape
- Andre Geim has also received the Ig Nobel prize: in physics (with Sir Michael Berry) for using magnets to levitate a frog.
  - “*The Ig Nobel Prizes honor achievements that first make people laugh, and then make them think*”
- Co-authored a journal article with this pet hamster Tisha
  - Geim, A. K.; Ter Tisha, H. A. M. S. (2001). "Detection of earth rotation with a diamagnetically levitating gyroscope". Physica B: Condensed Matter. 294-295: 736.

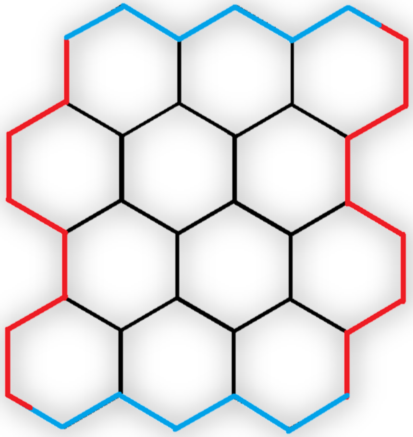


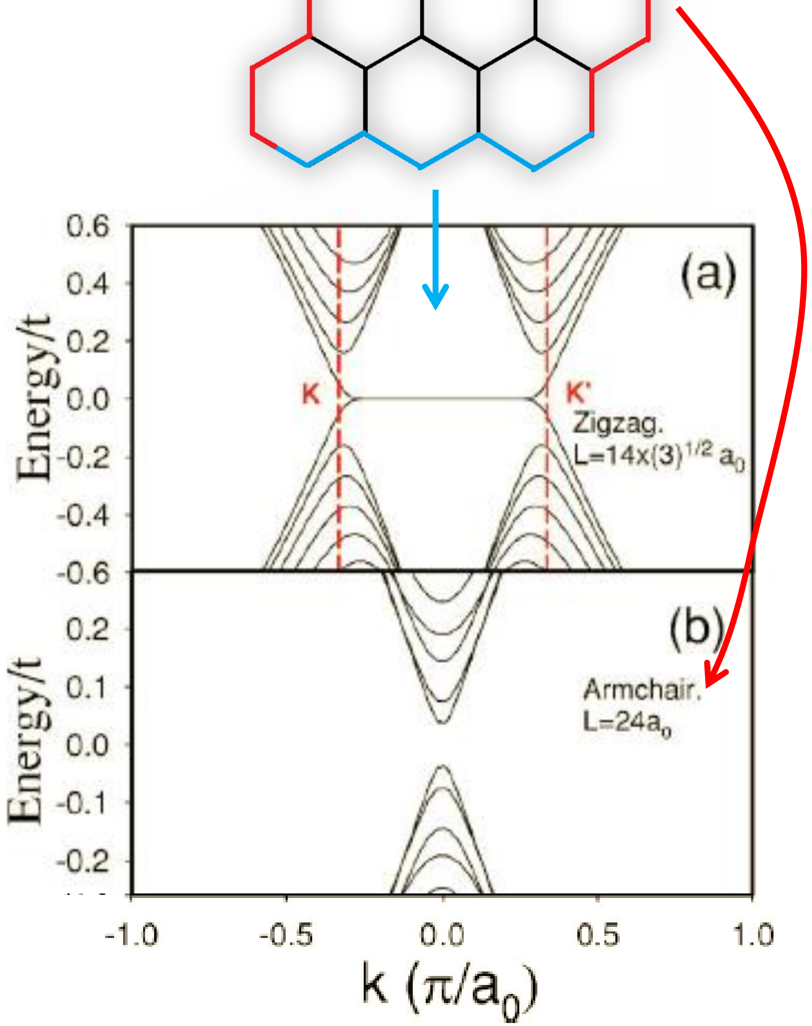
Nanostructured graphene

- Armchair edges
  - Simple quantum confinement
- Zigzag edges
  - Passivated zig-zag edges should support spin-polarized states
- Need atomically perfect samples!



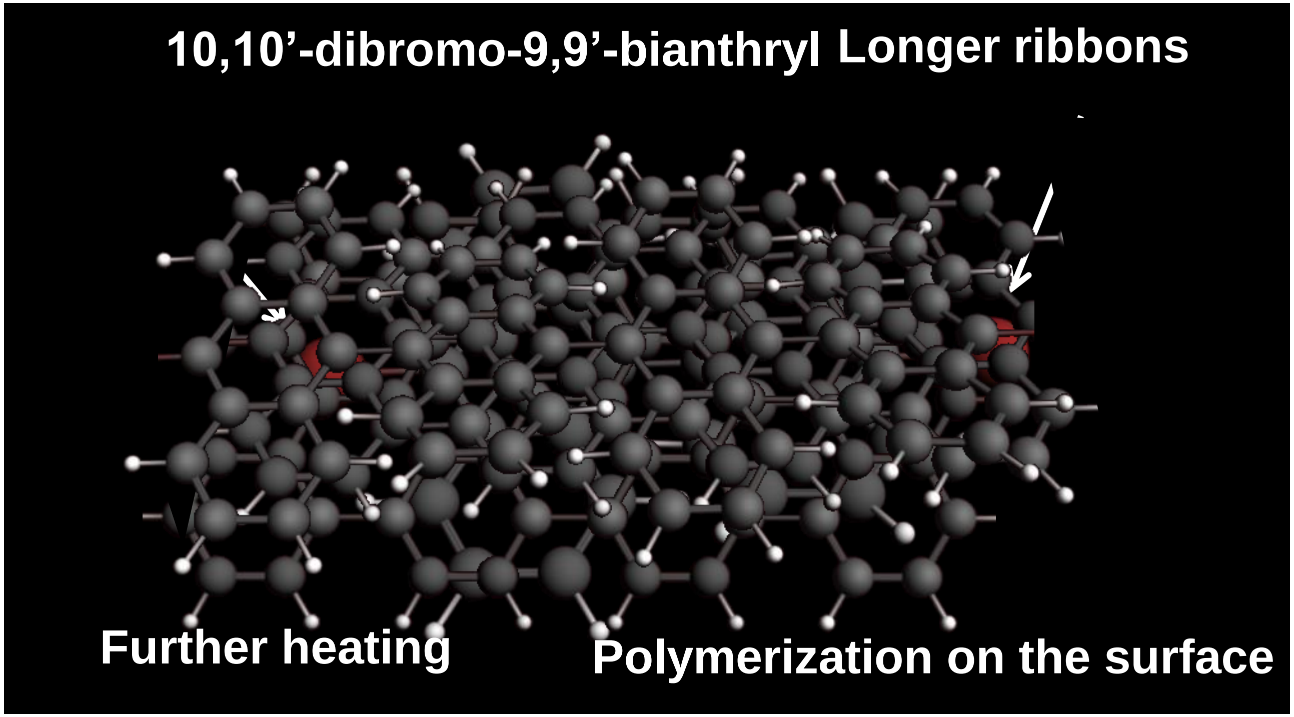
X. Zhang et al. ACS Nano **7,** 198–202 (2013).





