Graphene Edges; Unconventional Electronic and Magnetic Properties

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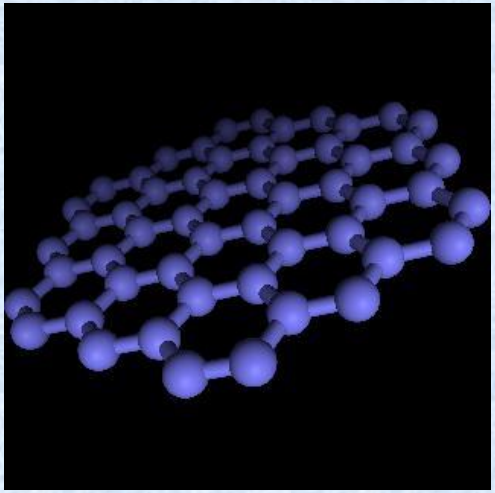
Tokyo Institute of Technology



nanographene edge

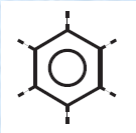
Fundamental Aspects of Graphene and Other Carbon Allotropes"
Kavli Inst. for Theor. Phys., Univ. of California, Santa Barbara
January 9 - 13, 2012

graphene and edge effect for chemists and physicists

chemistry aspect

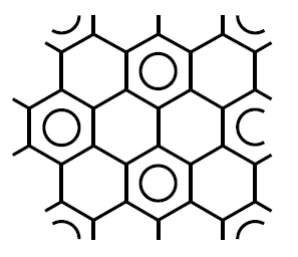
aromaticity

Clar's aromatic sextet rule



aromatic sextet

graphene



aromaticity 1/3

chemically active

physics aspect

massless Dirac fermion (relativistic wave equation)

in the bipartite lattice

zero-gap semiconductor
with linear bands ($\propto \mathbf{p}$)

