Universiteit Utrecht

[Faculty of Science
Chemistry]

# The atomic and electronic structure of well-defined graphene nanoribbons studied by scanning probe microscopy


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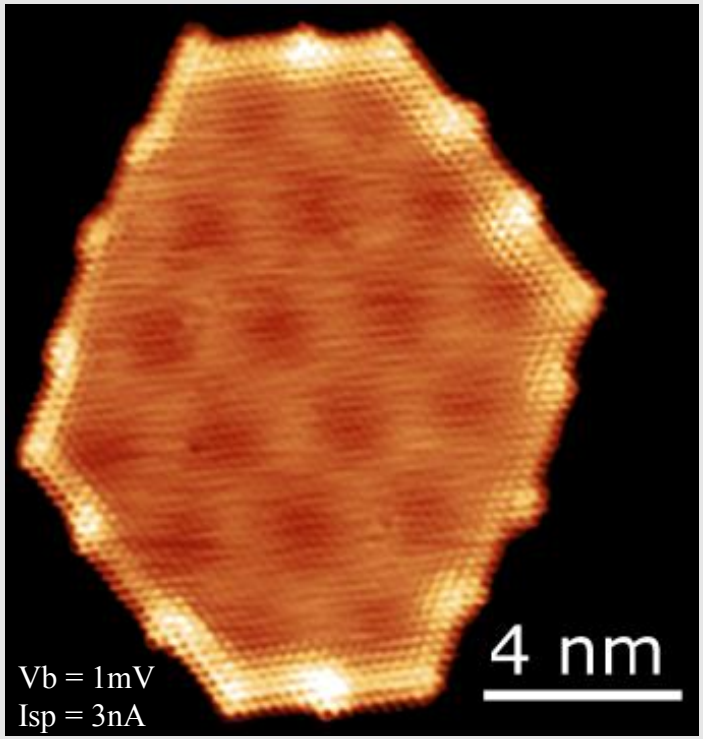
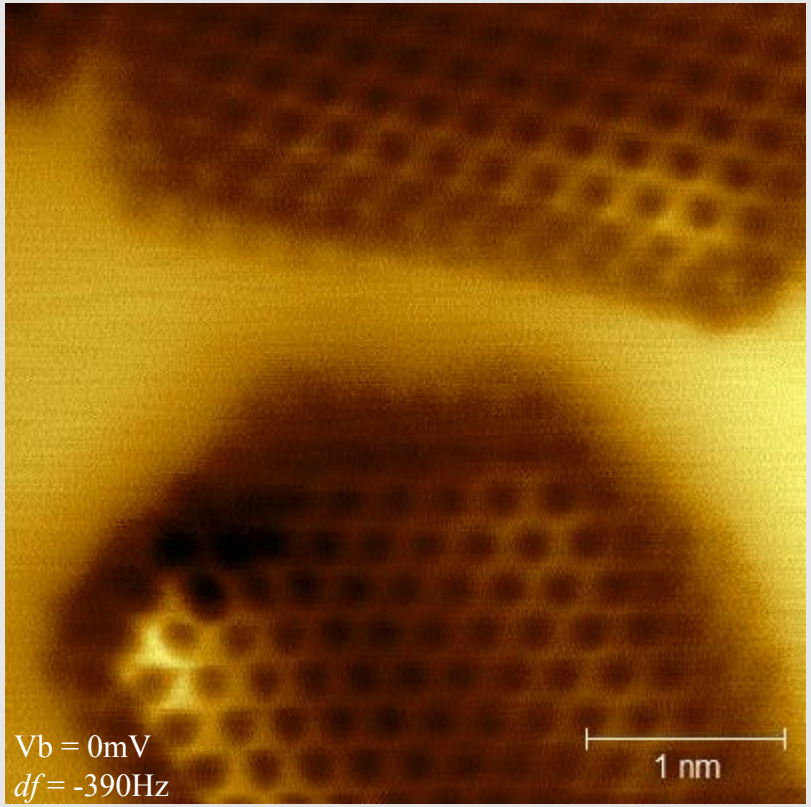
# How small can graphene be?

- Graphene as a promising candidate for future nanoelectronics
- However: limited experimental study of well-defined graphene nanostructures
- Relate atomic structure to electronic properties
- Control over the edge shape and chemistry?