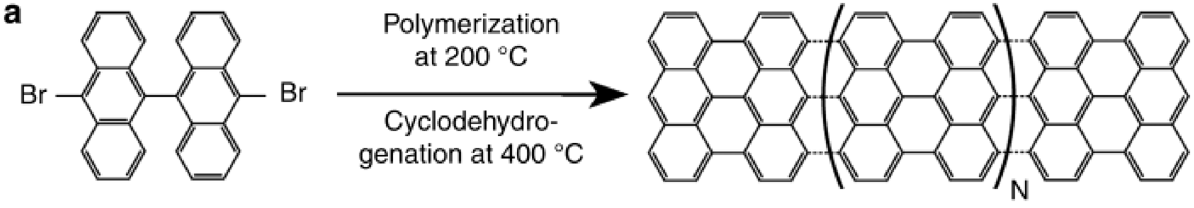
A.H. Castro Neto *et al*., Rev. Mod. Phys. **81**, 109 (2009)
Rycerz, A., Tworzydło, J. & Beenakker, C., *Nature Phys.* **3**, 172 (2007).

Bottom up synthesis of graphene nanoribbons



- Surface assisted polymerization
  - Evaporate precursor on Au(111) at 200ºC for surface assisted C-C coupling
  - Heat to 400ºC for cyclodehydrogenation

a



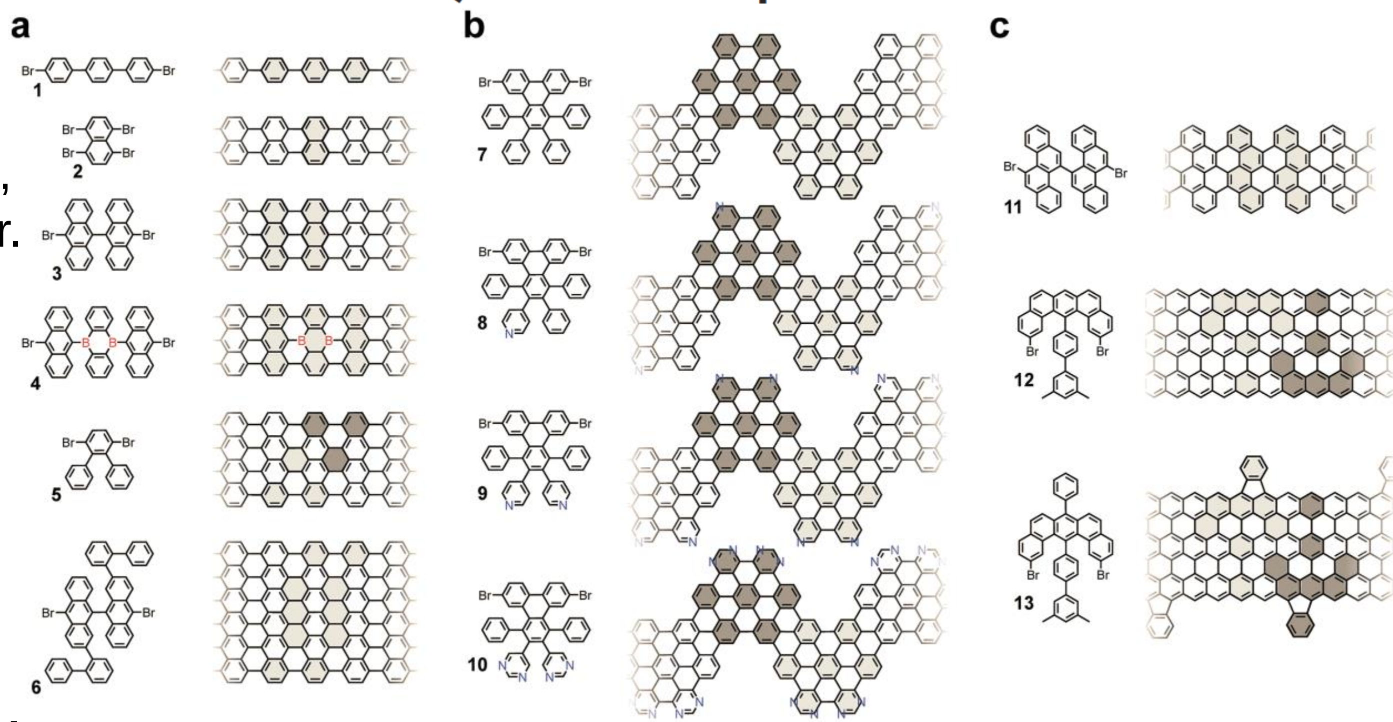
J. Cai *et al*...K. Müllen, R. Fasel, Nature **446**, 470-473 (2010)

Atomically precise graphene nanoribbons

- Precursor precisely determines the structure of the nanoribbon
- Precursor toolbox expanding rapidly