$$\mathscr{H} = v_F \sigma \mathbf{p}$$

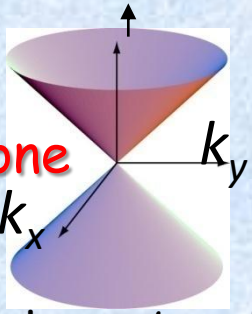
momentum $\mathbf{p}$

Fermi velocity $v_F \approx (1/300)c$

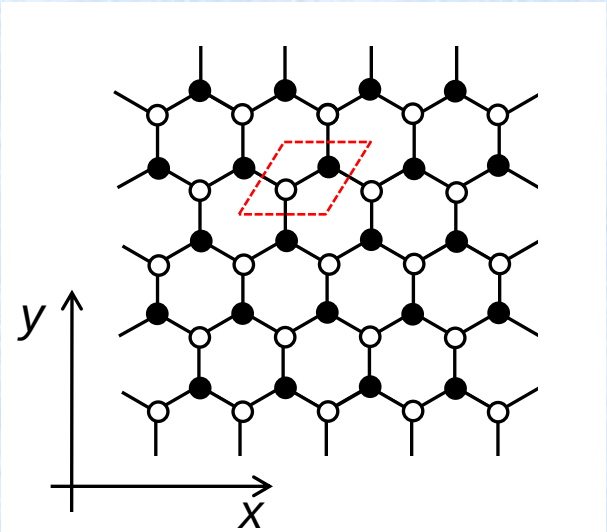
pseudo-spin σ ⬆⬇

degree of freedom; 2

conduction band



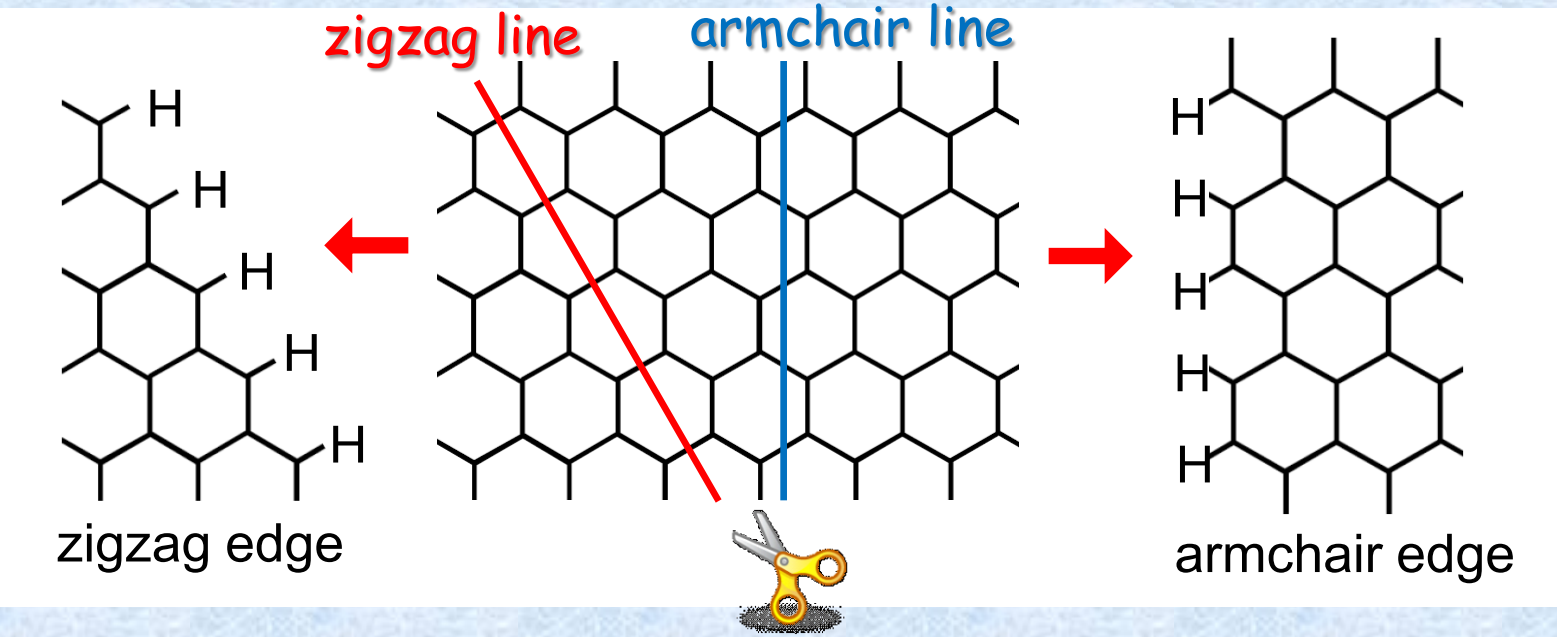
valence band

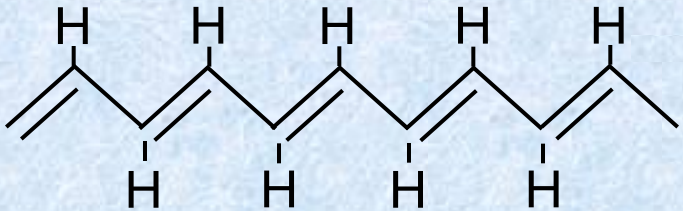


two sublattices A; ●, B; ○

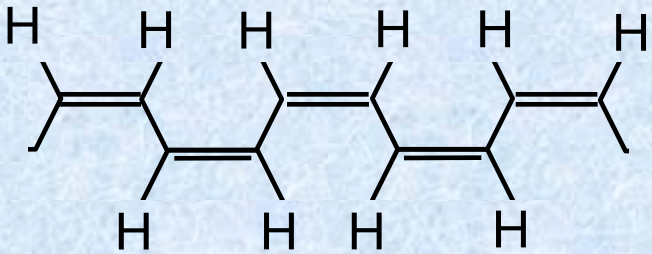
two sites in the unit cell

cutting a graphene sheet and terminating edge carbon atoms by hydrogen





trans-polyacetylene



cis-polyacetylene

Edge modifies the electronic structure in two manners

edge shape dependent (zigzag/armchair)

electron scattering/interference at the edge

superlattice pattern (STM)

Raman G-band (C-C stretching; 1600 cm^{-1})

localized non-bondings π state at the edge (edge state)

Outline

1. Edge state at **zigzag edge** and the magnetic structure of edge-state spins

   # spin-polarized edge state

   from theoretical and experimental understandings

   # what is the difference in the magnetic structure between the edge-state spins of π-electron origin and the σ-dangling bond spins

   nanographene (π) and fluorinated nanogrphene ($\pi+\sigma$)

2. Electron wave interference at **armchair edge**

   # resonance Raman G-band of armichair-edged graphene nanoribbons

   # STM superlattice and its fine structure in the vicinity of edge

3. Nanofabrication

   # graphene oxide, AFM tip **zigzag**-edged graphene nanoribbons

4. Conclusion

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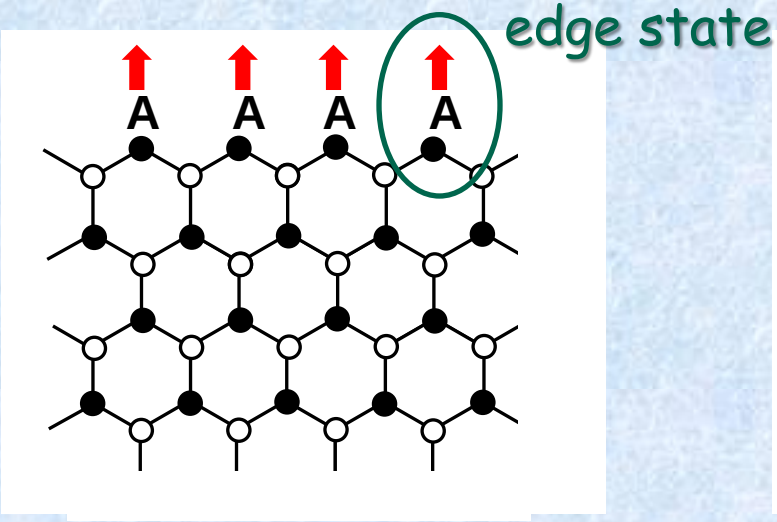
4. Conclusion

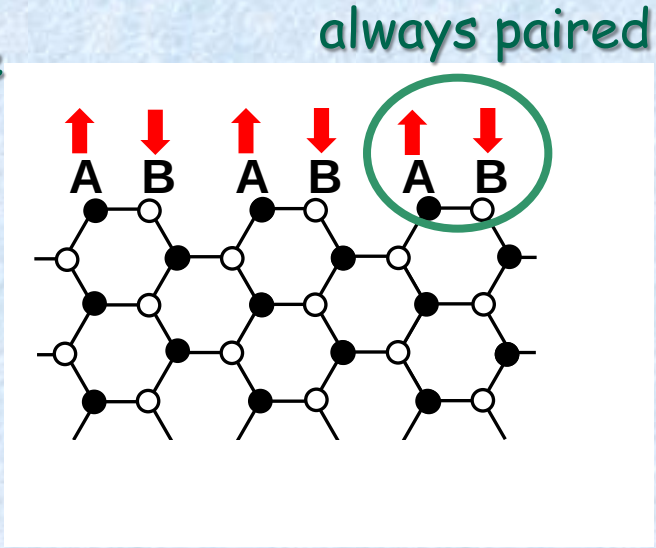
edge state

T. Enoki, S. Fujii, K. Takai, M. Kiguchi, *Bull. Chem. Soc. Jpn.*, (2012), in press.
T. Enoki, *Eur. Phys. Lett.*, (2012), in press.
T. Enoki, *Proc. Nobel Symp. on Graphene and Quantum Matters*, (2012), in press.
S. Fujii and T. Enoki, J. *Amer. Chem. Soc.*, (2012), submitted.

How physicists understand the edge state



zigzag edge



armchair edge

edge state (magnetic)

only one of the sublattices (A, B) exists in the zigzag edge

broken symmetry of the pseudo-spin ↑ in Dirac fermion

Clar's aromatic sextet rule (# of sextets)

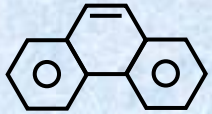
most stable structure

maximal number of the sextets separated by the entirely empty rings

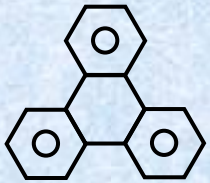
aromatic Kekulé molecules

armchair shaped

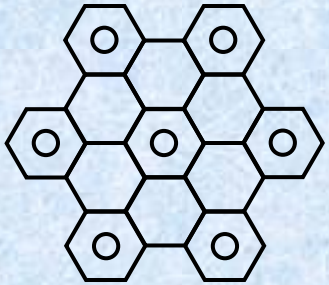
(1)



(2)

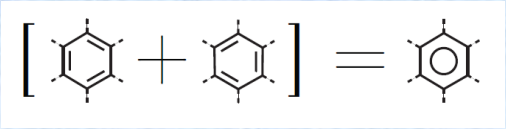


(3)