# Previous studies on nanoscale graphene: CVD growth

- Chemical vapor deposition
  - 1 problem: edges

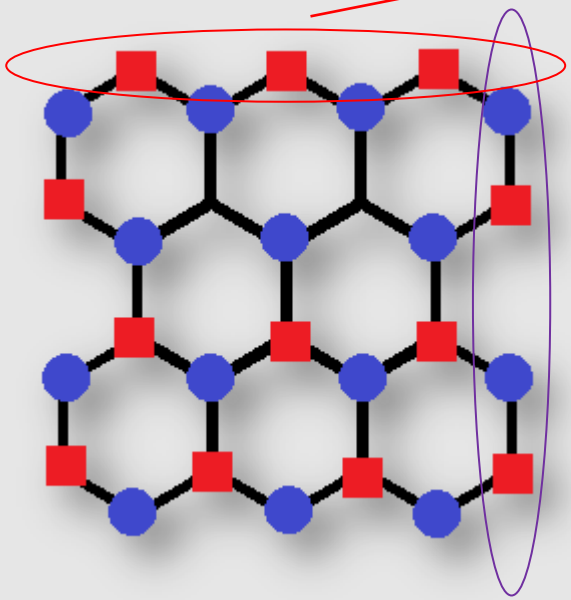


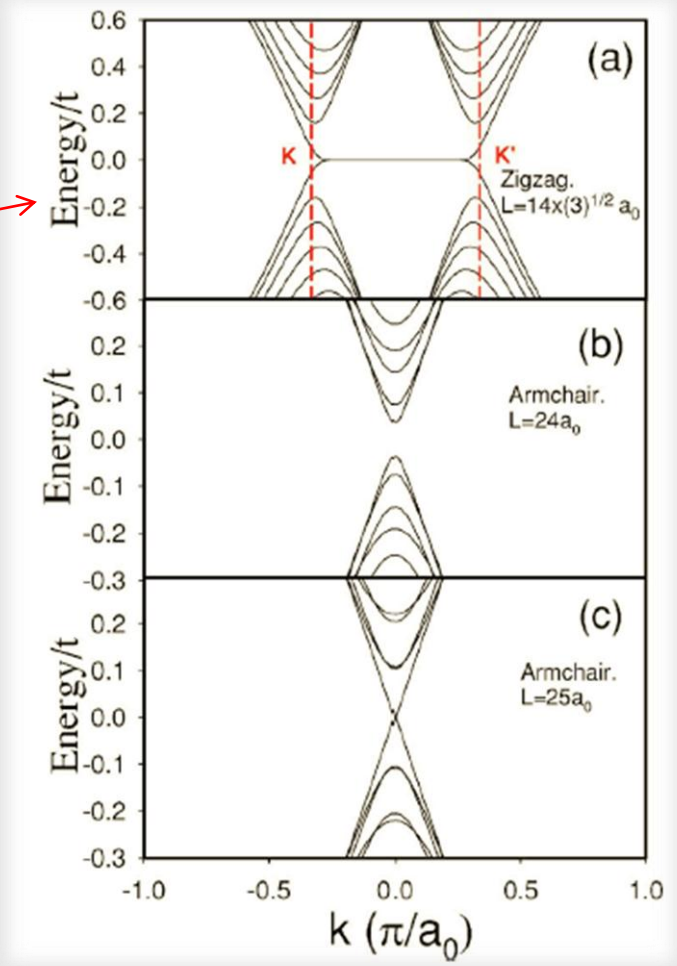




S. Hämäläinen *et al.*, Phys. Rev. Lett. **107**, 236803 (2011)
S. Phark *et al.*, ACS nano **5**, 8162, (2011)
D. Subramaniam *et al.*, Phys. Rev. Lett. **108**, 046801 (2012)
B. Wang *et al.*, Nano lett. **11**, 424-30 (2011)

# Why do edges matter?

- Edges and edgestates
  - Contribution of different sublattices





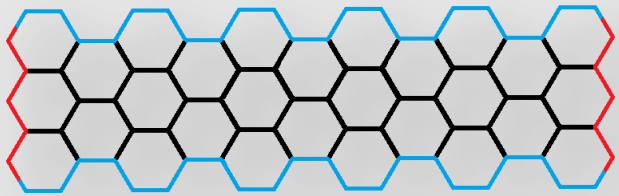




A.H. Castro Neto *et al*., Rev. Mod. Phys. **81**, 109-162 (2009)
L. Brey and H.A. Fertig, Phys. Rev. B **73**, 235411 (2006)

# Chemically prepared graphene derivatives: nanoribbons

- Surface assisted polymerization
  - Synthesize and evaporate precursor on Au(111) at 200°C for surface assisted C-C coupling
  - Heat to 400°C for cyclodehydrogenation
- Full control over edges!
  - Shape: armchair
  - Chemistry: hydrogen terminated