On-Surface Synthesis of Atomically Precise Graphene Nanoribbons

L. Talirz, P. Ruffieux, R. Fasel, Adv. Mater. 28, 6222 (2016)

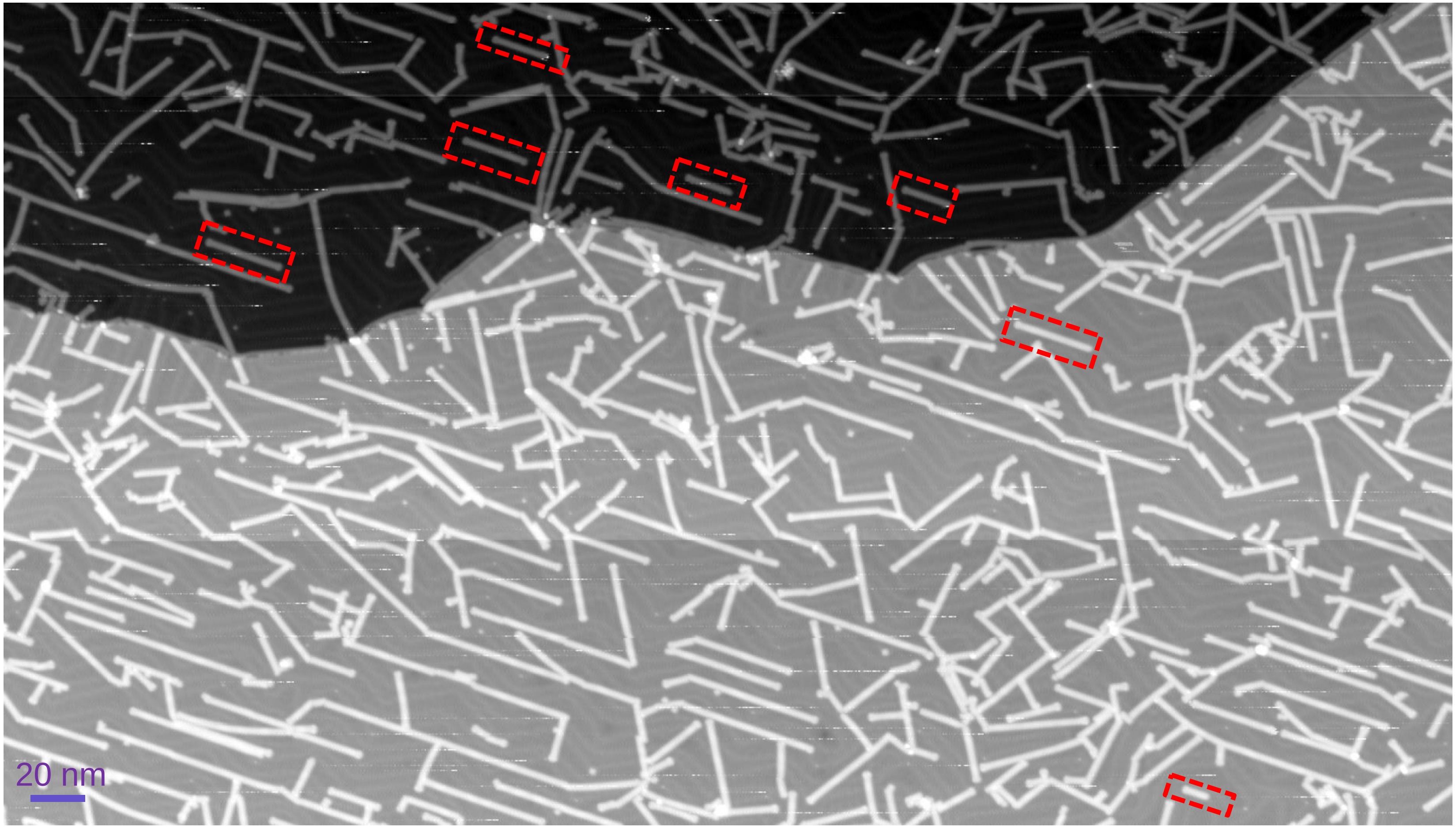


- Challenges:
  - Longer ribbons, decoupling with the substrate, transfer into device structures

Typical sample

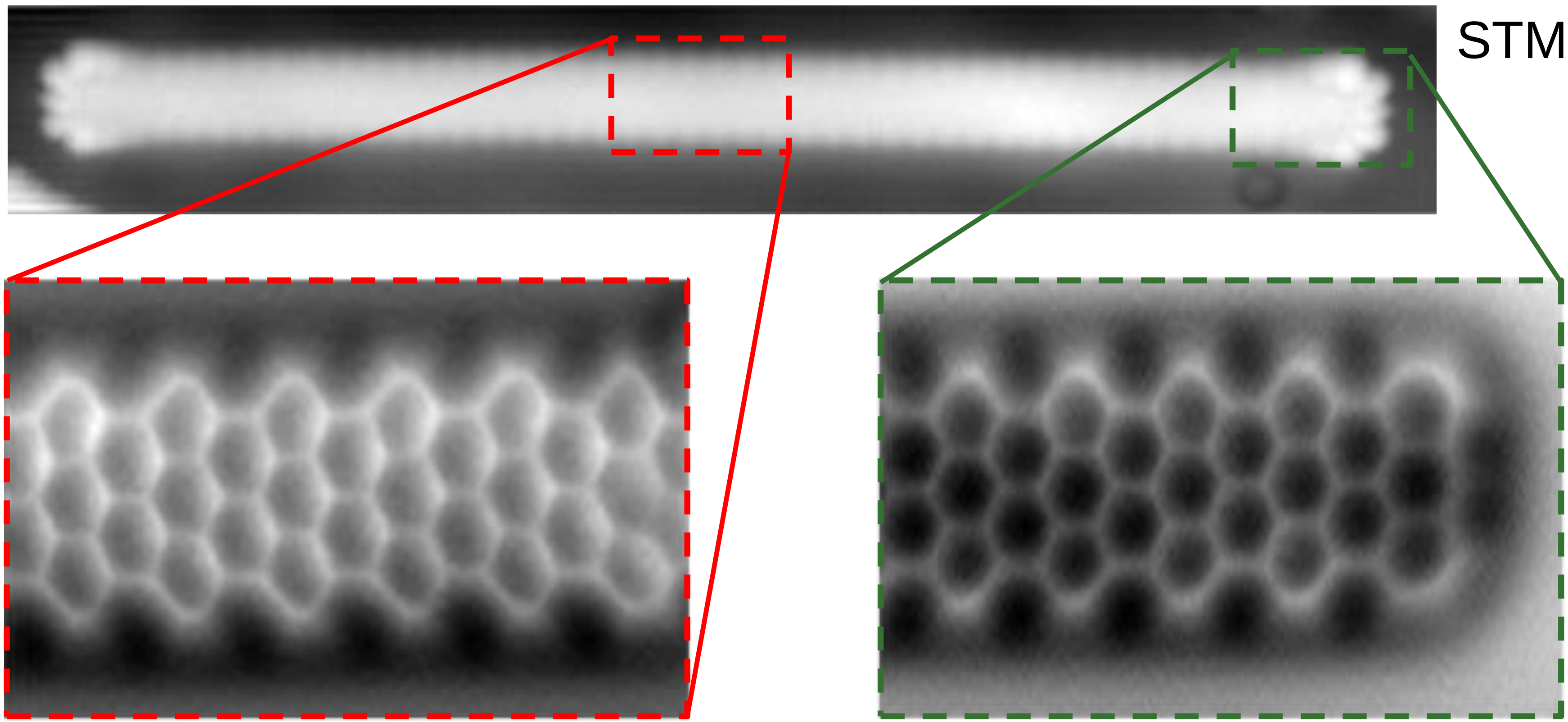
- Isolated ribbons can be found
- They are easily manipulated along ribbon axis ⇒ weak interaction with the underlying Au(111) substrate

Typical imaging parameters: V = 50 mV, I = 10 pA



Geometric structure of the ribbons

- STM gives LDOS close to Fermi level
- AFM gives map of total electron density (through Pauli repulsion)
  - All experiments in UHV at T = 5K, Qplus AFM