(7)

well stabilized

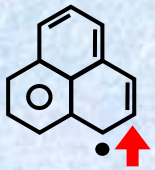


sextet

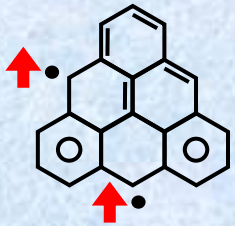
benzene ring with C atoms singly bonded to the surrounding

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

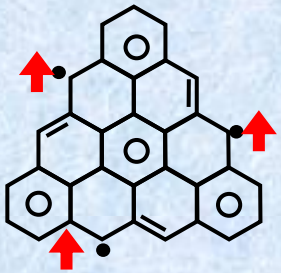
zigzag shaped



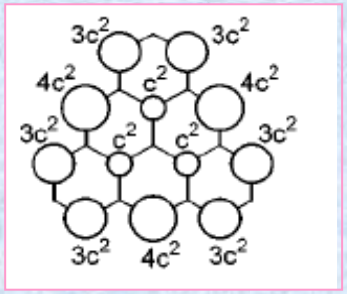
S=1/2
(1)



S=1
(2)



S=3/2
(4)

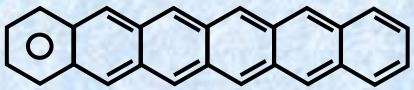


localized around zigzag edges

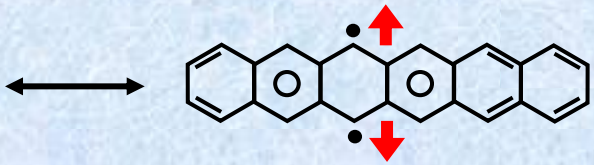
less stabilized ferromagnetic

Hund rule

less stabilized antiferromagnetic (open shell singlet)



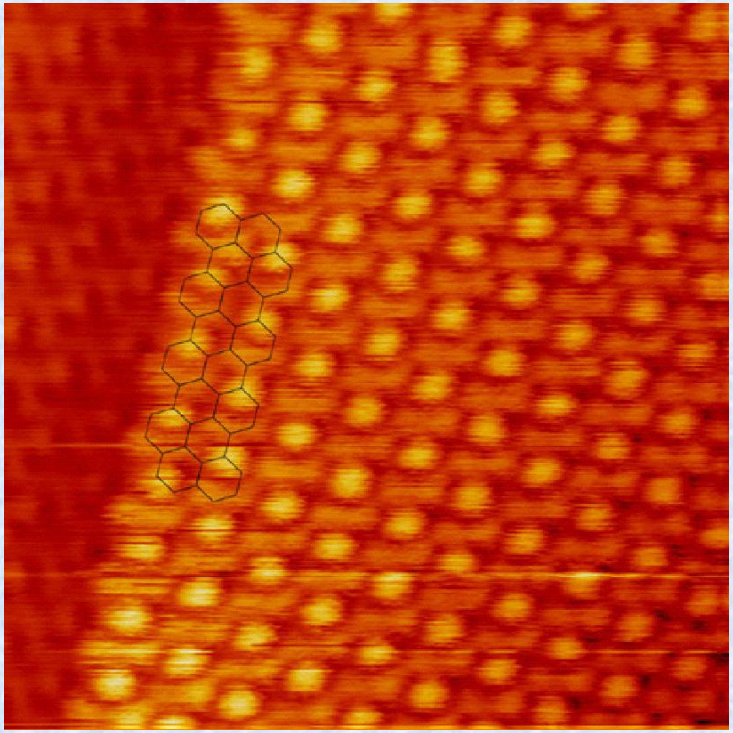
(1)

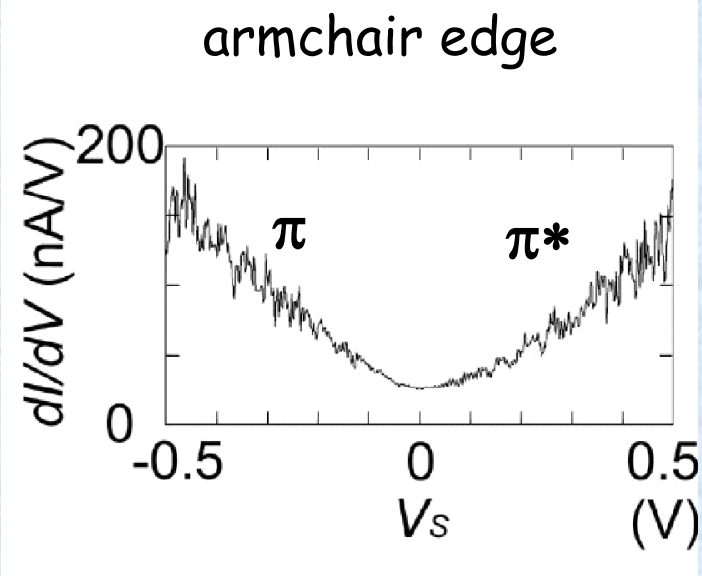


edge state

electronic state of graphene edges
hydrogen-terminated

experimental evidence of edge state (ultra-high vacuum-STM/STS)



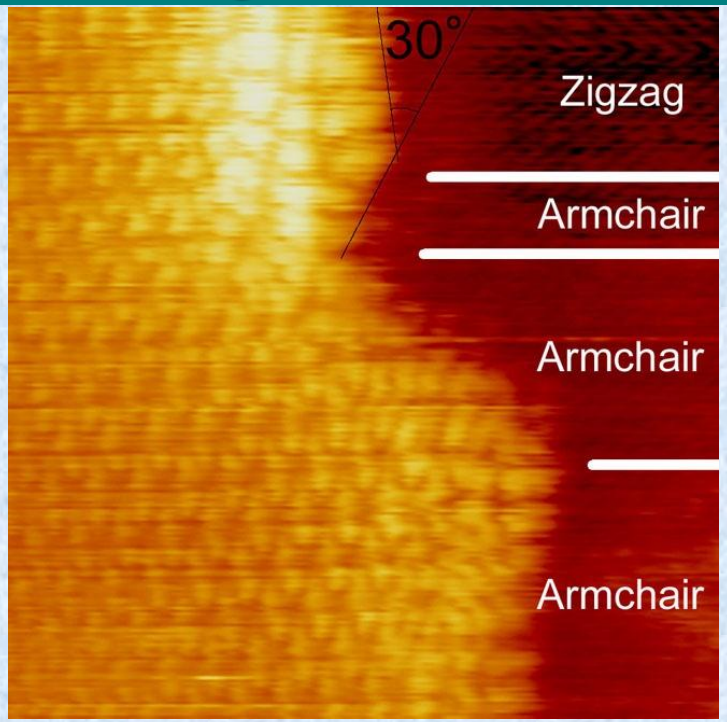


armchair edge: long and continuous, energetically stable (aromatic)