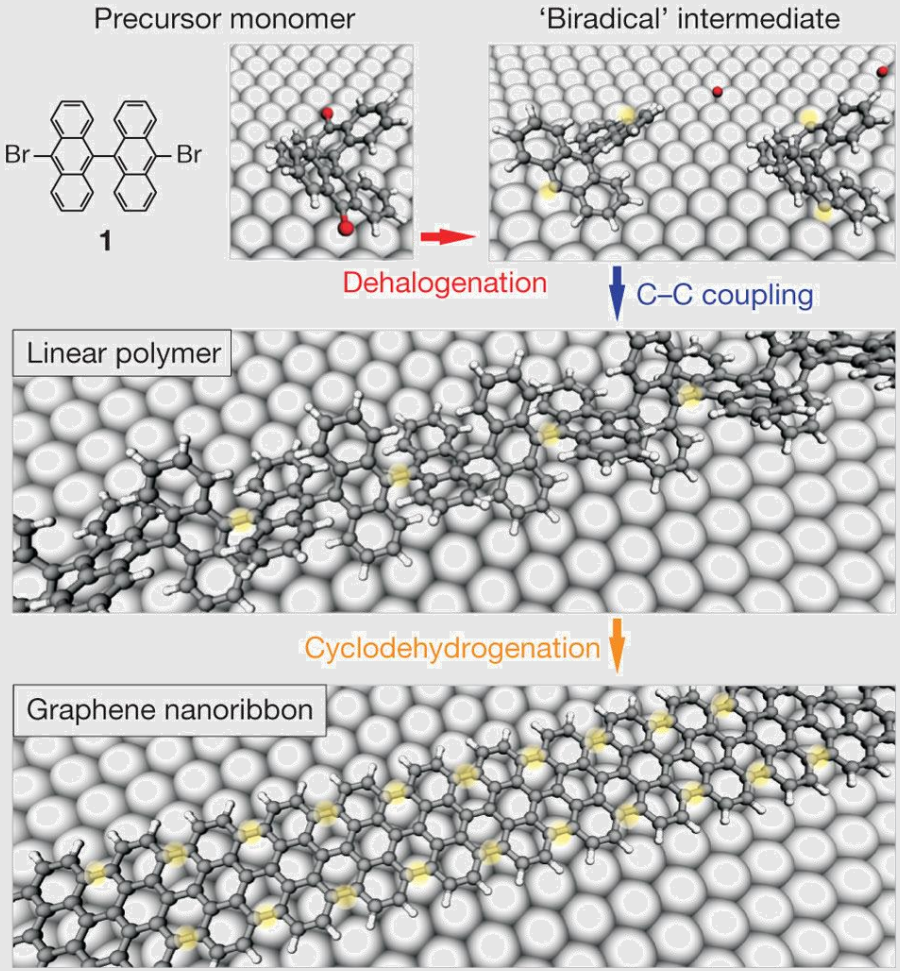
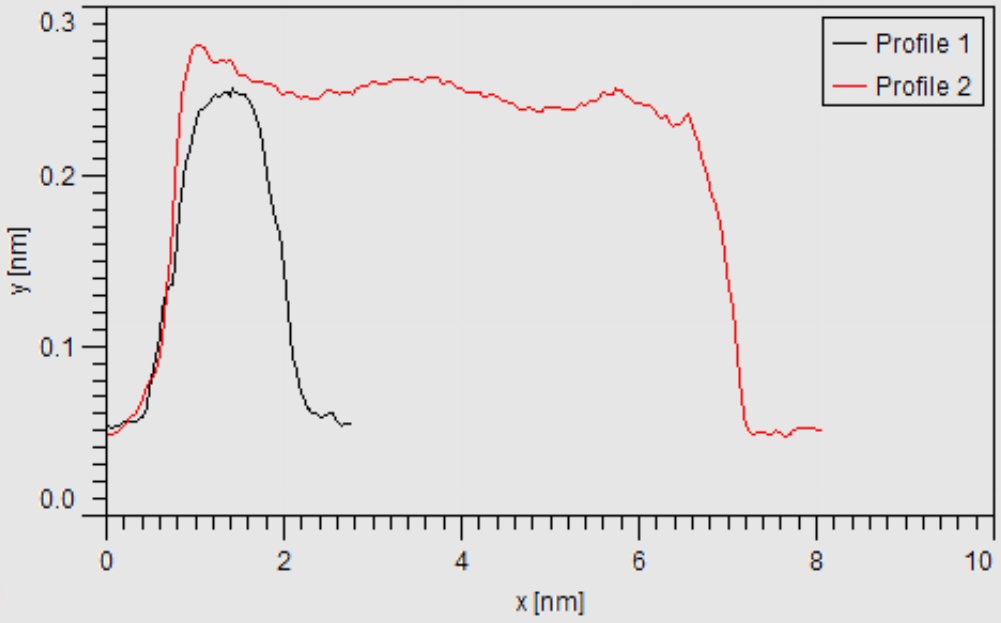


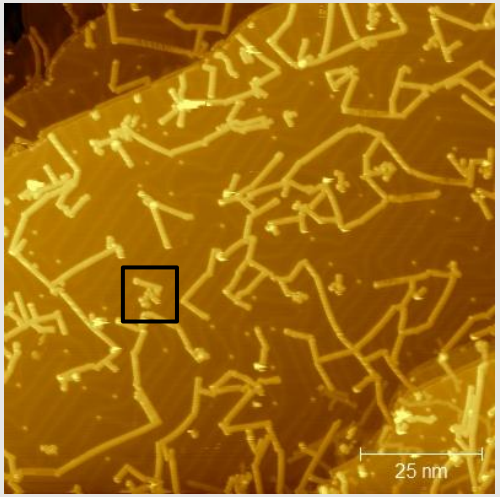


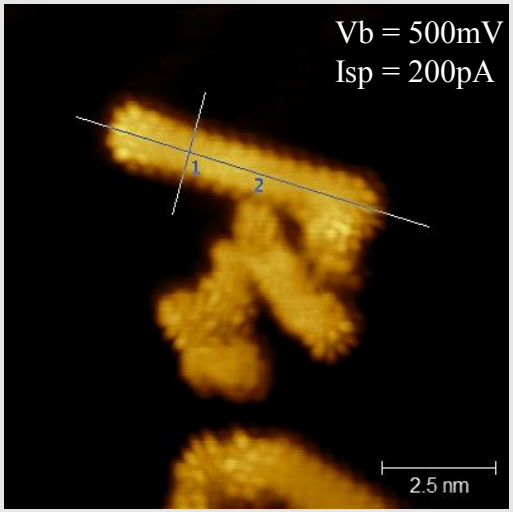

Image taken from J. Cai *et al.*, Nature **466**, 470-473 (2010)

# Growth results

- Growth yields ~5-15nm long ribbons
- Apparent width ~1.5nm
- Apparent height ~0.25nm

