Graphene edges and nanographene
- electronic structure and nanofabrications -

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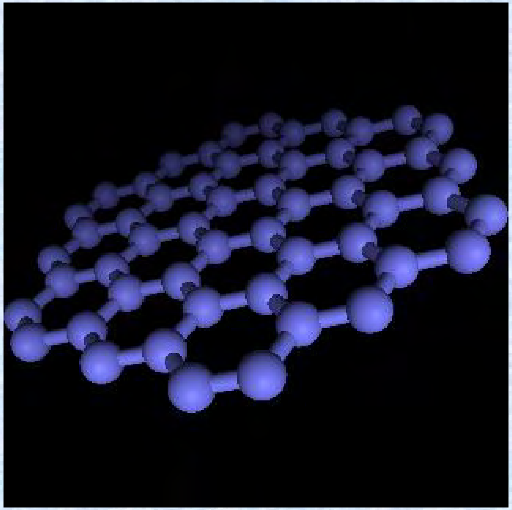
Carbon Materials for Today and Future Turkish-Japanese
Joint Symposium March 18-19, 2010
Istanbul Technical University, Istanbul, Turkey

nanographene



condensed polycyclic hydrocarbon molecules
extended to nano-dimension

electronic structure   shape dependent

edge state

electronic, magnetic, chemical activities

Outline

1. Introduction
   edge state in nanographene edges
   aromaticity in condensed polycyclic hydrocarbon

2. Preparation of nanographene and structural characterizations
   resonance Raman experiments

3. Experimental evidence of edge state
   scanning tunneling microscopy/spectroscopy (STM/STS)
   near edge x-ray absorption fine structure (NEXAFS)
   electron spin resonance (ESR)

4. Nanofabrications
   graphene oxide
   non-contact atomic force microscopy (AFM)

5. Conclusion

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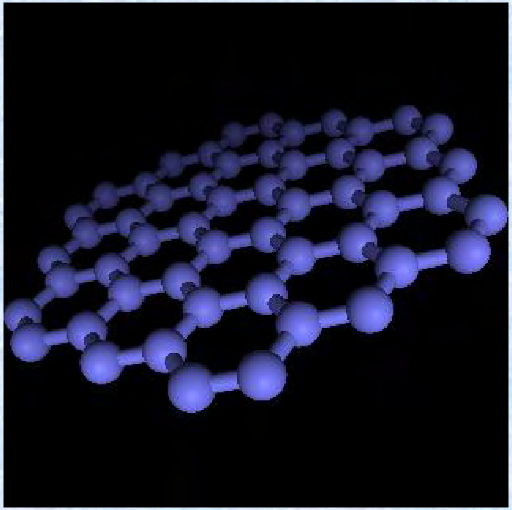
nanographene

open edge

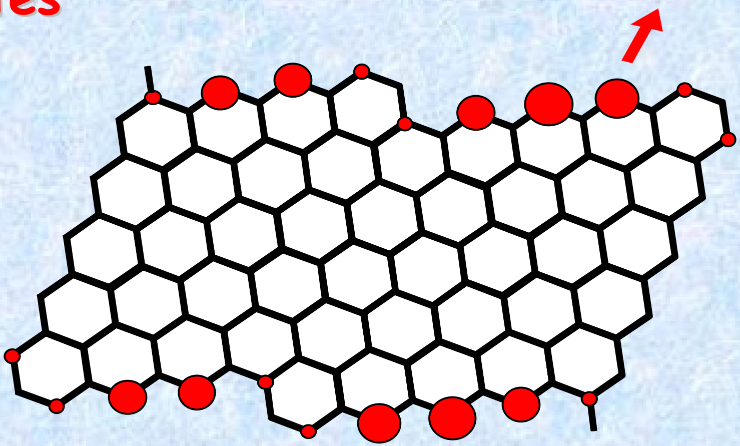
contrasted to other members;
graphene (infinite), nanotubes, fullerenes



nanographene

shape effect → edge states

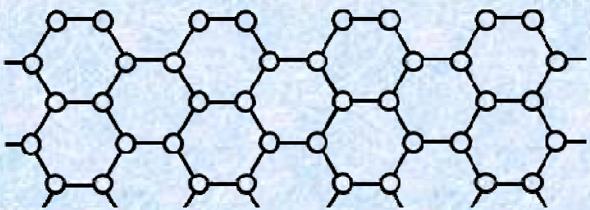
Yamabe et al.
Fujita, Wakabayashi et al.



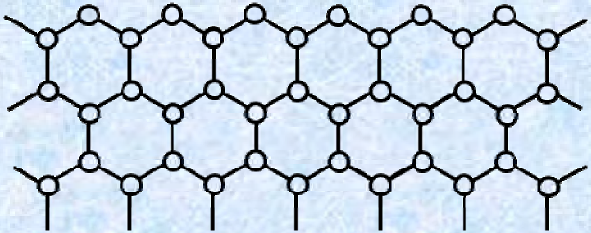
localized π-spins

↓

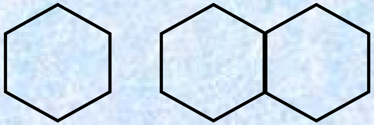
enhanced magnetism



armchair edge



zigzag edge

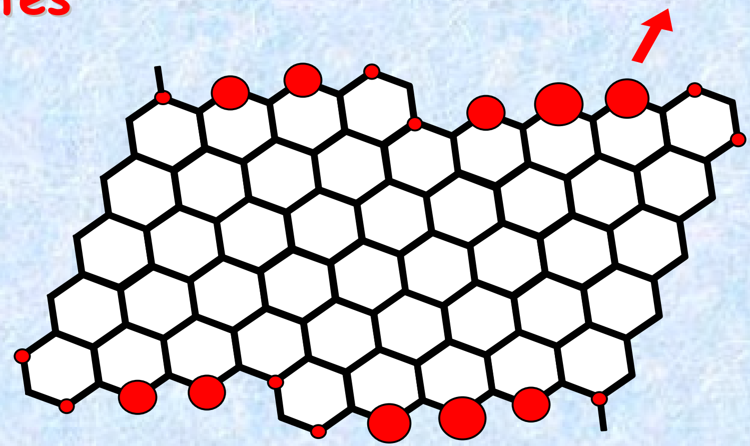


nonmagnetic
(Kékule structure)

nanographene

Yamabe et al.
Fujita, Wakabayashi et al.

shape effect → edge states



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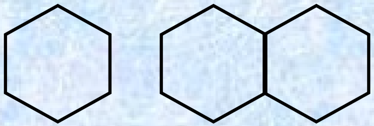
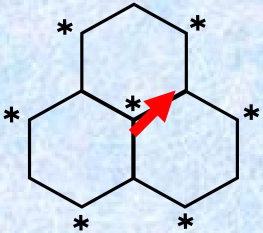
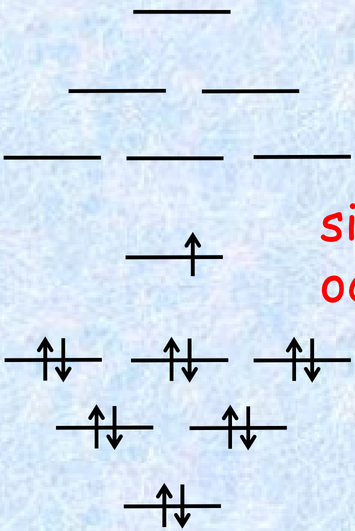


nonmagnetic
(Kékule structure)



non-Kékule structure
nonbonding π-state (s=1/2)