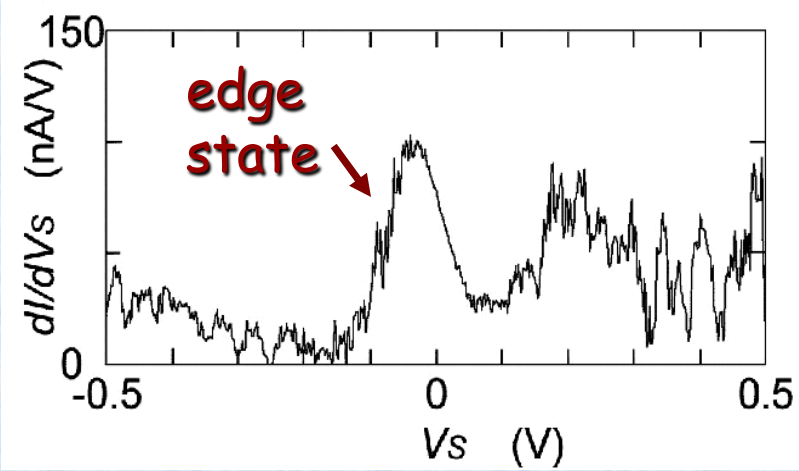
Kobayashi, Fukui, Enoki, et al., *Phys. Rev. B* (2005)

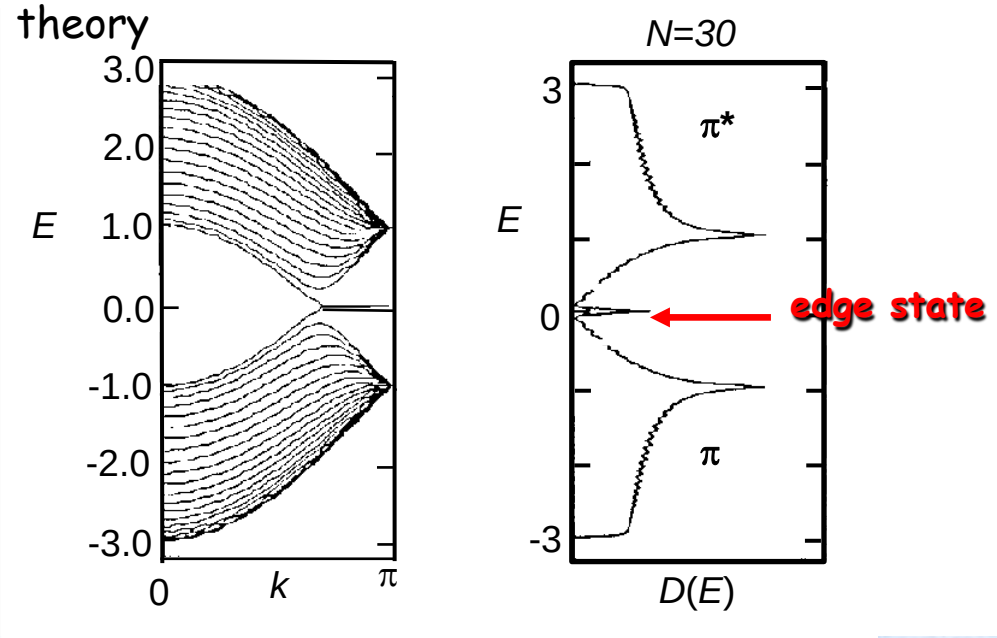
electronic state of graphene edges
hydrogen-terminated

experimental evidence of edge state
(ultra-high vacuum-STM/STS)



zigzag edge





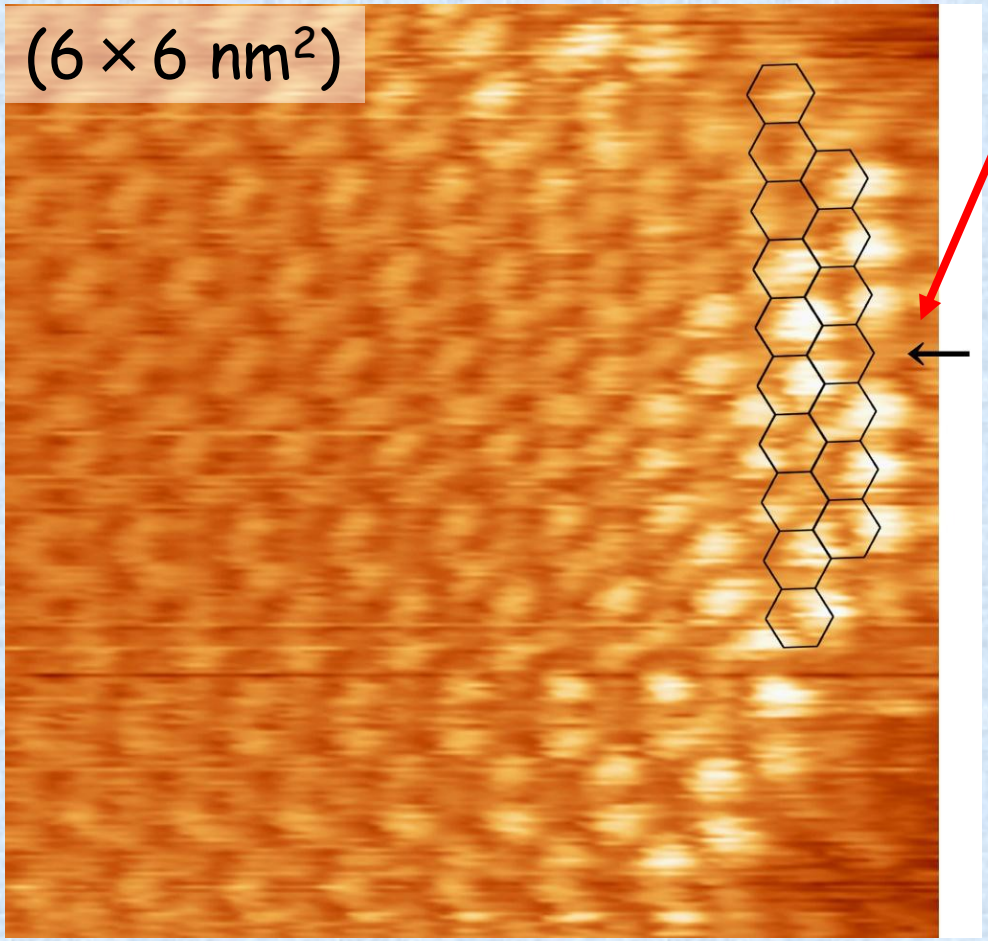
zigzag edge: short and defective, energetically unstable (less aromatic)