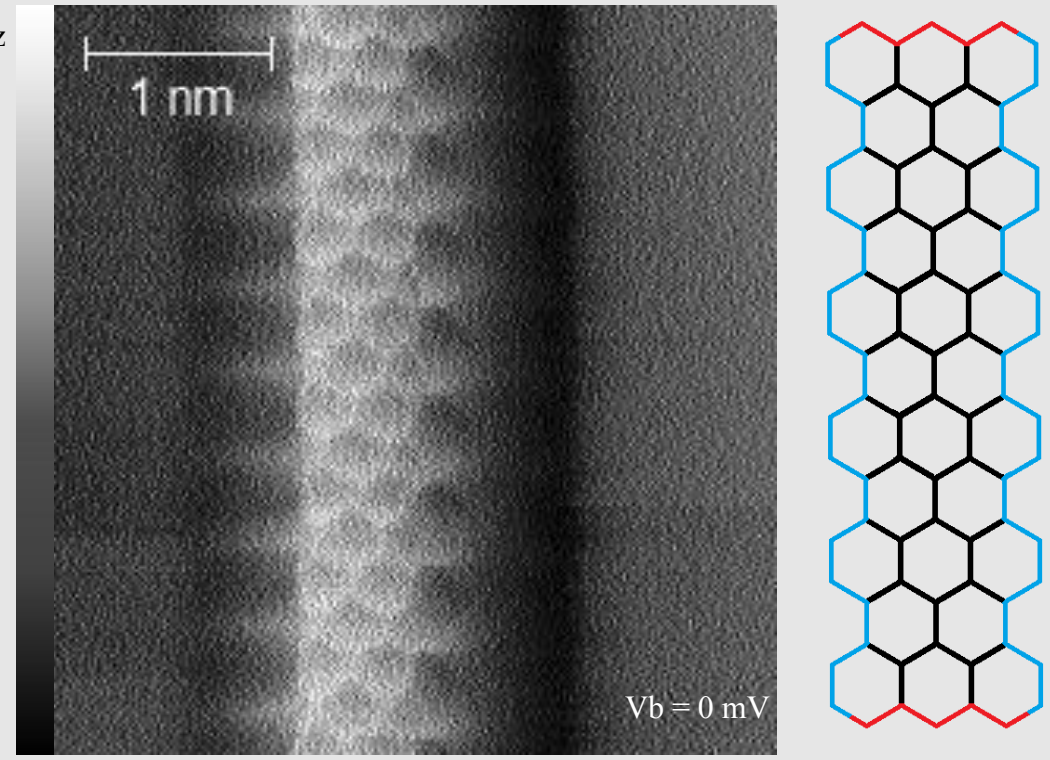


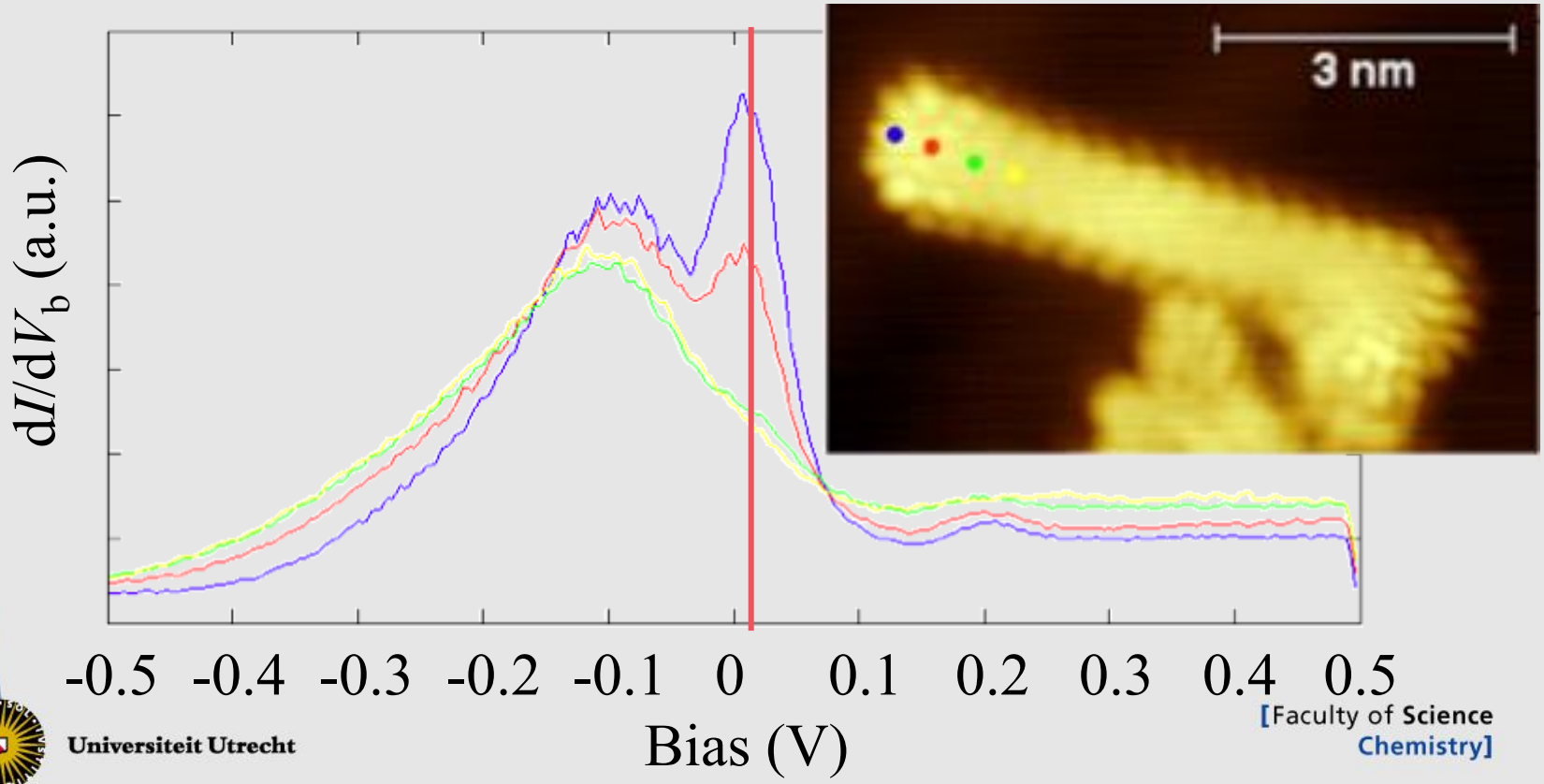
# Looking at the atomic structure

- STM probes the LDOS close to fermi level
- For atomic backbone rather use AFM

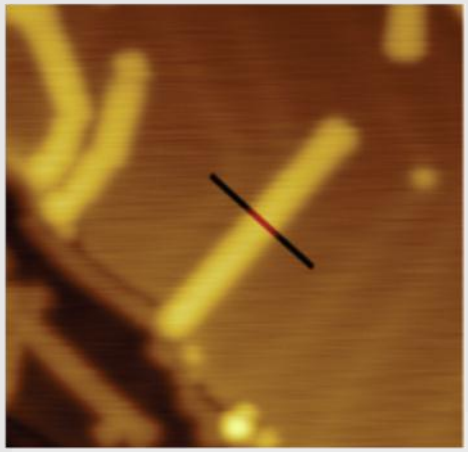


# Looking at the electronic structure

- Ribbon ends: zigzag terminated
- End state close to Dirac point