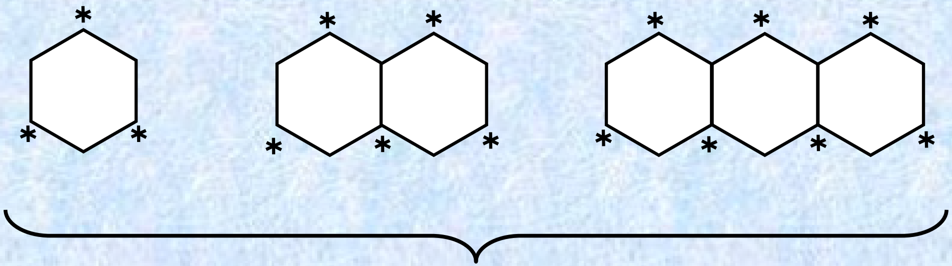


singly occupied

edge state ~ non-bonding π-state in hydrocarbon molecules

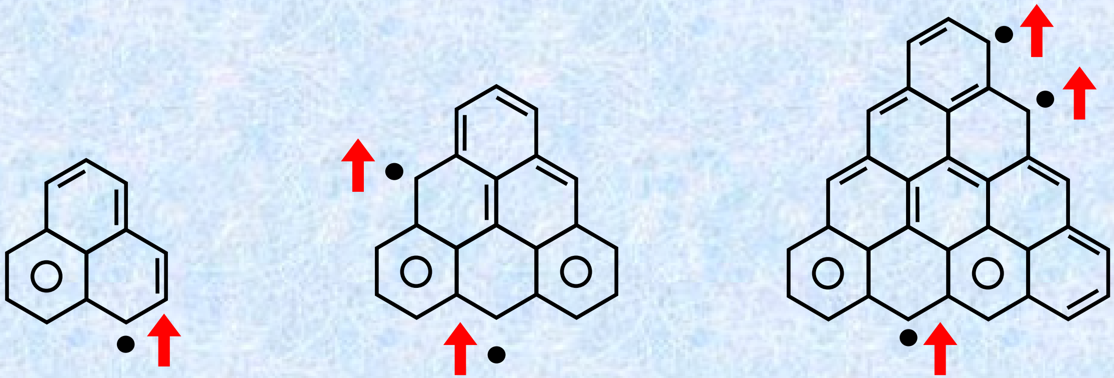
Lieb's theorem (No. of non-bonding π-states) = $|N_{*} - N_{un*}|$

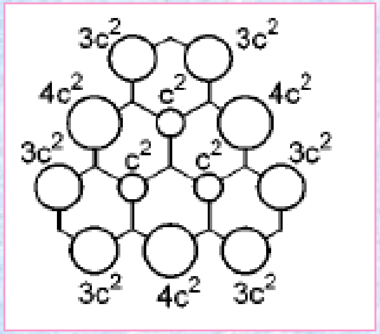
spin state $S = |N_{*} - N_{un*}|/2$ Hund rule



Kekulé molecules
nonmagnetic

$S = 0$ (0)





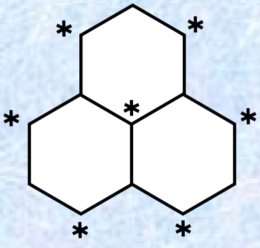
localized around
zigzag edges

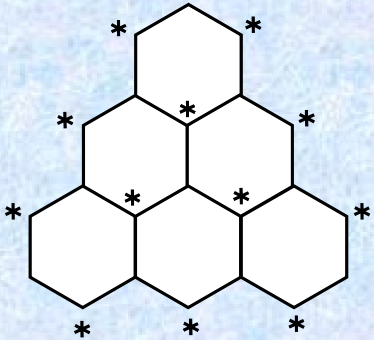
edge state ~ non-bonding π-state in hydrocarbon molecules

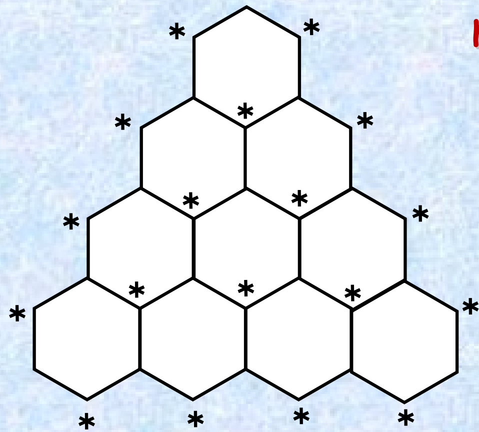
Lieb's theorem (No. of non-bonding π-states) = $|N_{*} - N_{un*}|$

spin state $S = |N_{*} - N_{un*}|/2$ Hund rule

non-Kekulé molecules
magnetic



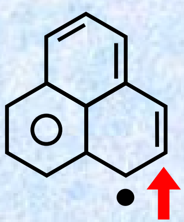


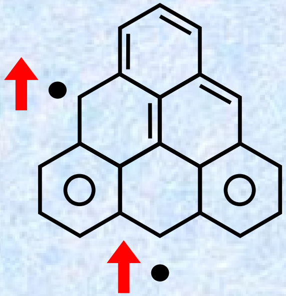


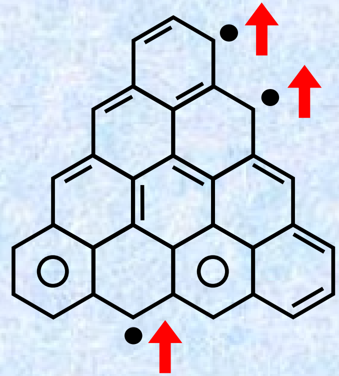
S = 1/2 (1)

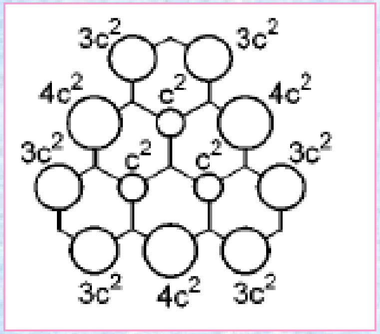
S = 1 (2)

S = 3/2 (3)









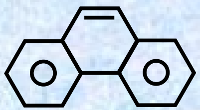
localized around
zigzag edges

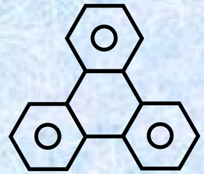
Clar's aromatic sextet rule (# of sextets)   most stable structure