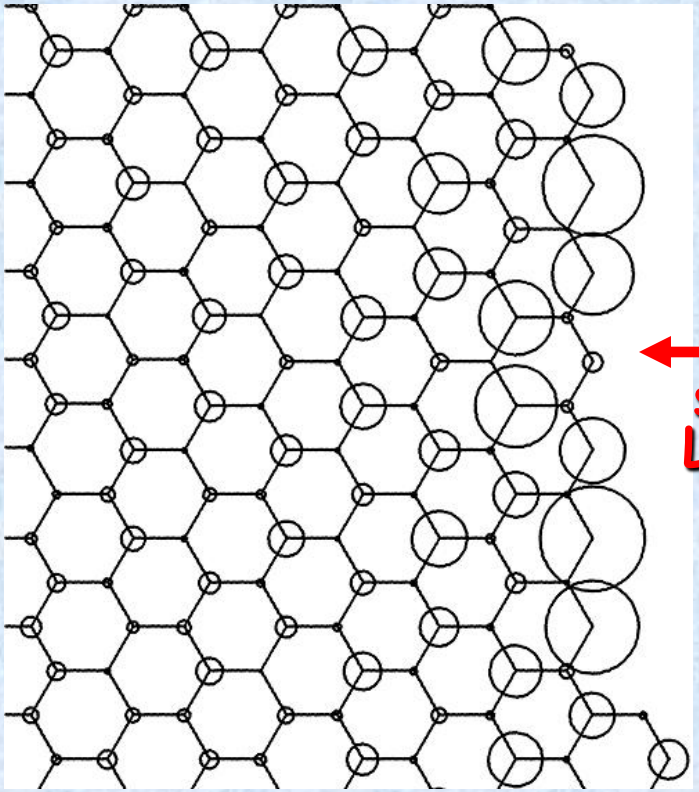
Kobayashi, Fukui, Enoki, et al., *Phys. Rev. B* (2005)

Fujita, et al. *J. Phys. Soc. Jpn.* (1996)

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, Fukui, Enoki, et al., *Phys. Rev. B* (2006)

edge state of π-electron origin
topological origin from the pseudo-spin in Dirac fermion

σ-dangling bond
defect origin in the sp^3 backbone

What difference?