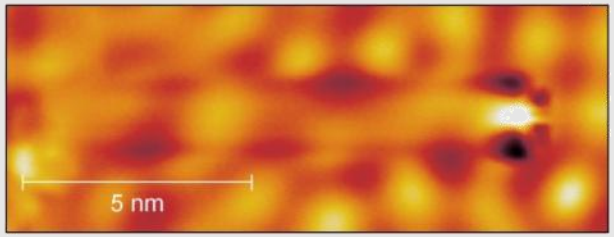


# Looking at the electronic structure

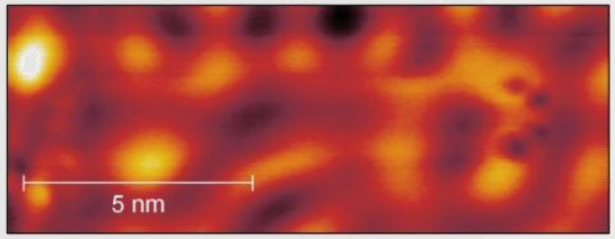


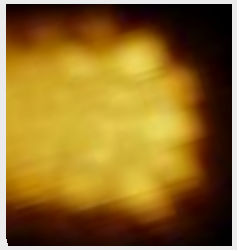
- dI/dV mapping of the ribbons
  - 'End state' at the zigzag ends of the ribbon close to the Dirac point
  - Increased intensity at the armchair edges of the ribbon far away from the Dirac point