AFM
with a CO-terminated tip

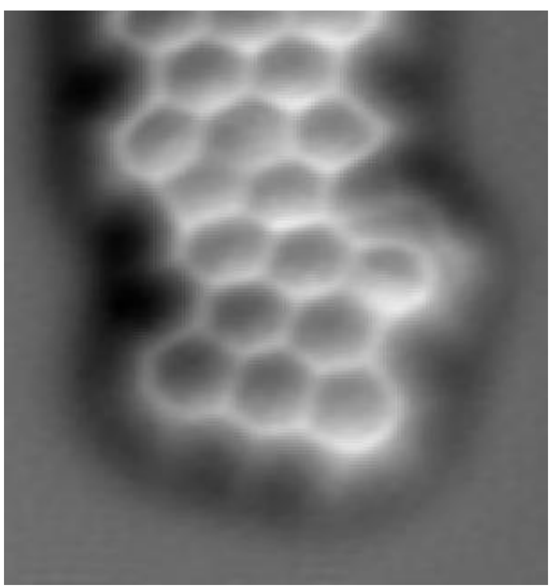
AFM

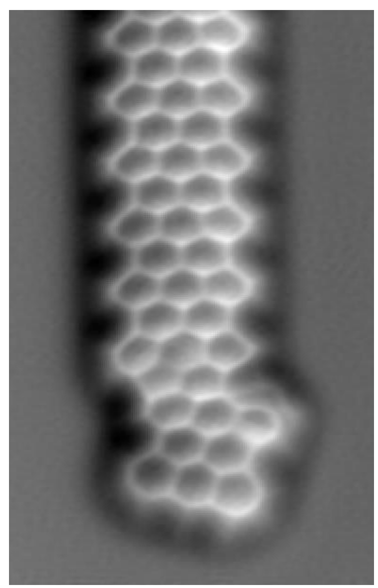
J. van der Lit et al. *Nature Comm.* 4, 2023 (2013).

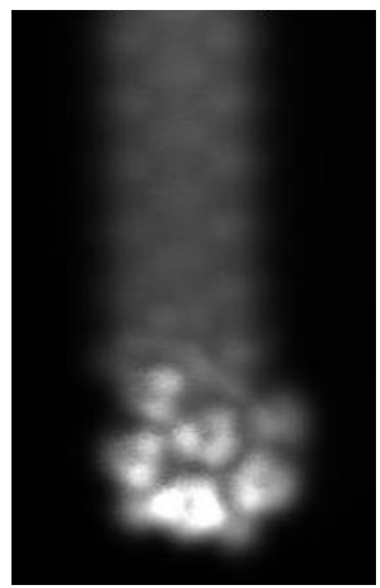
Why do we need AFM?

- Defects etc. are not easy to identify

Atomically resolves images of a molecule with 798 atoms



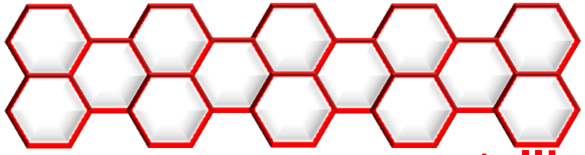




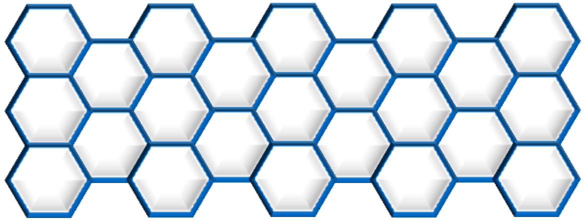
CO terminated tip

Armchair nanoribbons

- Nanoribbon width also important
  - Armchair nanoribbons can be either metallic or insulating
  - Wide gaps when *N* = 3*p* or *N* = 3*p*+1
  - Small gaps when the width is *N* = 3*p*+2
  - Zero gap in nearest neighbor tight-binding



metallic

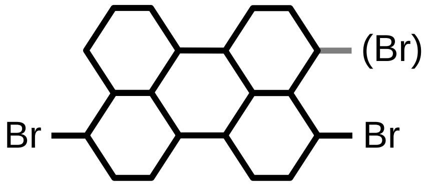


insulating

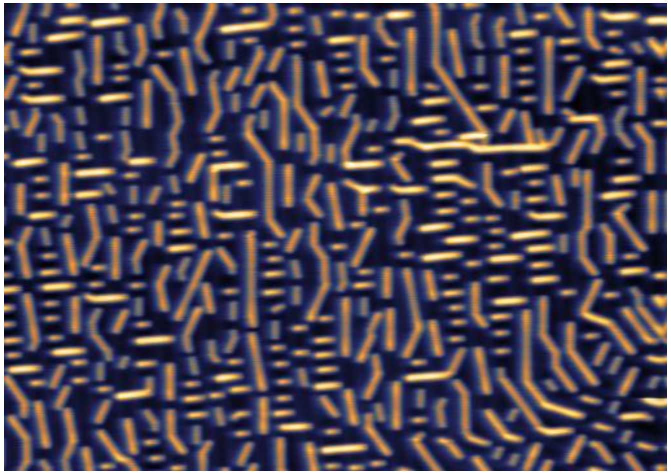
A.H. Castro Neto *et al*., Rev. Mod. Phys. **81**, 109 (2009)
Nakada, Fujita, Dresselhaus, Dresselhaus, Phys. Rev. B **54,** 17954 (1996).

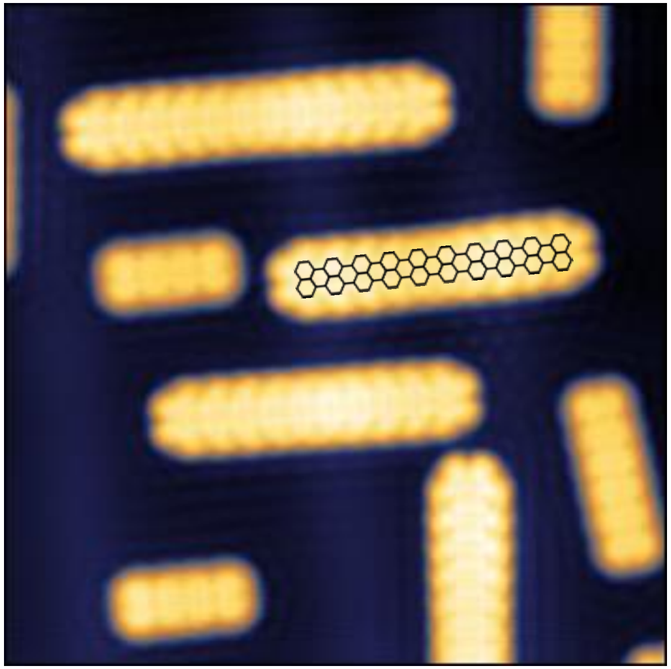
N = 5 nanoribbons

- Grown through on-surface polymerization (deposition at 200°C, annealing at 320°C)
  - On-surface synthesis of rylene-type graphene nanoribbons. J. Am. Chem. Soc. 137, 4022 (2015).
- Isolated ribbons can be found
- easy to manipulate along ribbon axis: weak interaction with the underlying Au(111) substrate