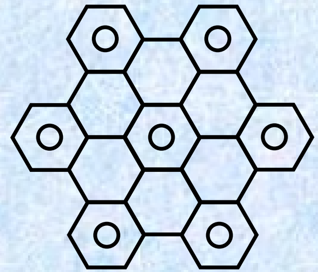
maximal number of the sextets separated by the entirely empty rings

aromatic Kekulé molecules


(1)

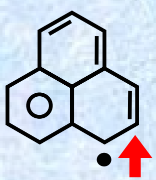

(2)

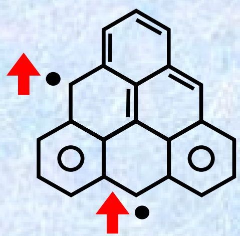

(3)

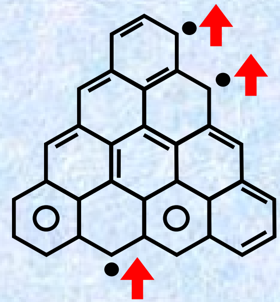

(7)

well stabilized

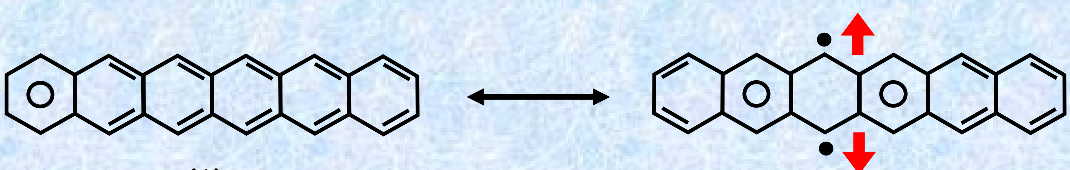
non Kekulé molecules (non-bonding π-state (π-radical))


S=1/2
(1)


S=1
(2)


S=3/2
(2)

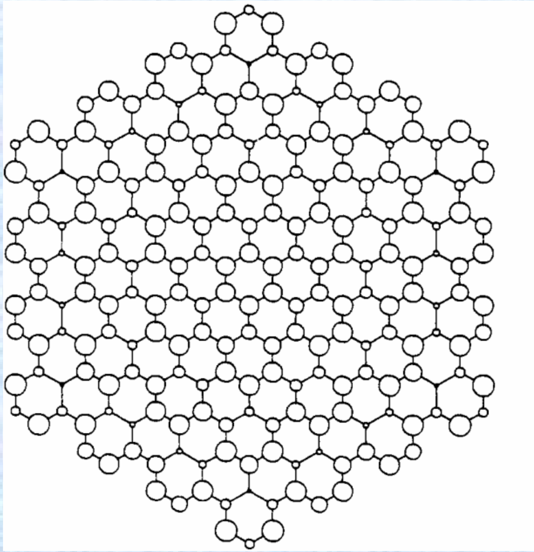
less stabilized
ferromagnetic


(1)

less stabilized
antiferromagnetic
(open shell singlet)

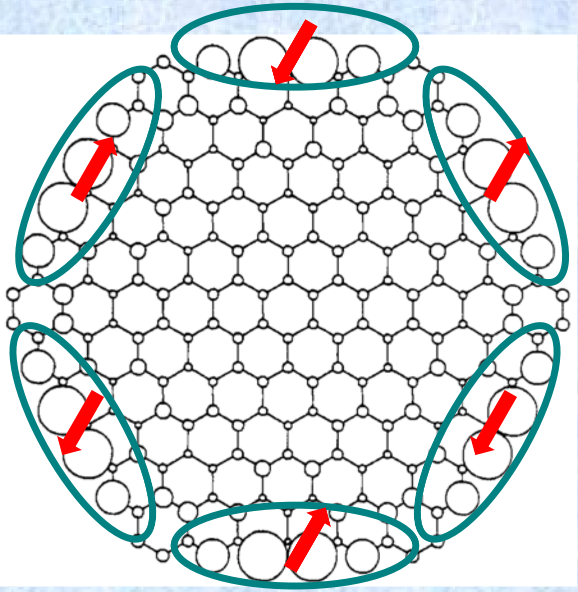
spatial distributions of the HOMO levels
for armchair-edged and zigzag-edged nanographene sheets

Stein & Brown, *JACS* (1986)



armchair-edged

uniform
distribution

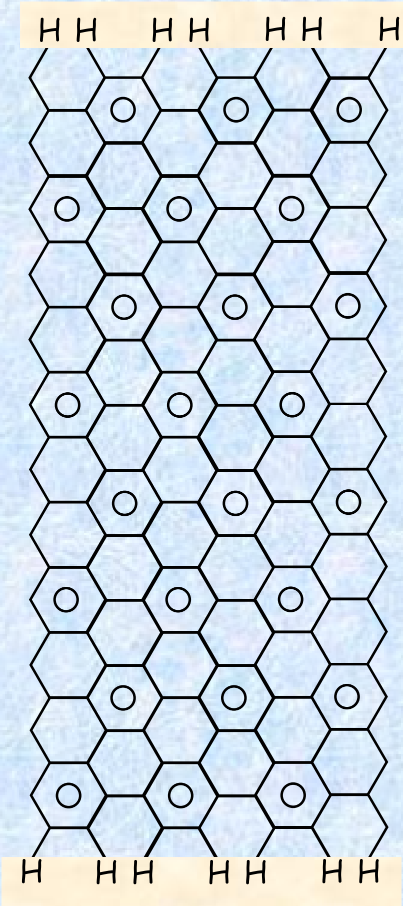


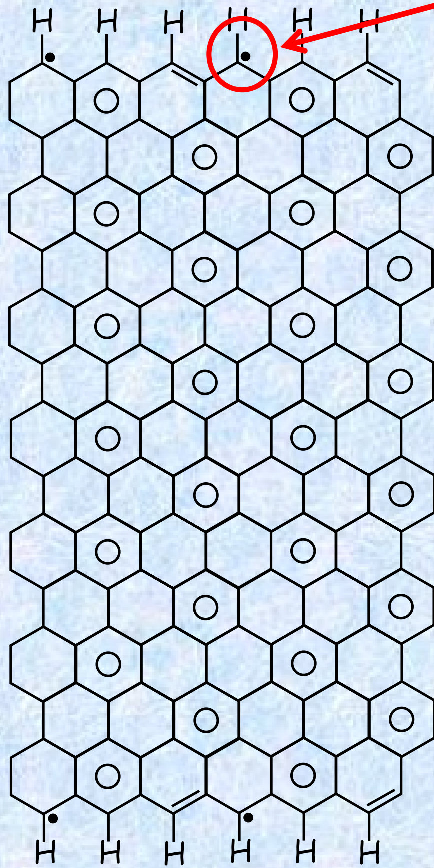
zigzag-edged

non-bonding π-state (edge state) in the zigzag edges

unconventional nanographene-based magnetism

nanographene ribbon Clar's sextet formula





radical spins at zigzag edges

magnetically
electronically
chemically
active

$\sqrt{3}\times\sqrt{3}$ superlattice in the interior

armchair edge

same to infinite graphene

nonmagnetic

zigzag edge

magnetic (edge-state spins)