**+0.05V**

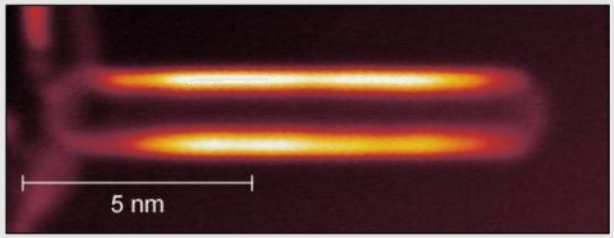



**-0.10V**

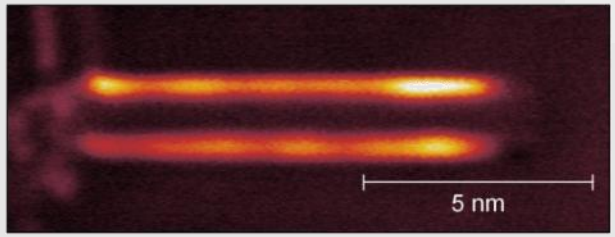


**+1.70V**

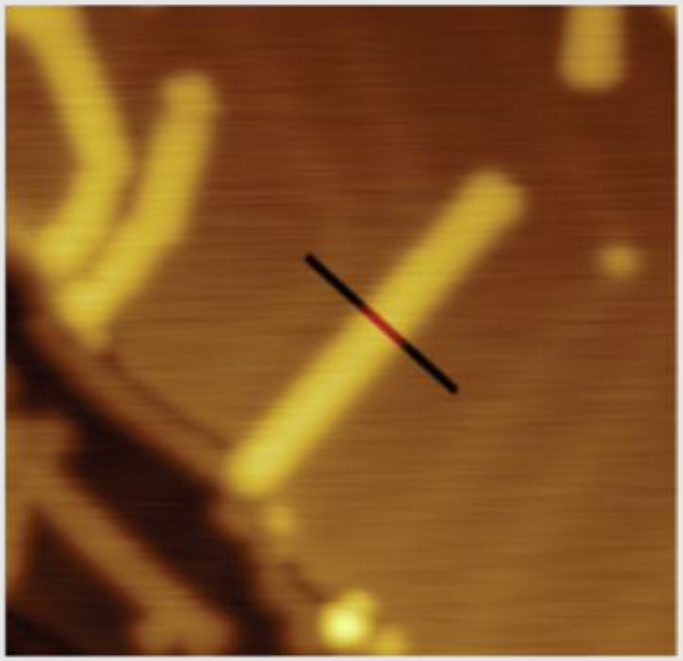


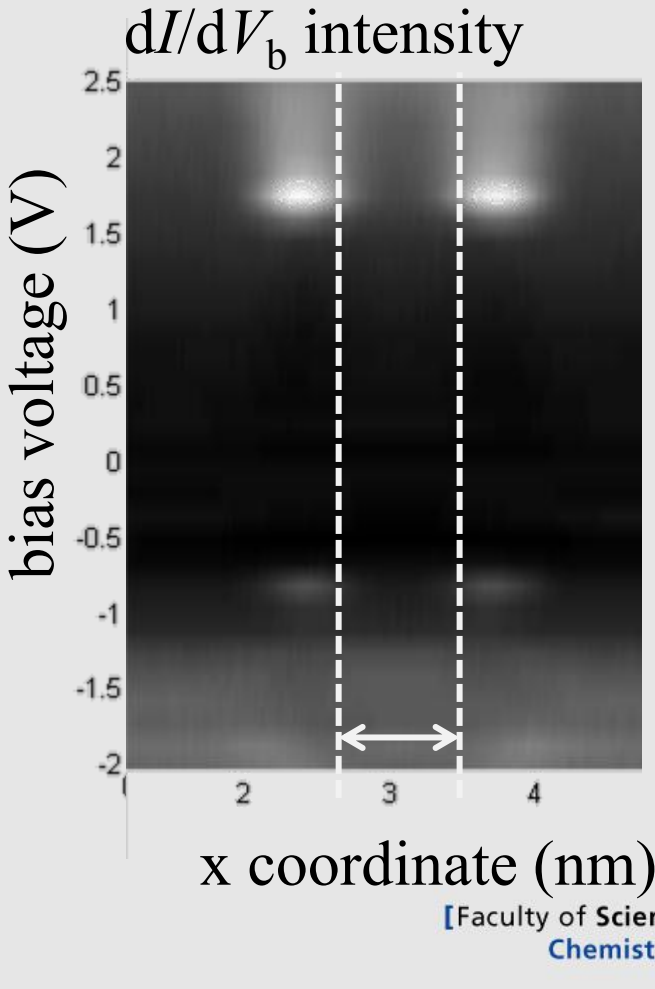

**-0.85V**



# Looking at the electronic structure

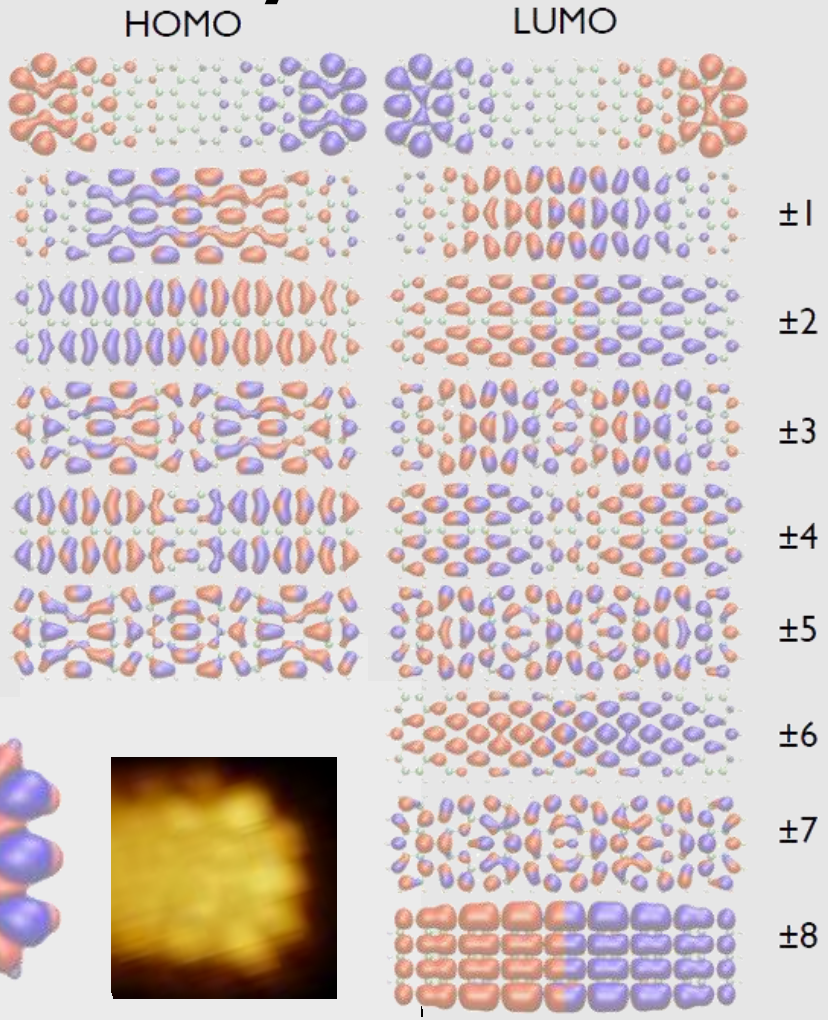
- Linescans of dI/dV as a function of V
- States along the armchair edges protrude atomic backbone