fluorination of nanographene

M. Kiguchi, V. L. J. Joly, K. Takai, T. Enoki, R. Sumii, K. Amemiya, *Phys. Rev.* **B84**, 045421 (2011)

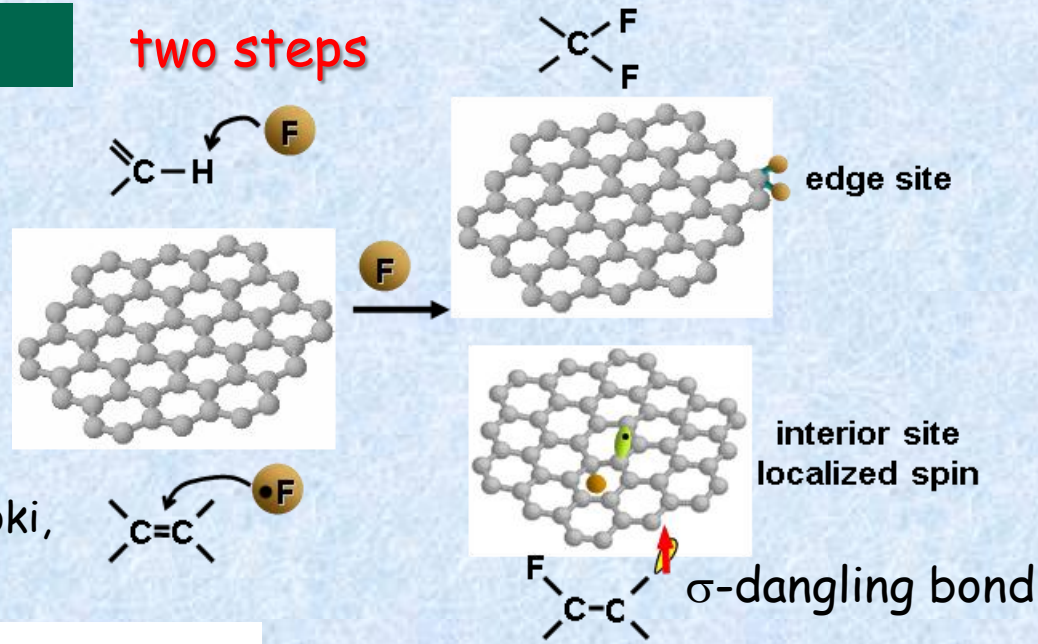
fluorination of nanographene

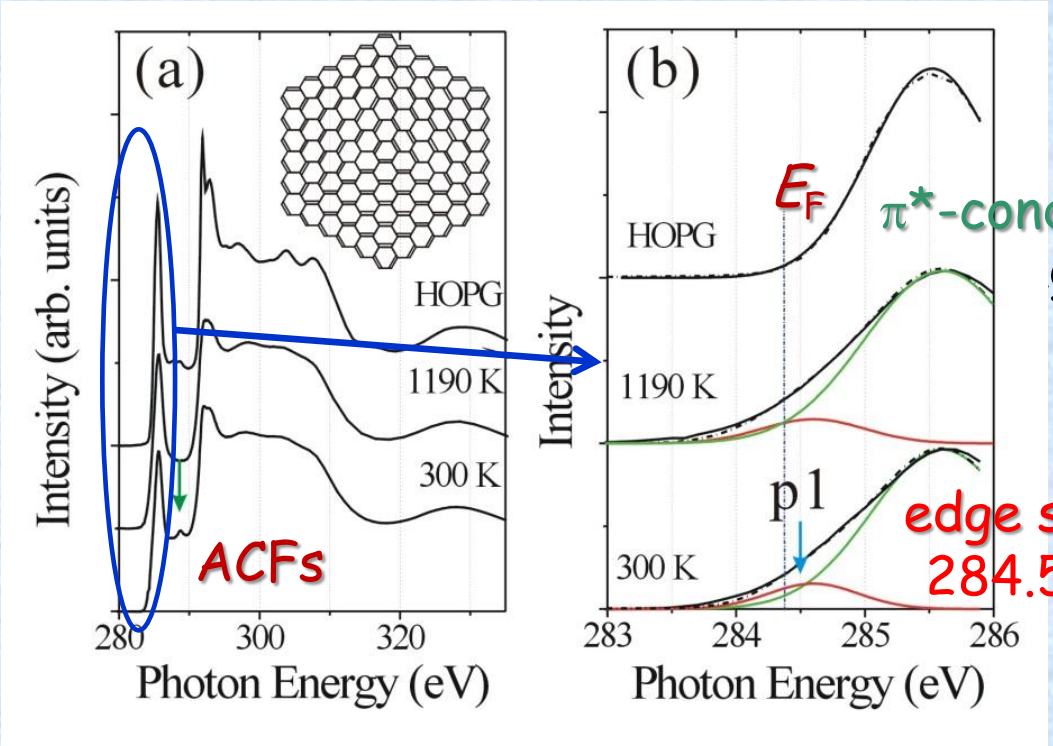
two steps

two kinds of nonbonding state having localized spin

edge state of π-electron
σ-dangling bond of defect

M. Kiguchi, V. L. J. Joly, K. Takai, T. Enoki, et al., *Phys. Rev.* B84, , 045421 (2011)





π*-cond. band 285.5 eV

gnetism

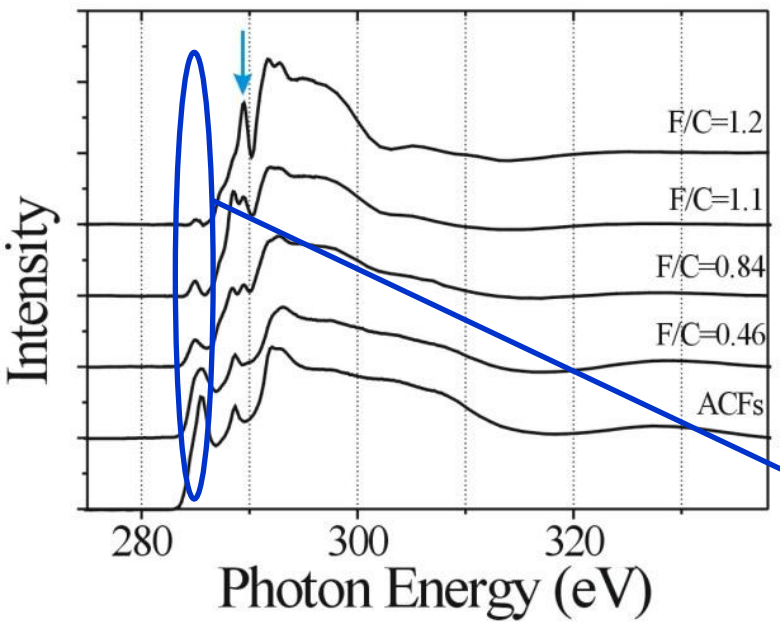
edge state
284.5 eV

near edge X-ray absorption fine structure (NEXAFS)

nanographene in activated carbon fibers (ACF)

pristine ACFs
heat-treated ACFs (1190 K)

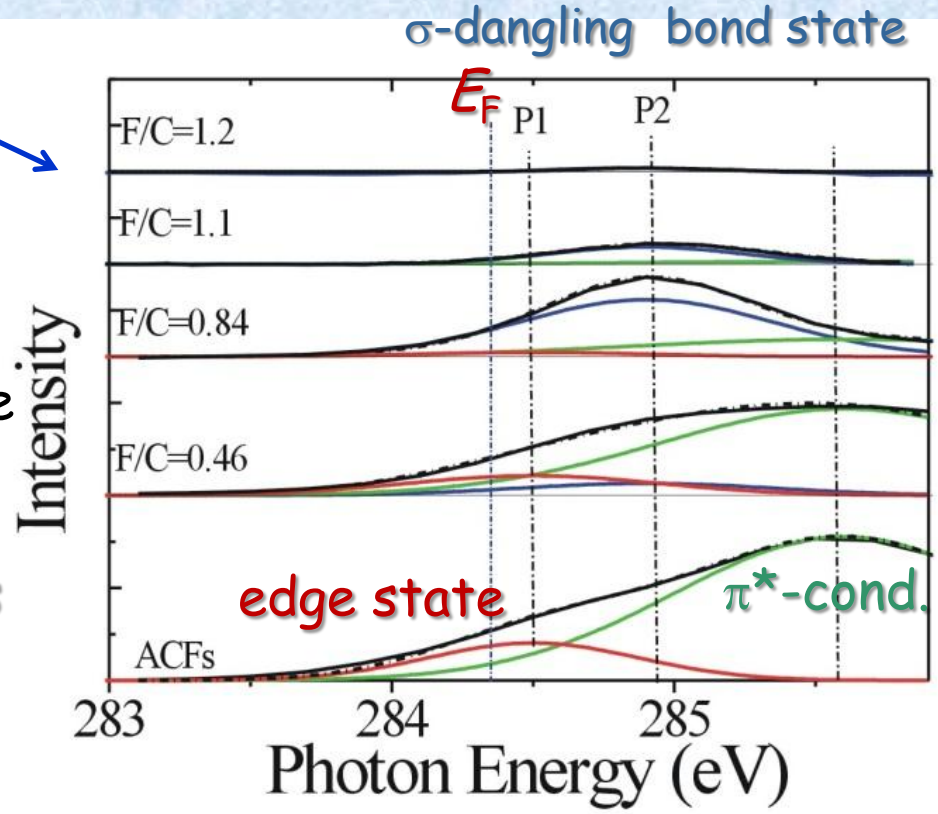
NEXAFS fluorinated ACFs (F/C= 0 – 1.2)



σ-dangling bond state (284.9 eV) appears independent from edge state
0.4 < F/C < 1.2
with a maximum intensity at F/C ~ 0.8

edge state of π-electron
chem. shift 284.5 eV more negative from π* conduction band
large screening effect
large local density of states

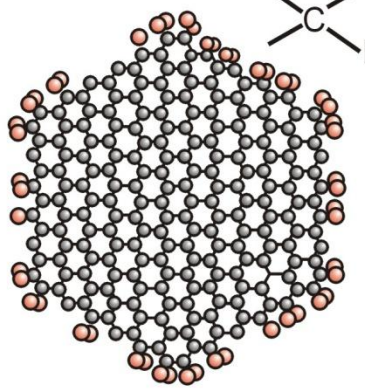
σ-dangling bond
chem. shift 284.9 eV less negative
weak screening effect