Wassmann, Mauri, et al. *JACS* (2010)

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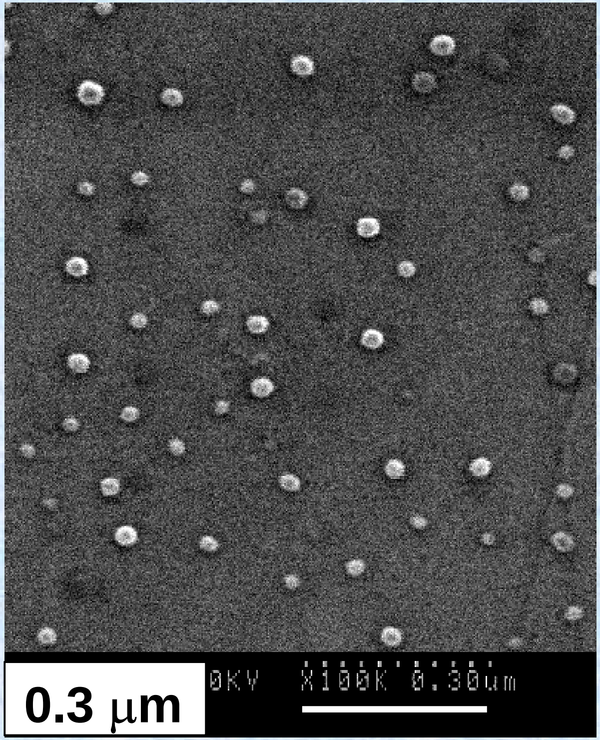
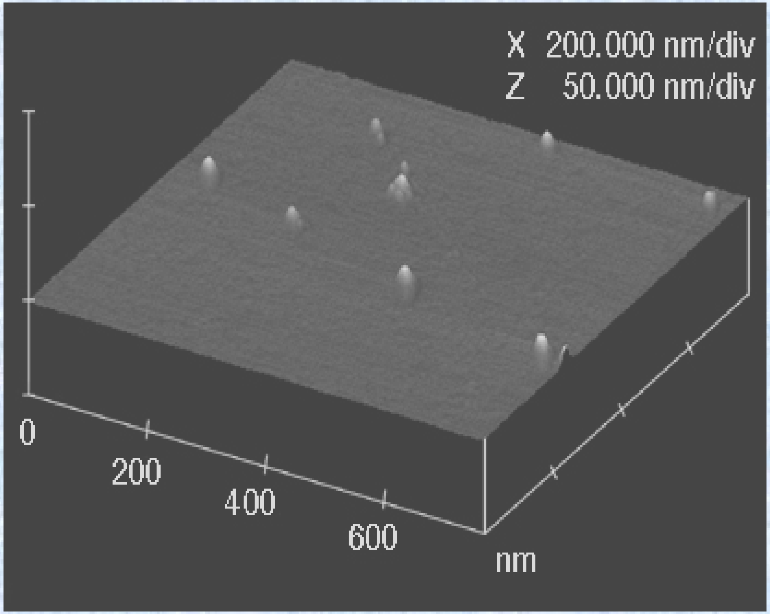
nanodiamond particles deposited by electrophoretic technique

Affoune, Enoki, et al. *Chem. Phys. Lett.* (2000)

SEM image



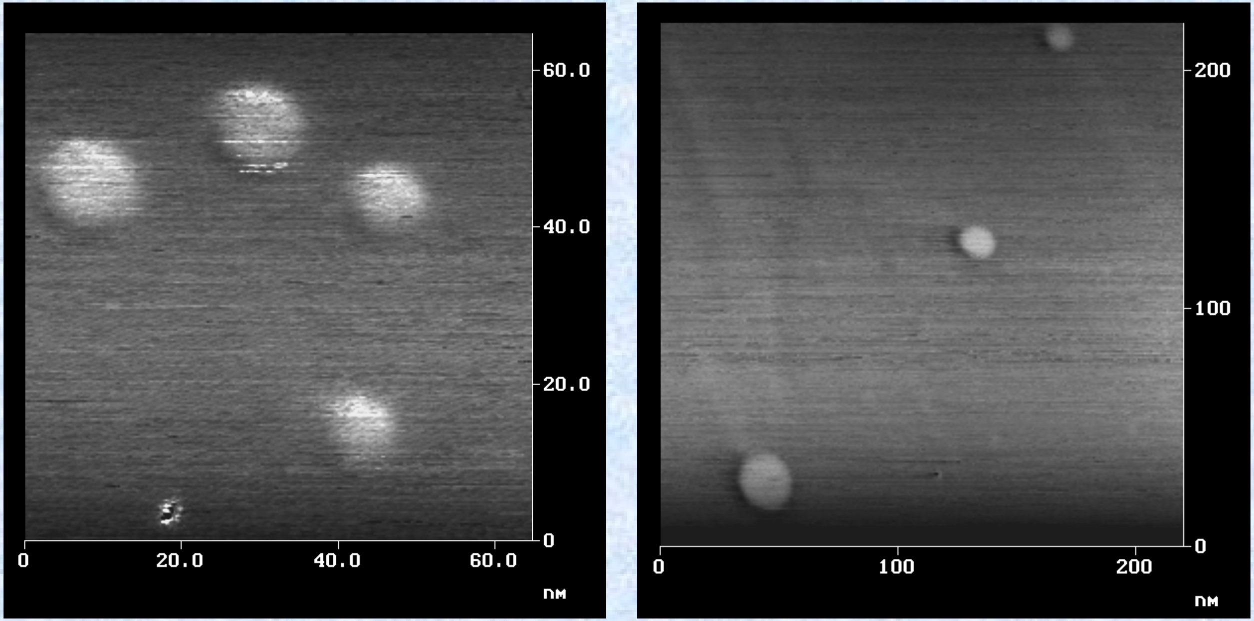
AFM image



spherical shape with particle sizes (several 10 nm) larger than those observed for the primary particles by TEM (5 nm)