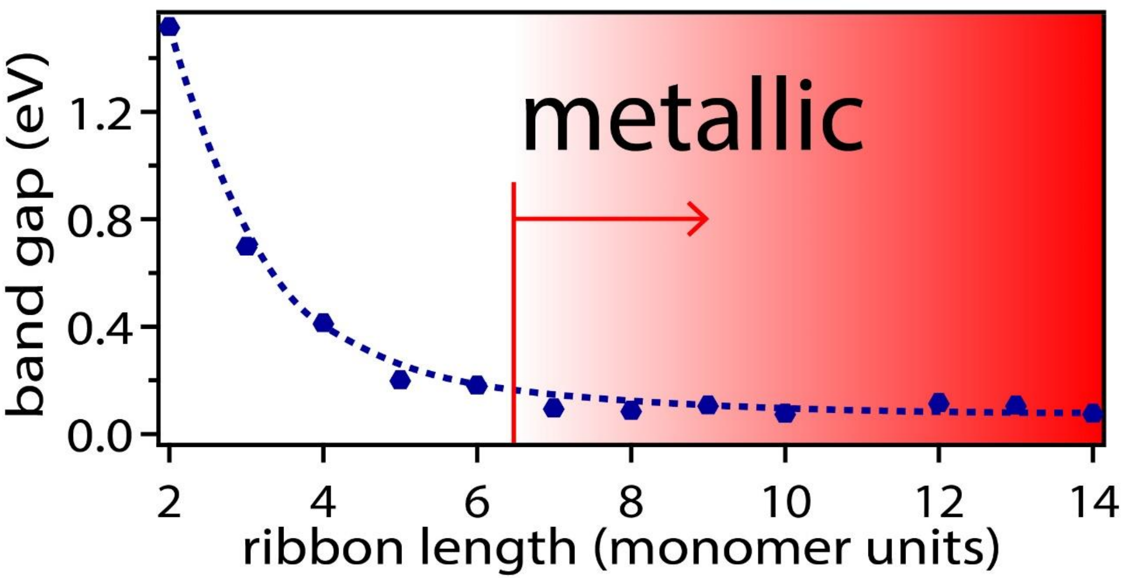
DBP (dibromoperylene) $C_{20}H_{10}Br_2$

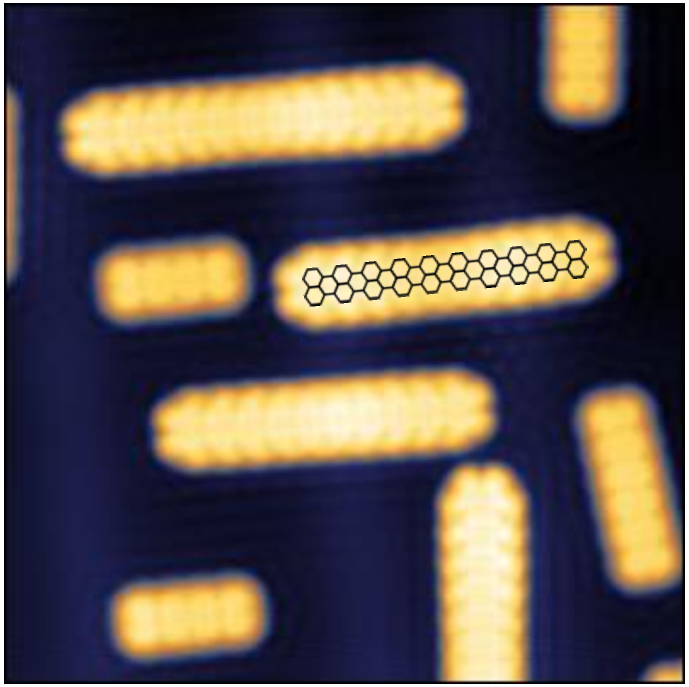




Gaps as function of ribbon length

- Energy gap goes down as a function of ribbon length
- Gap down to ~ 0.1 eV in > 6 monomer ribbons
- Use as metallic leads – heterostructures?





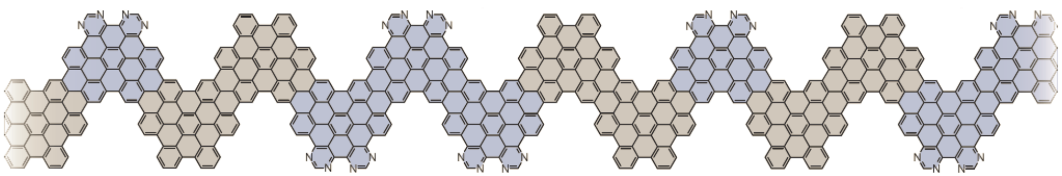
A. Kimouche *et al*. Nat. Commun. 6, 10177 (2015).

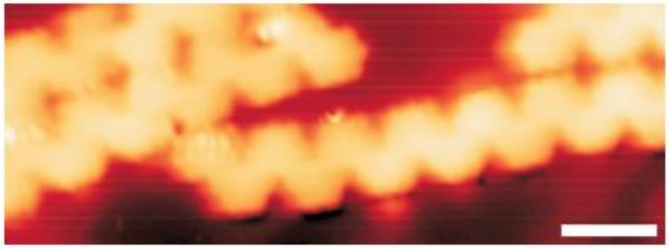
GNR heterostructures

- Covalently connect two different types of GNRs
- So far: only semiconductor-semiconductor junctions

Graphene nanoribbon heterojunctions Nature Nano. 9, 896 (2014)

Jinming Cai[1†], Carlo A. Pignedoli[1], Leopold Talirz[1], Pascal Ruffieux[1], Hajo Söde[1], Liangbo Liang[2], Vincent Meunier[2], Reinhard Berger[3], Rongjin Li[3], Xinliang Feng[3], Klaus Müllen[3]* and Roman Fasel[1,4]*