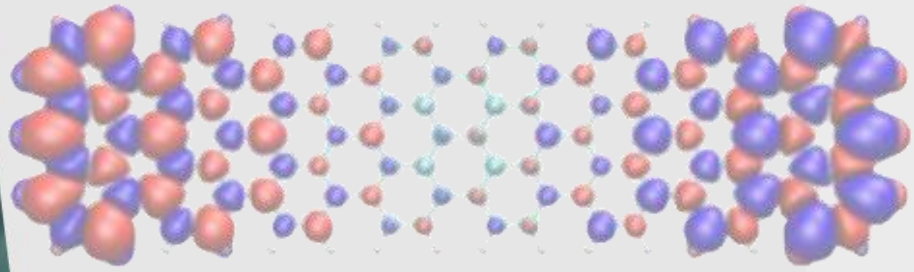


# What does DFT say?

- Comparison with DFT
  - In energy all states are spin degenerate
  - HOMO & LUMO localized at zigzag ends
  - Spin polarized

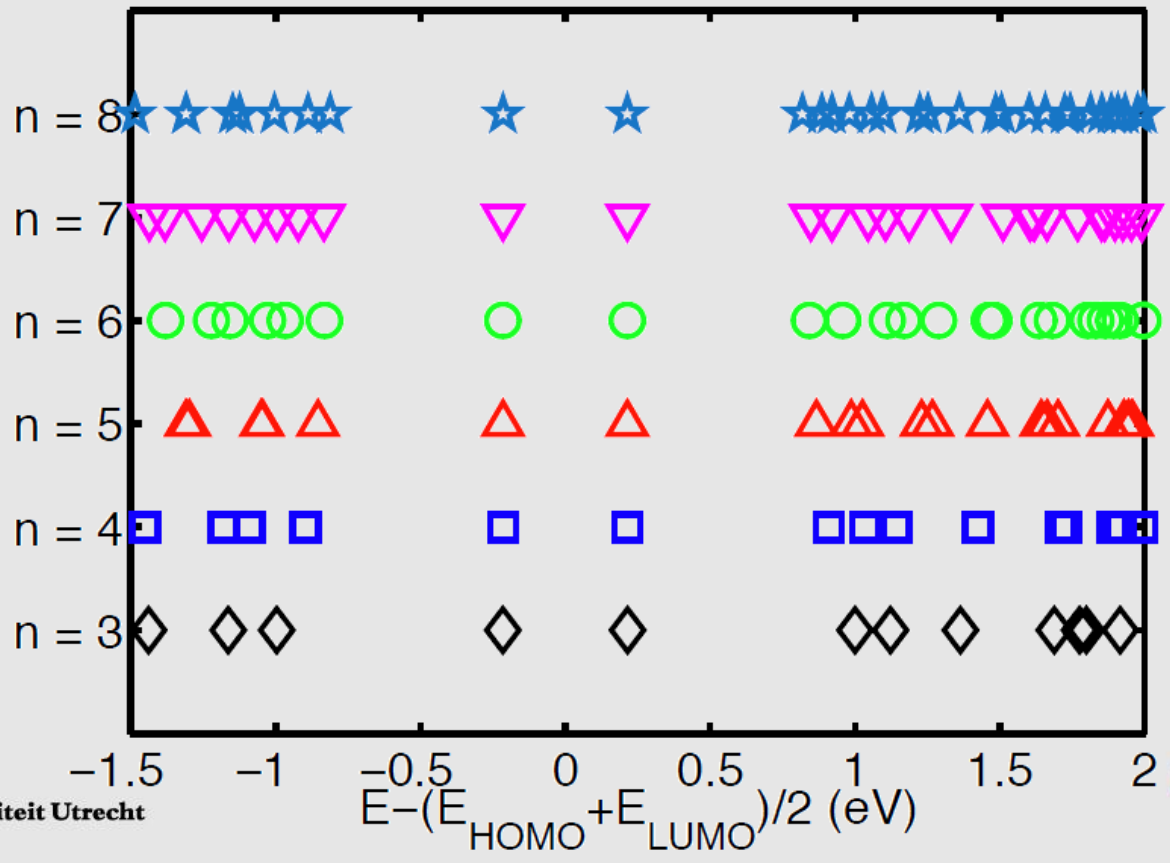



spin-density



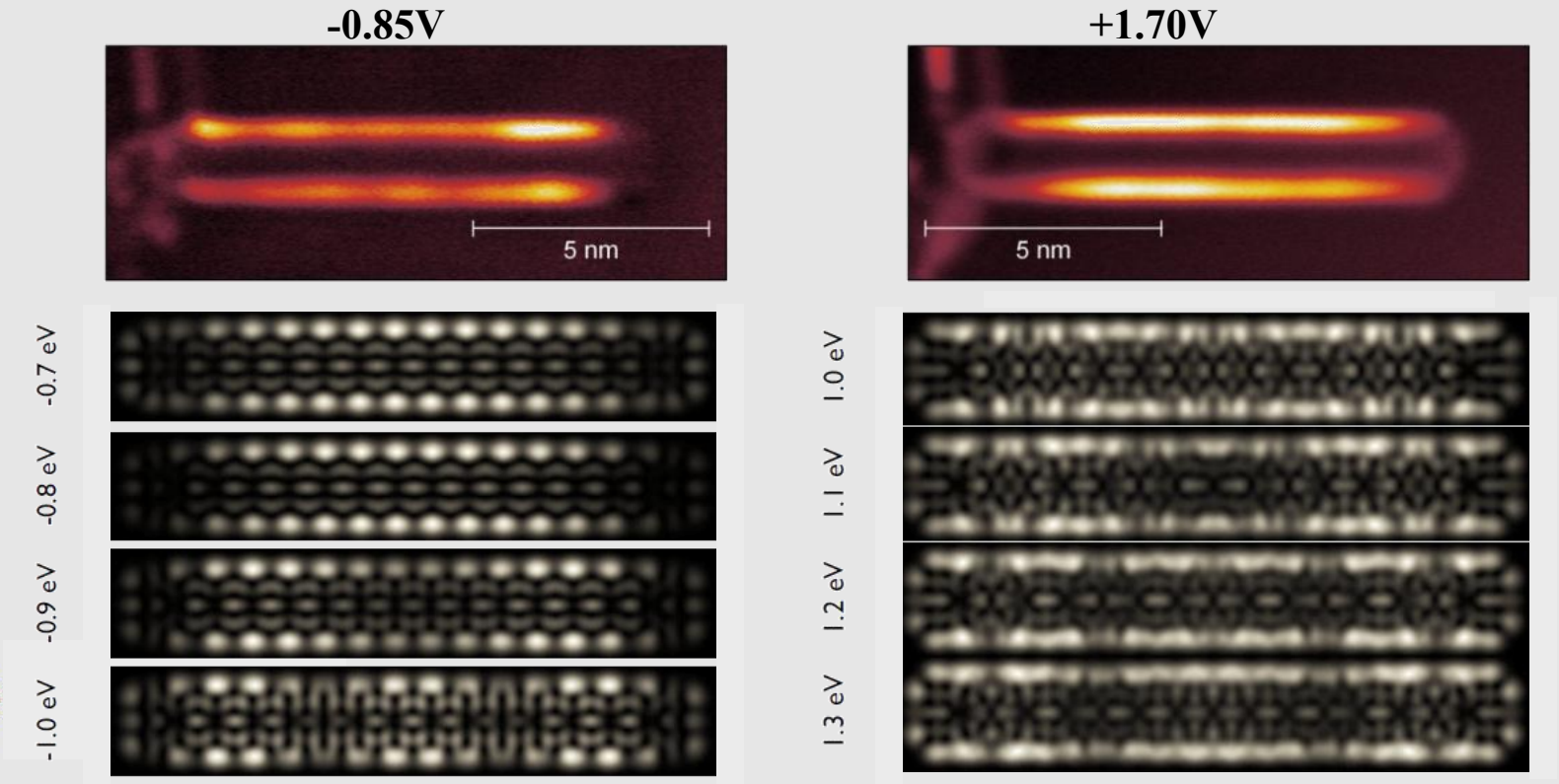
# Calculated energies

- End states ('HOMO/LUMO') are in the gap
- Relative dense spectrum



# Comparison LDOS maps with experiment

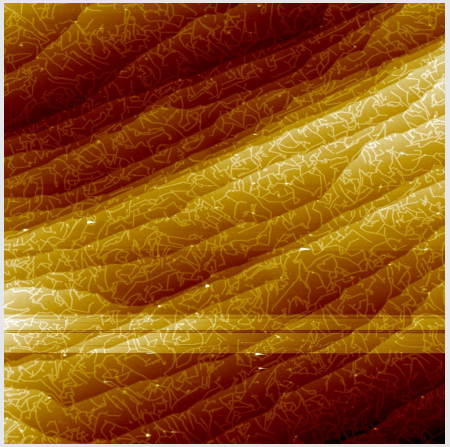
- Extension of wavefunctions into the vacuum
- Highest intensity protrude the atomic backbone
- Qualitative agreement with calculations



# Conclusions

- Chemical approaches allow control over edge shape and chemistry
- STM (nc-AFM) allows to simultaneously resolve the atomic positions and electronic properties of the graphene nanoribbons
- Zigzag ends of the ribbon show strongly localised states close to the Dirac point
  - According to DFT these states should have strong spin polarization
- States further away from the Dirac point are mainly localized at the armchair edge

# Questions



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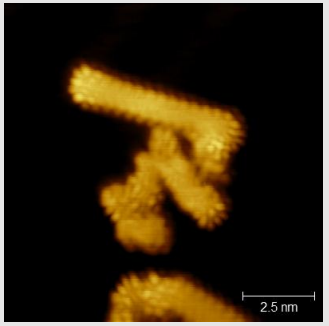


Further questions: M.P.Boneschanscher@uu.nl