absorbed solvent molecules on the surface of particles

nanographene and STM analysis

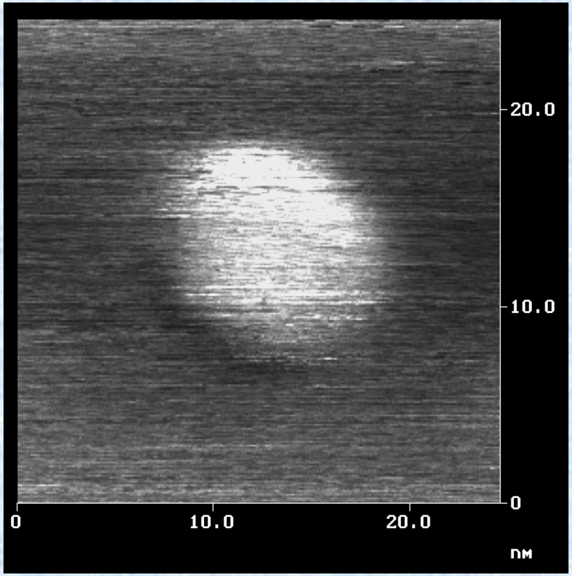


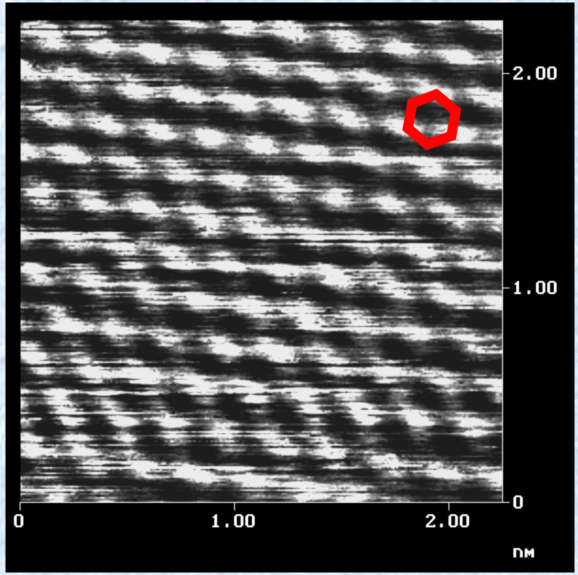
STM images after heat-treatment at 1600 °C in Ar atmosphere

nanographene ⟹ flat single layer sheet

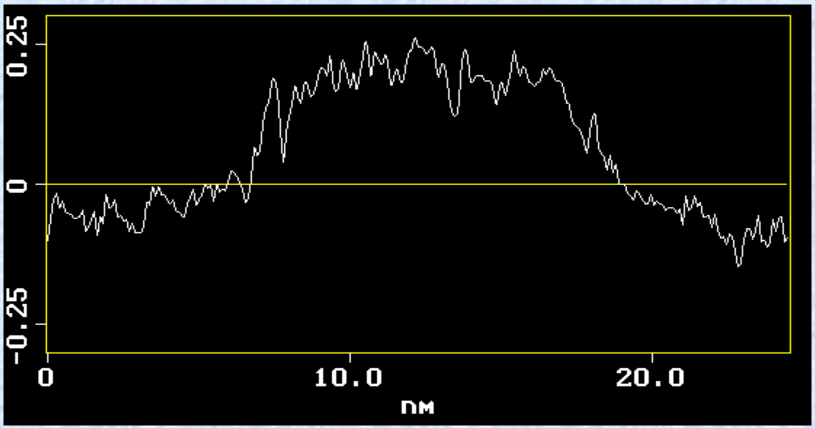
mean in-plane size of 10 nm

nanographene on HOPG substrate and STM Analysis

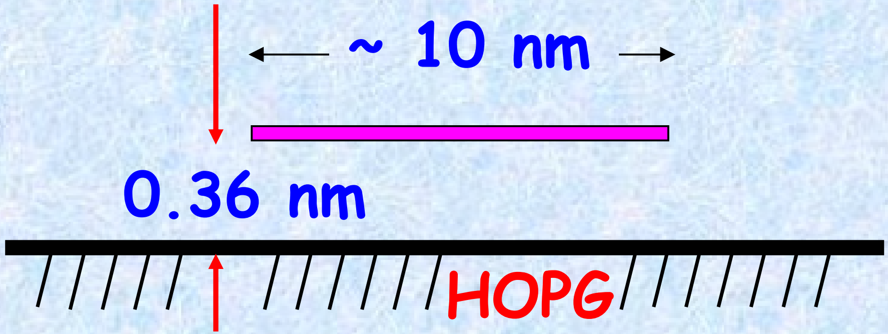




current image



cross-sectional profile



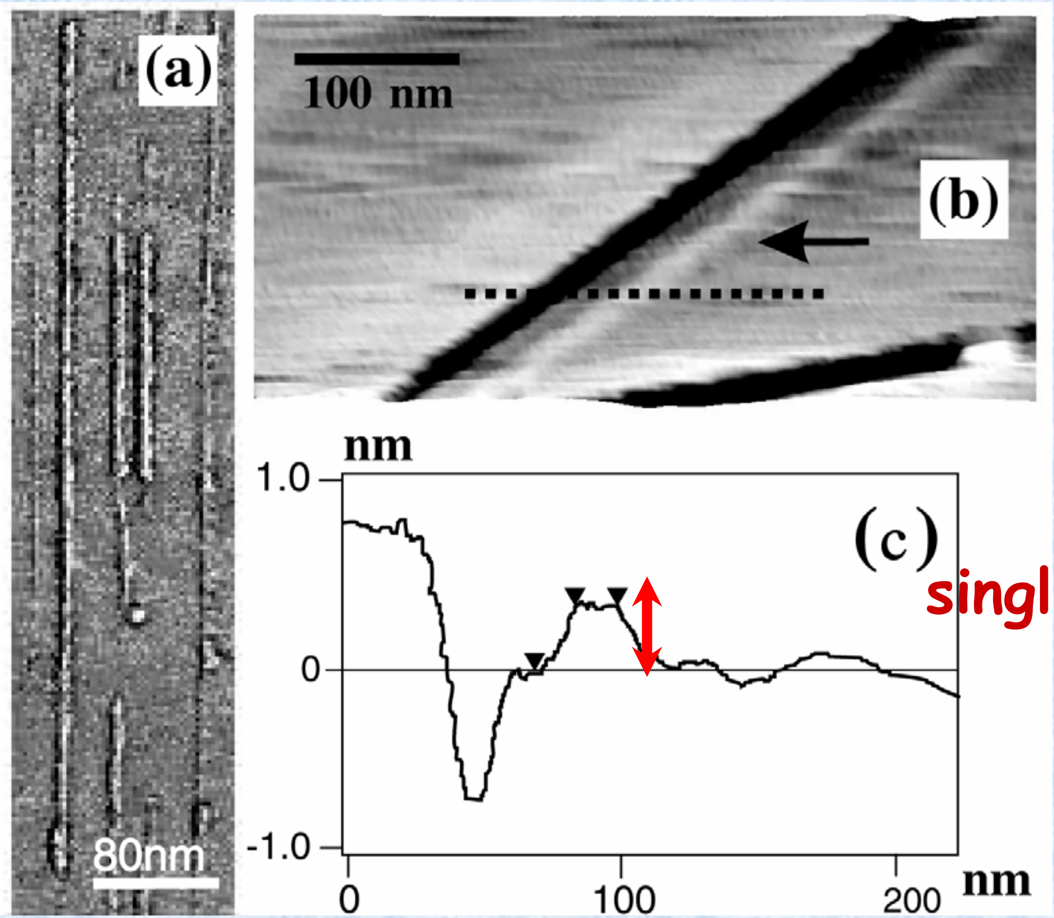
monolayer of nanographene

nanographene ribbon observed by resonance Raman experiments

Cançado, Enoki, et al., *PRL* (2003)