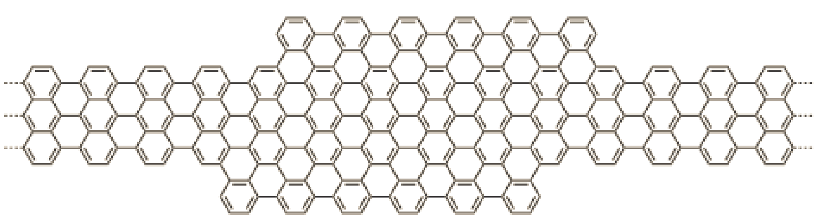


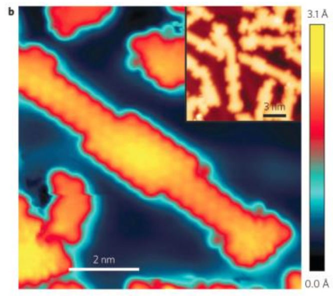


Molecular bandgap engineering of bottom-up synthesized graphene nanoribbon heterojunctions

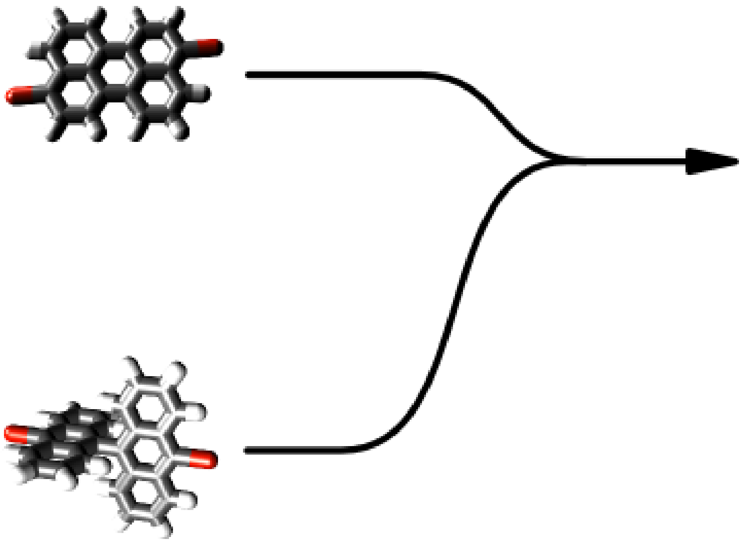
Nature Nano. 10,156 (2015)

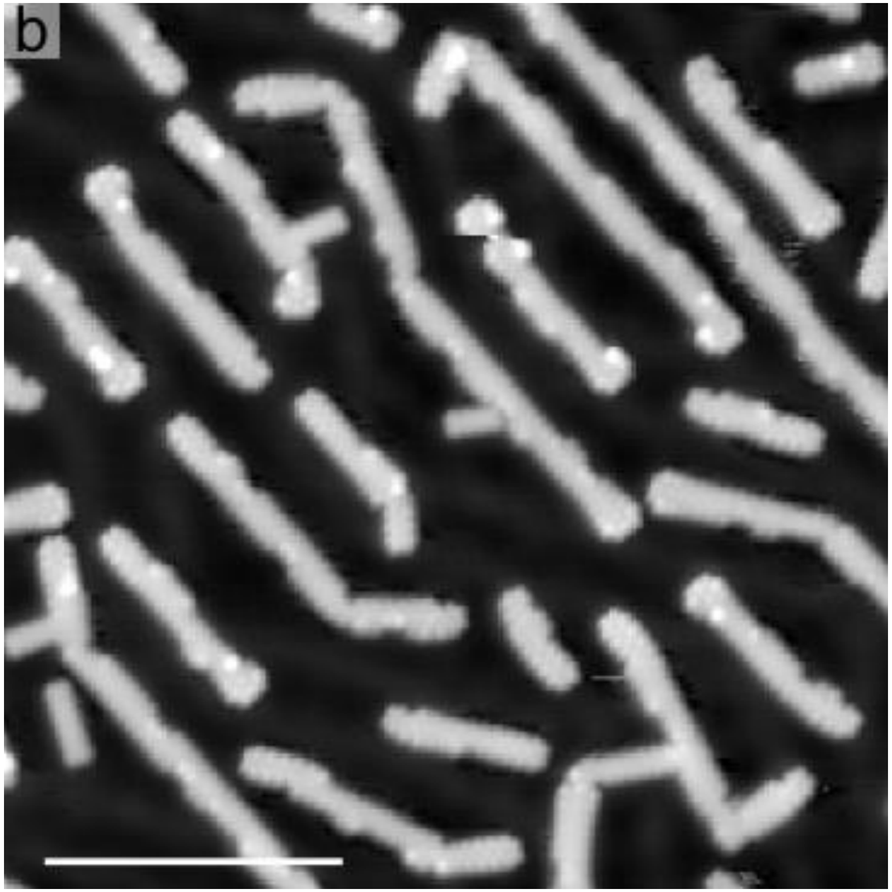
Yen-Chia Chen[1,2], Ting Cao[1,2], Chen Chen[3], Zahra Pedramrazi[1], Danny Haberer[1], Dimas G. de Oteyza[1,4], Felix R. Fischer[2,3,5]*, Steven G. Louie[1,2]* and Michael F. Crommie[1,2,5]*