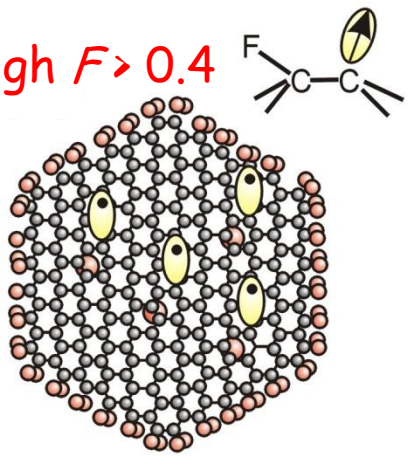
fluorine concentration dependence of NEXAFS intensity and localized spin

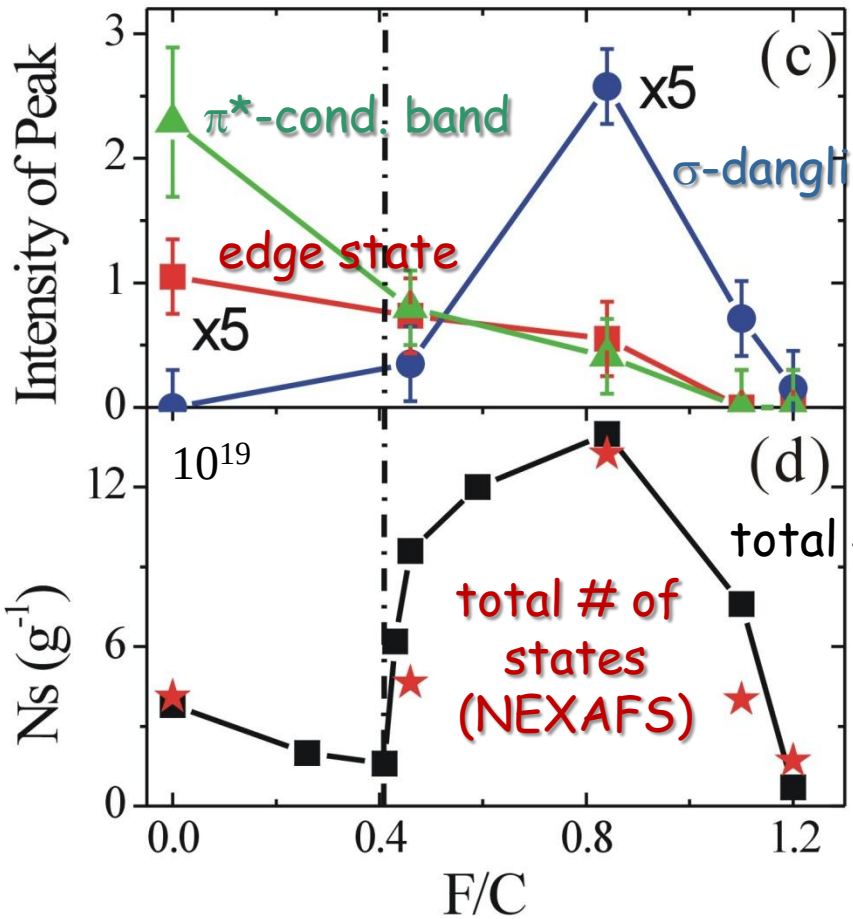
# of Carbon atoms ~200~300 (nanographene 2-3 nm)

low $F < 0.4$



high $F > 0.4$





electronic state NEXAFS

magnetism

total # of localized spins (magnetism)

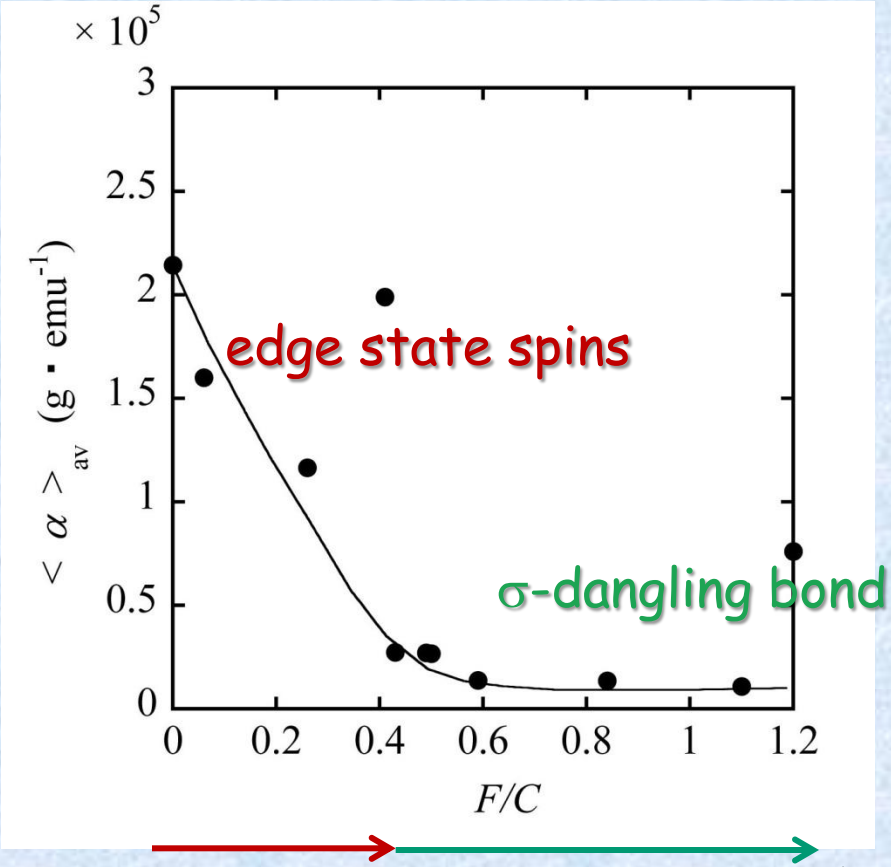
max conc. of dangling bond spins at F/C~0.8

1/2 of interior C atoms fluorinated

edge C → interior C → fluorinated

magnetism; edge state and σ-dangling bond state

internal exchange field

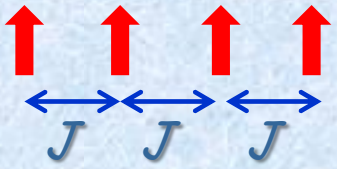


edge C → interior C → fluorinated

edge state spins

topological origin

interacting with each other through exchange interaction



σ-dangling bond spins

defect origin

isolated with no interaction

K. Takai, H. Sato, T. Enoki, N. Yoshida, F. Okino, H. Touhara, M. Endo, *J. Phys. Soc. Jpn.* **70**, 175 (2001).

Outline

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   # STM superlattice and its fine structure in the vicinity of edge