AFM image of single nanographene ribbon

single sheet of nanographene ribbon at a step edge

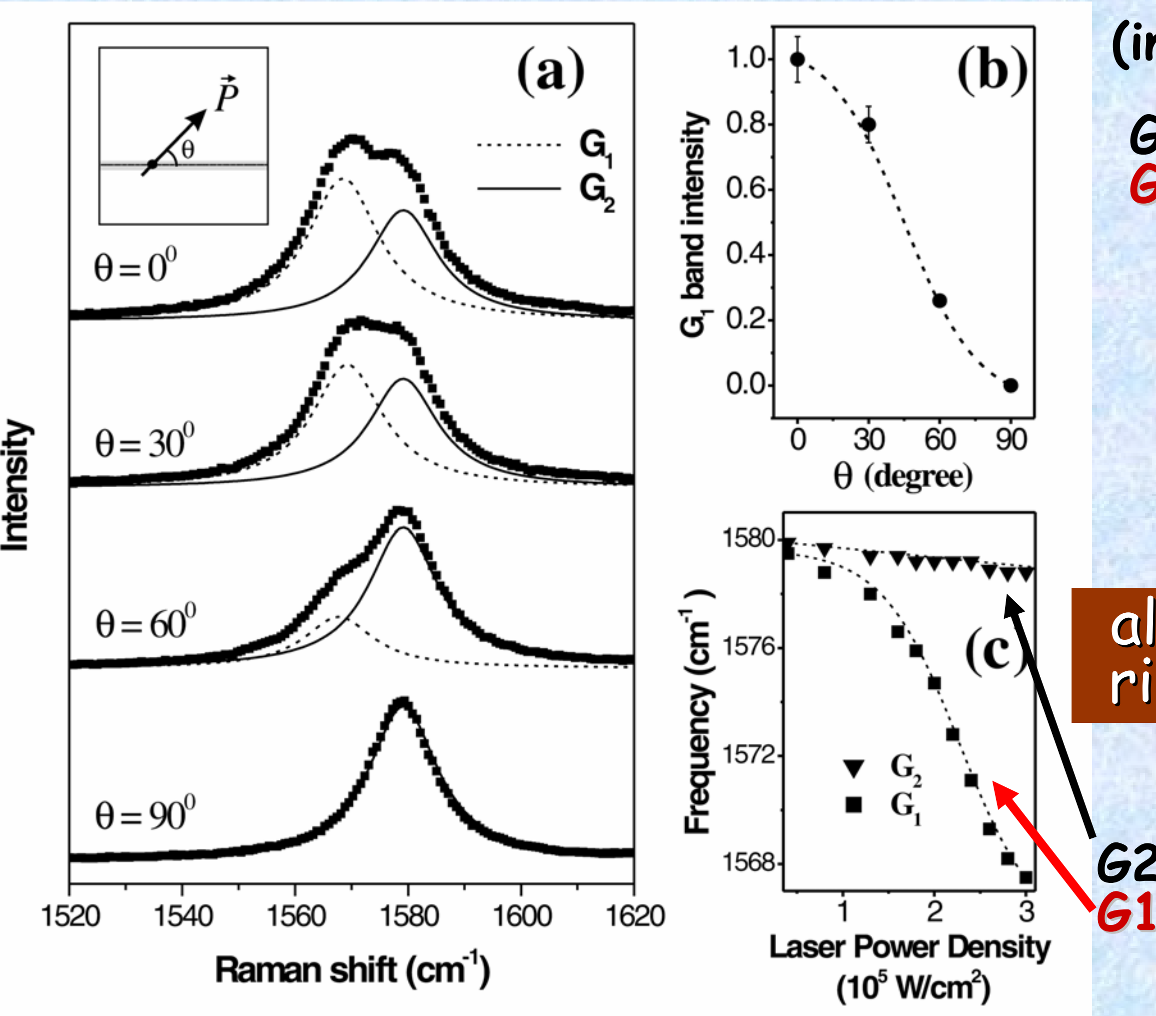


single sheet

ribbon size

8 nm x >1 μm

Resonance Raman experiments with polarized light

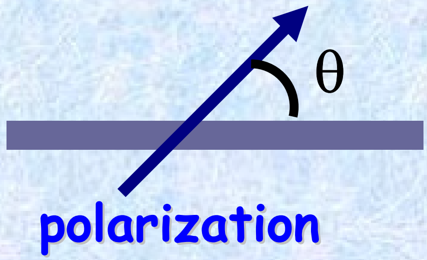


G band

(intralayer C-C stretching)

G2: substrate HOPG

G1: nanographene ribbon



alignments of individual ribbons are determined

small nanographene ribbon can be easily heated by light

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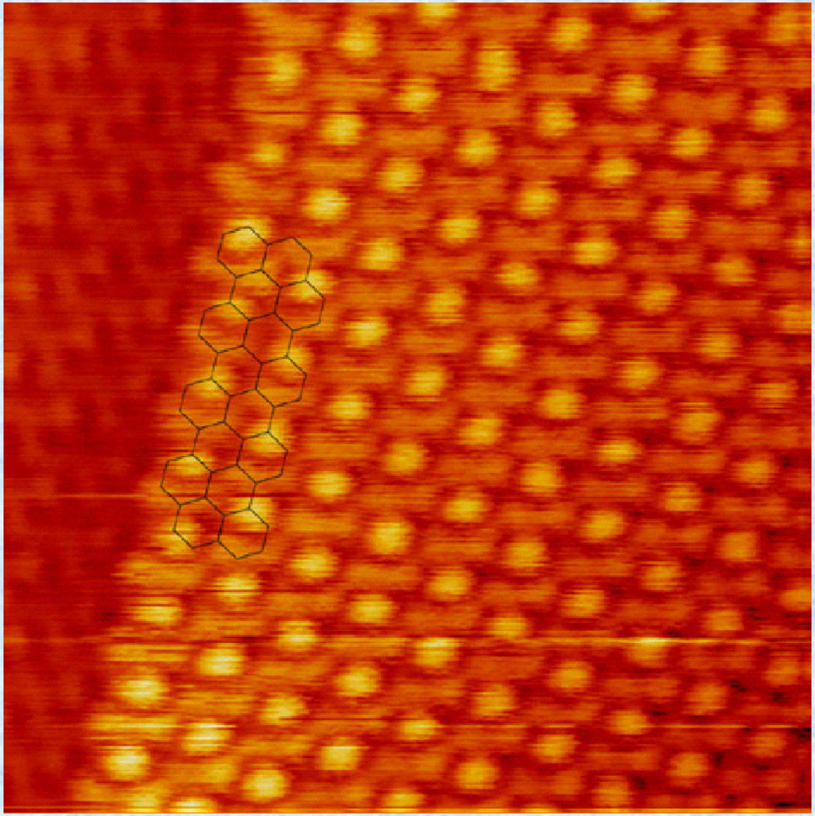
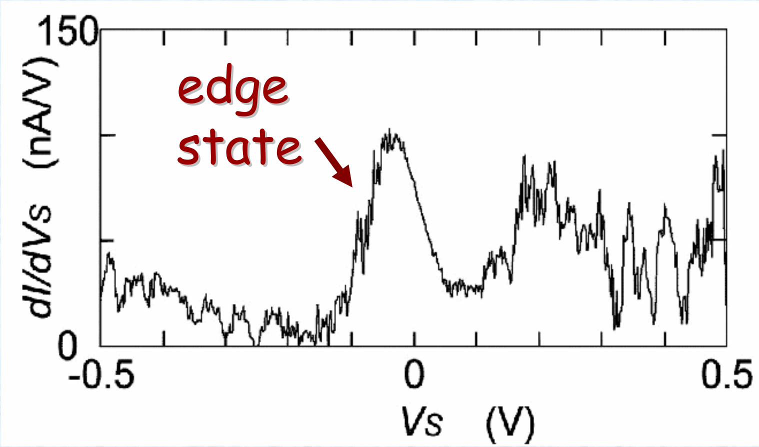
electronic state of graphene edges