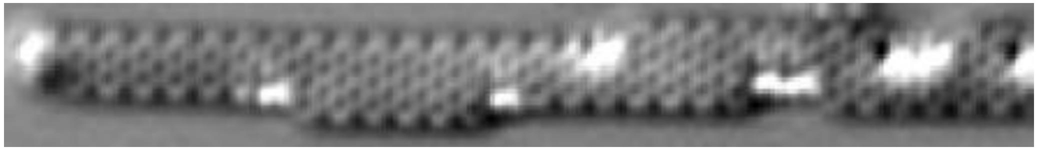


5-GNR / 7-GNR heterostructures



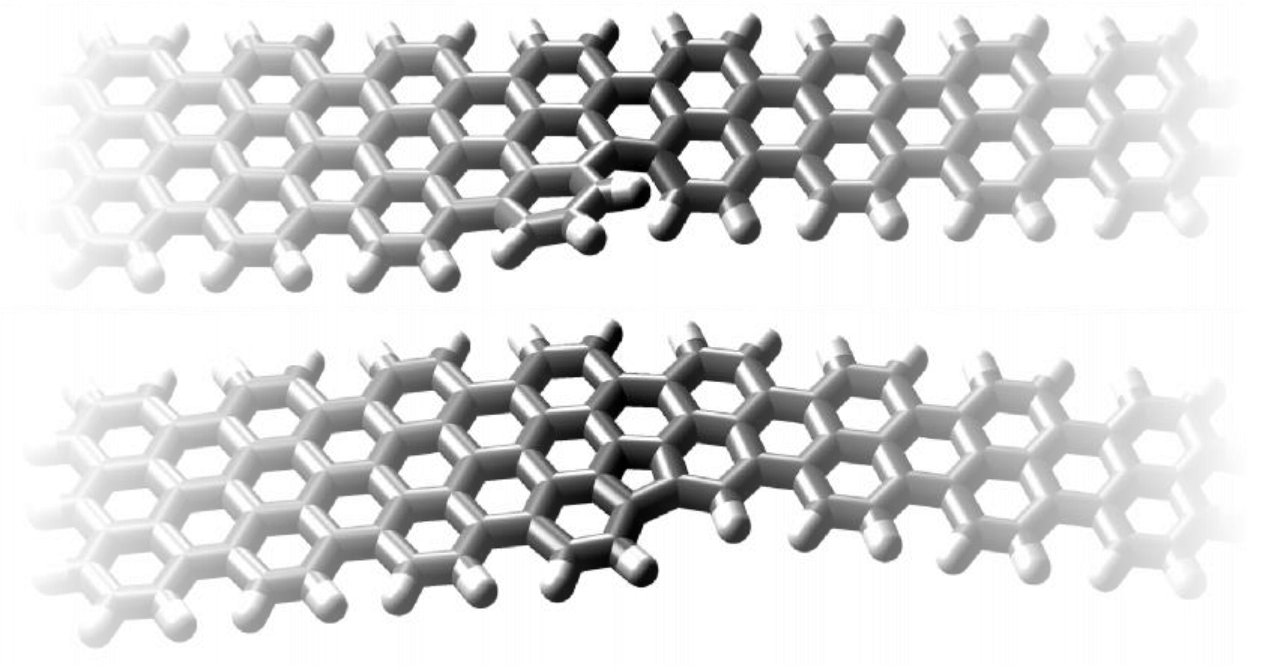


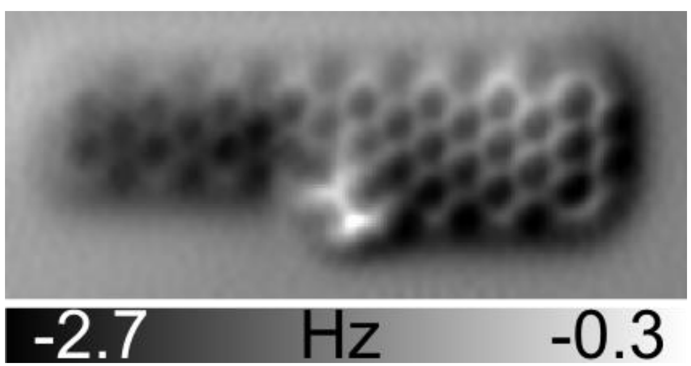
- GNR equivalent of a metal-semiconductor junction
- Co-deposition of DBBA and DBP onto Au(111) surface at T = 480 K
- Anneal to T = 570 K for 5 minutes to induce cyclodehydrogenation

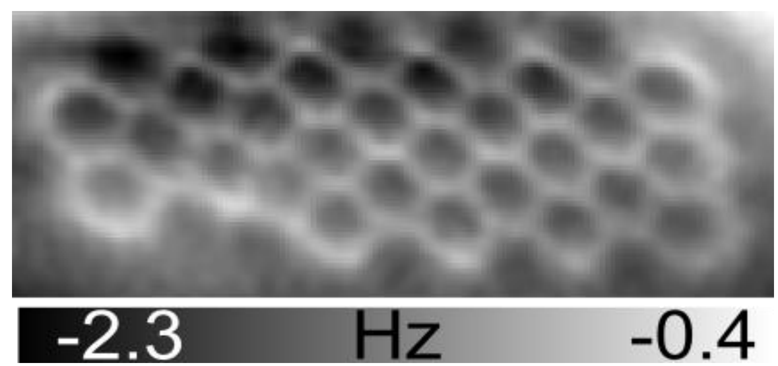


Junction geometry?

- Both non-planar and planar junctions
- Pentagon-hexagon pair
- Heating more (*T*=600 K) gives predominantly planar junctions







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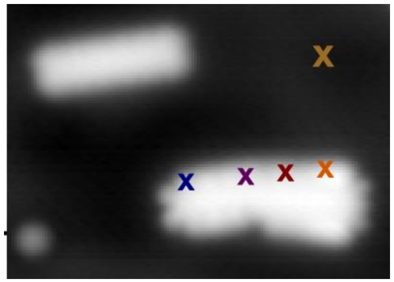
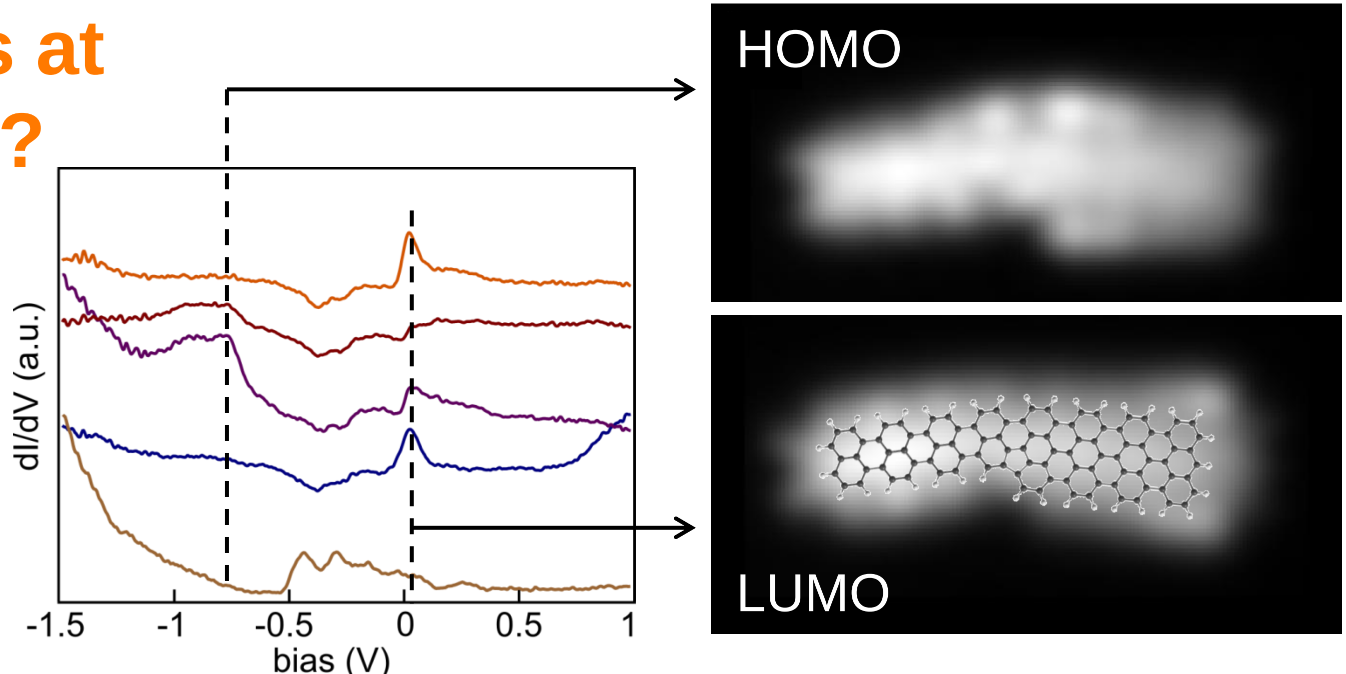
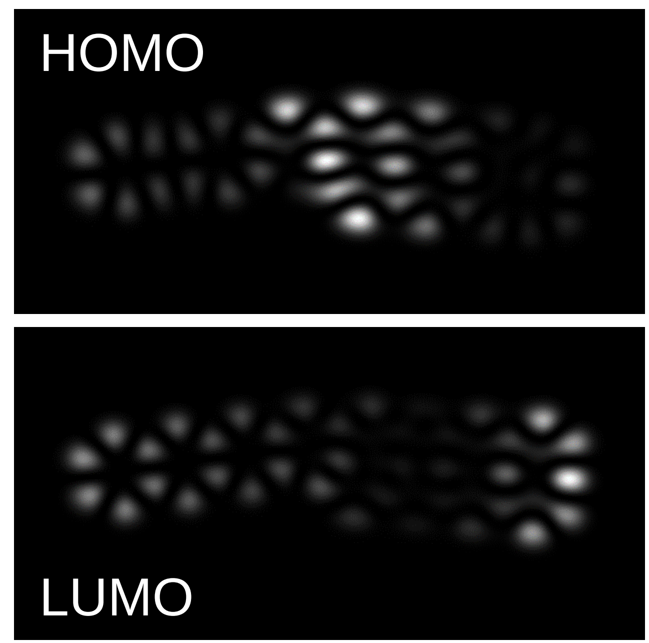
Energy levels at the junctions?