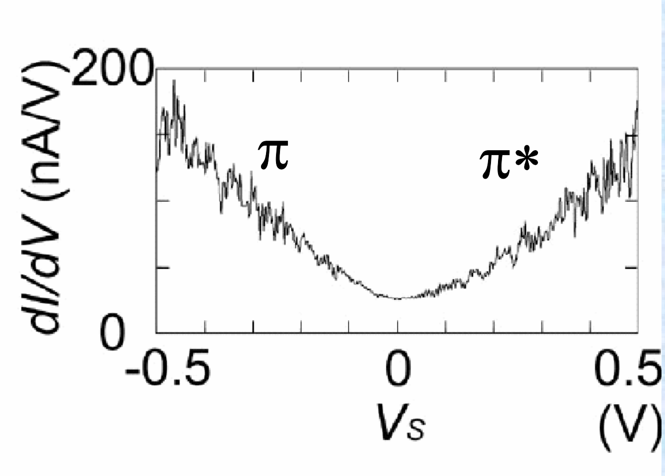
experimental evidence of edge state



zigzag edge



armchair edge

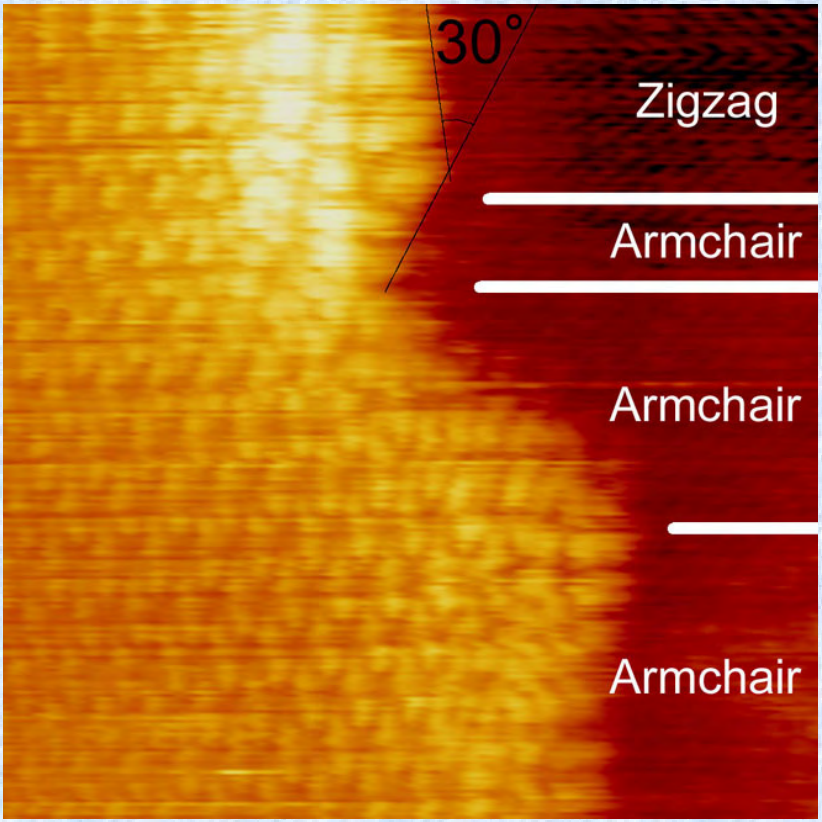


zigzag edge: short and defective, energetically unstable

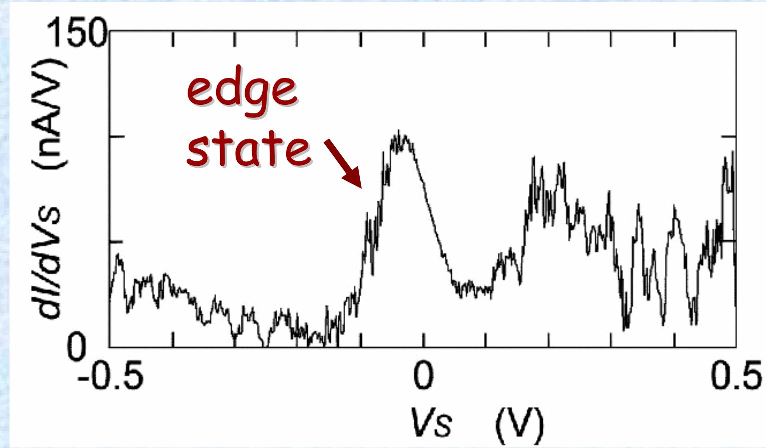
Kobayashi, Enoki, et al., *PRB* (2005)