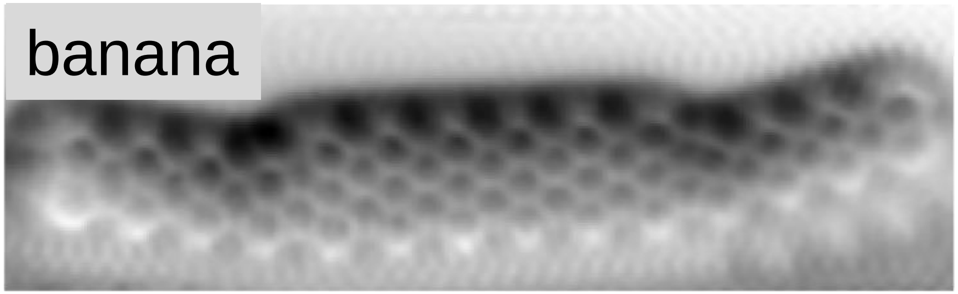




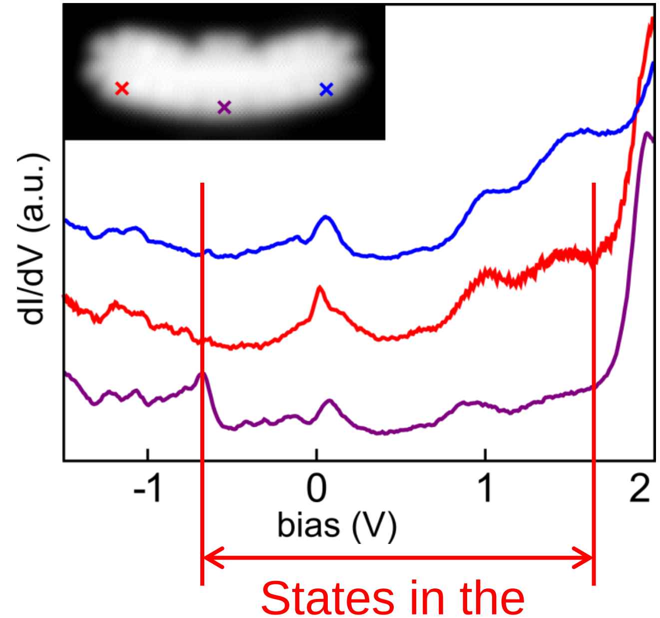


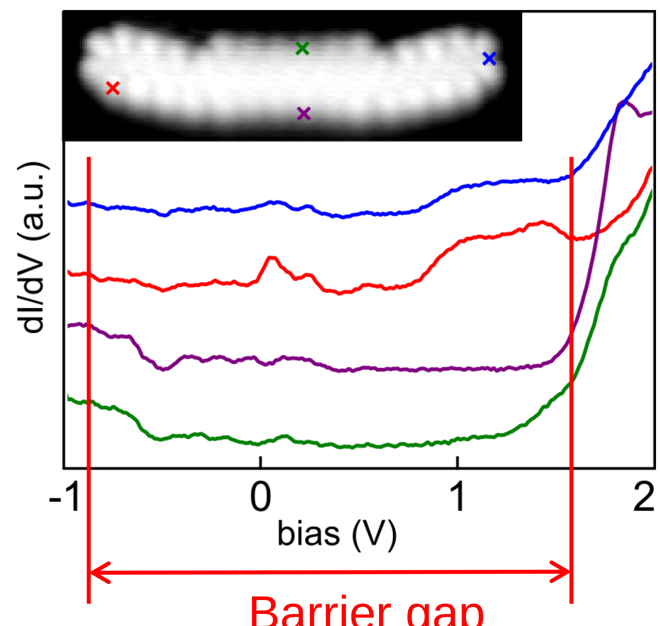
- LUMO: superposition of the 7-GNR end states and a hybridized 5-GNR state
- HOMO: 7-GNR end-state at the connected end and hybridized with a lower-energy orbital of the 5-GNR

Metal-semiconductor junctions in ribbons



- Model of a metal-semiconductor-metal structure embedded in a single graphene nanoribbon
- Acts as a ”tunnel barrier” if the semiconducting part is sufficiently wide (3 monomer units)
- New types of electronic components?





P.H. Jacobse et al. Nat. Commun. 8, 119 (2017).

Conclusions

- Wide variety of atomically precise graphene nanoribbons can be realized through on-surface synthesis
- Heterojunctions allow incorporation of more functionality into a single GNR, e.g. tunnel barrier
- Towards complete electrical device embedded in a single nanoribbon for GNR-based electronics