electronic state of graphene edges

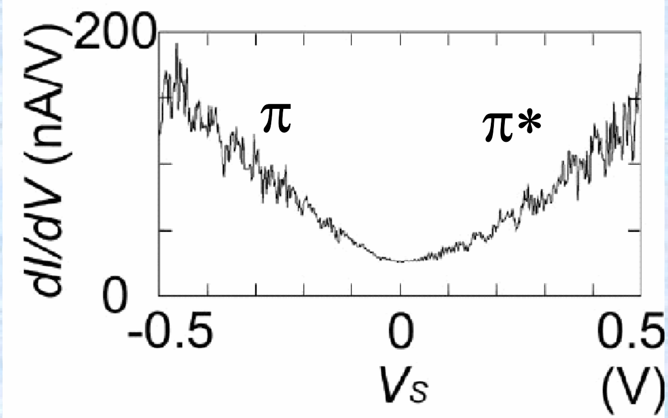
experimental evidence of edge state



zigzag edge



armchair edge

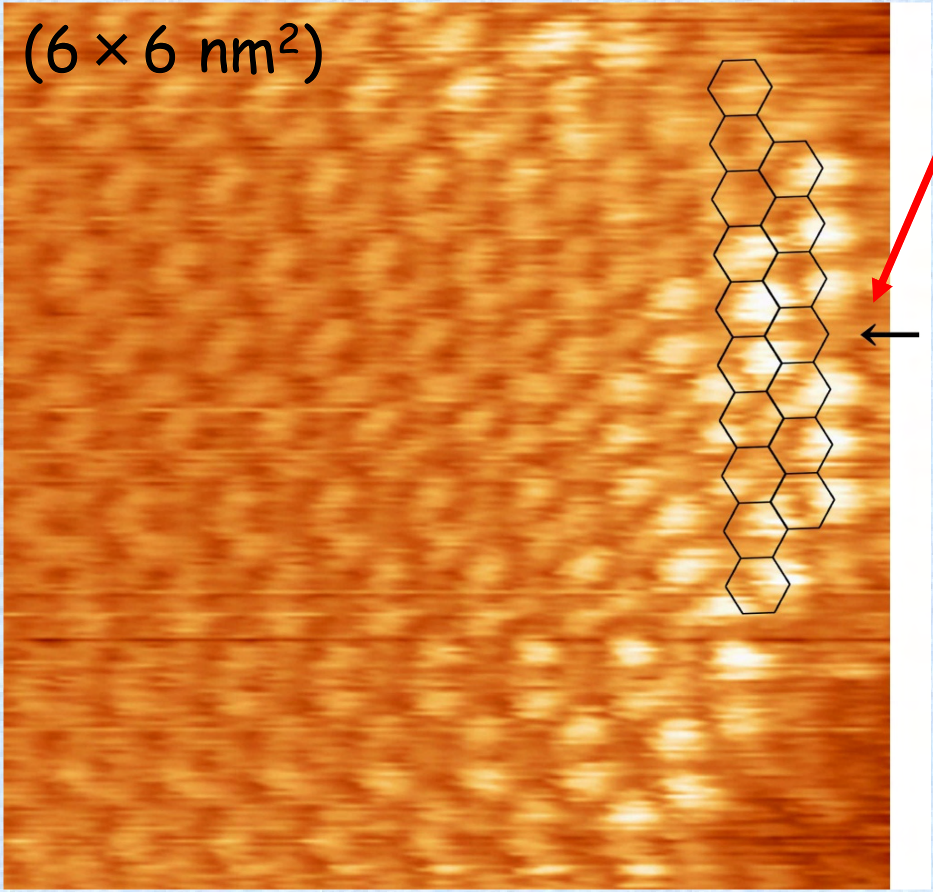


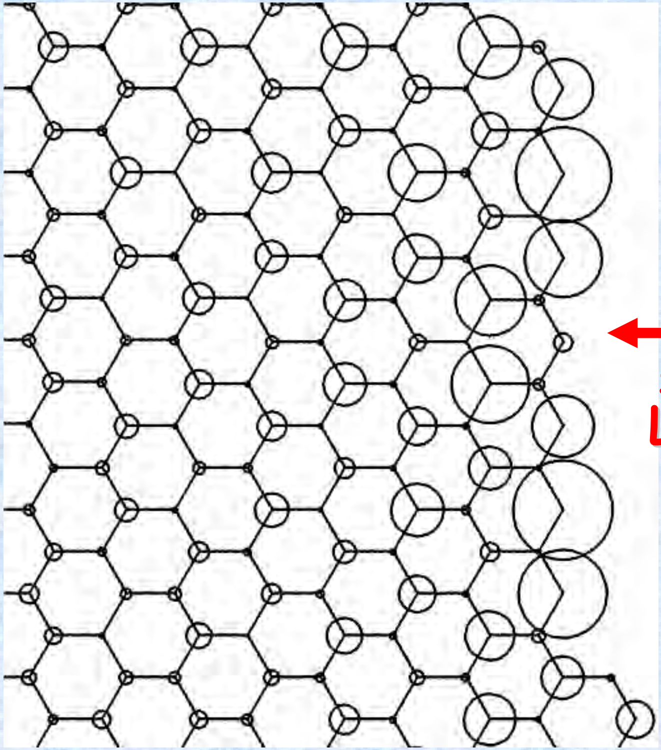
zigzag edge: short and defective, energetically unstable

Kobayashi, Enoki, et al., *PRB* (2005)

electron confinement effect in zigzag edges

edge-state-absent site at zigzag edge
(small local density of states (LDOS))





small
LDOS

node of the wave function

Kobayashi, Enoki, et al., *PRB* (2006)

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Conclusion

nanographene

non-bonding π-electron state (edge state)

↓

graphene edges

electronic, magnetic, chemical activities

nanoscopic graphene-based magnetism

various types

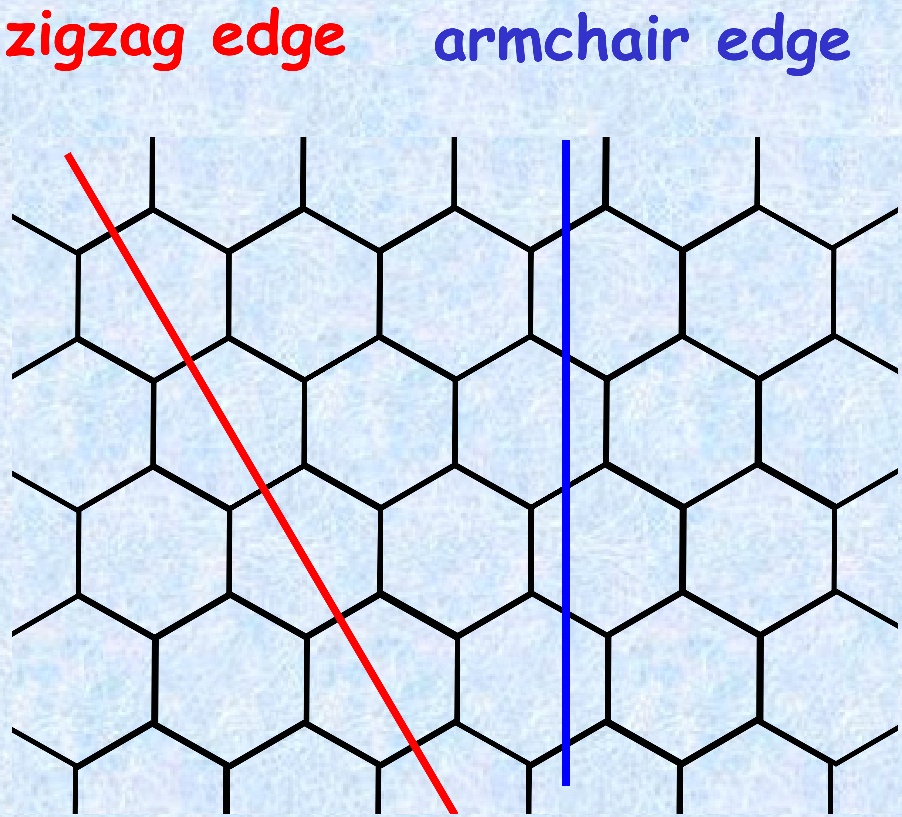
ferromagnetic/antiferromagnetic/ferrimagnetic

magnetic functions

gas adsorption induced magnetic switching, He sensor

nanofabrications with microprobe techniques

nanographene-based molecular devices



electron beam lthography

zigzag magnetic line

armchair nonmagnetic line

chemical modifications

CH itinerant magnetism

CH_2 localized magnetism

CF nonmagnetic

C=O conducting line

chemical functions

future promising molecular devices

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SURFACE SCIENCE
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