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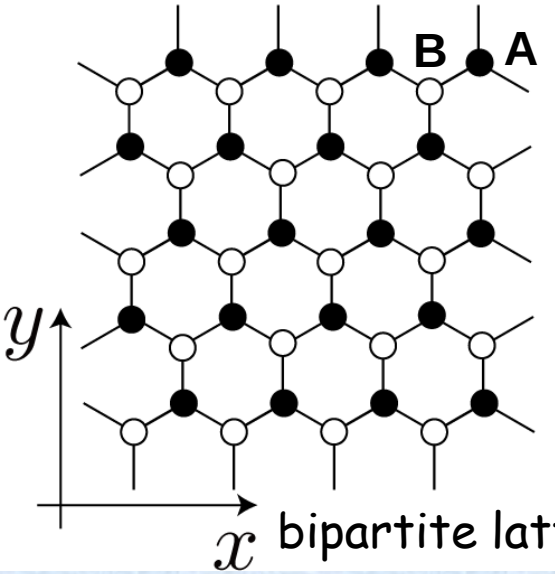
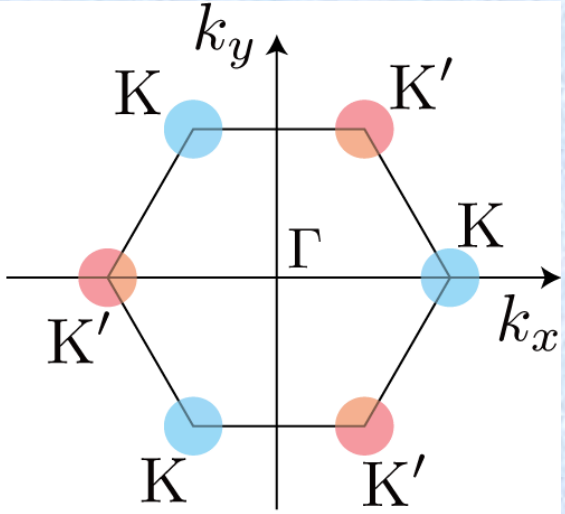
   # graphene oxide, AFM tip zigzag-edged graphene nanoribbons

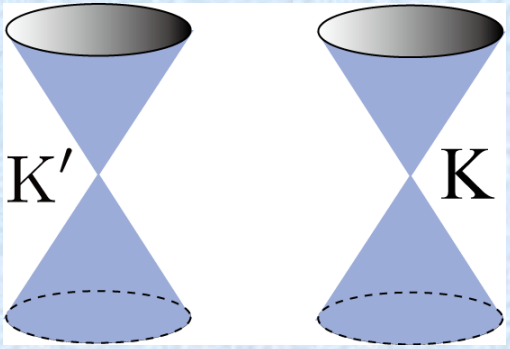
4. Conclusion

electron scattering at edges and interference

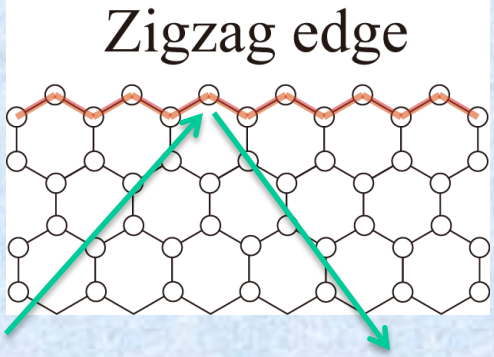


bipartite lattice





two Dirac cones

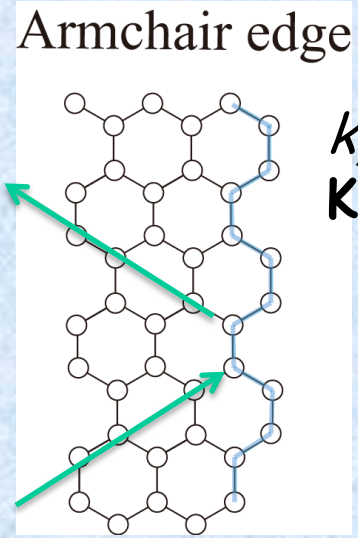


$k_y \rightarrow -k_y$

K → K

intra-valley scattering

no interference



$k_x \rightarrow -k_x$

K → K′

interference between K and K′

$$\psi_A(\mathbf{R}_A) \approx 0$$

$$\psi_B(\mathbf{R}_B) \propto \left(-\exp\left(-\underline{i\mathbf{K}}\mathbf{R}_B\right) + \exp\left(\underline{i\mathbf{K}'}\mathbf{R}_B\right)\right)$$

inter-valley scattering

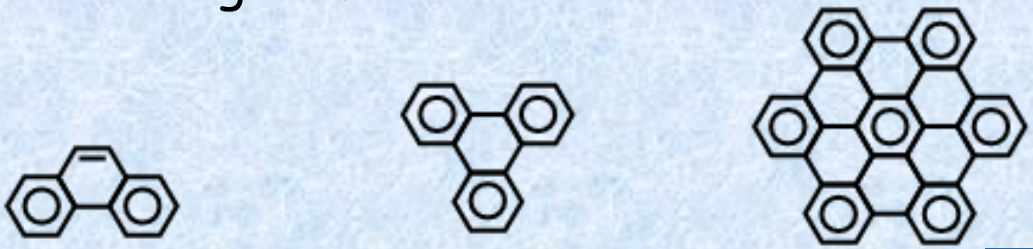
interference from chemistry aspect (Clar's representation)

infinite size graphene

3 states degenerate

$\sqrt{3} \times \sqrt{3}$ superlattice

armchair-edged molecules

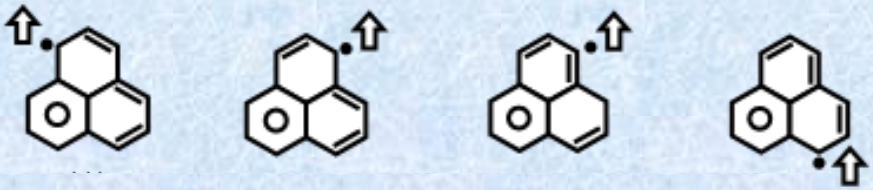


only one unique state

standing wave

electron wave interference

zigzag-edged molecules



12 states degenerate

(three fold symmetry: 4x3=12)

S=1/2 [1]

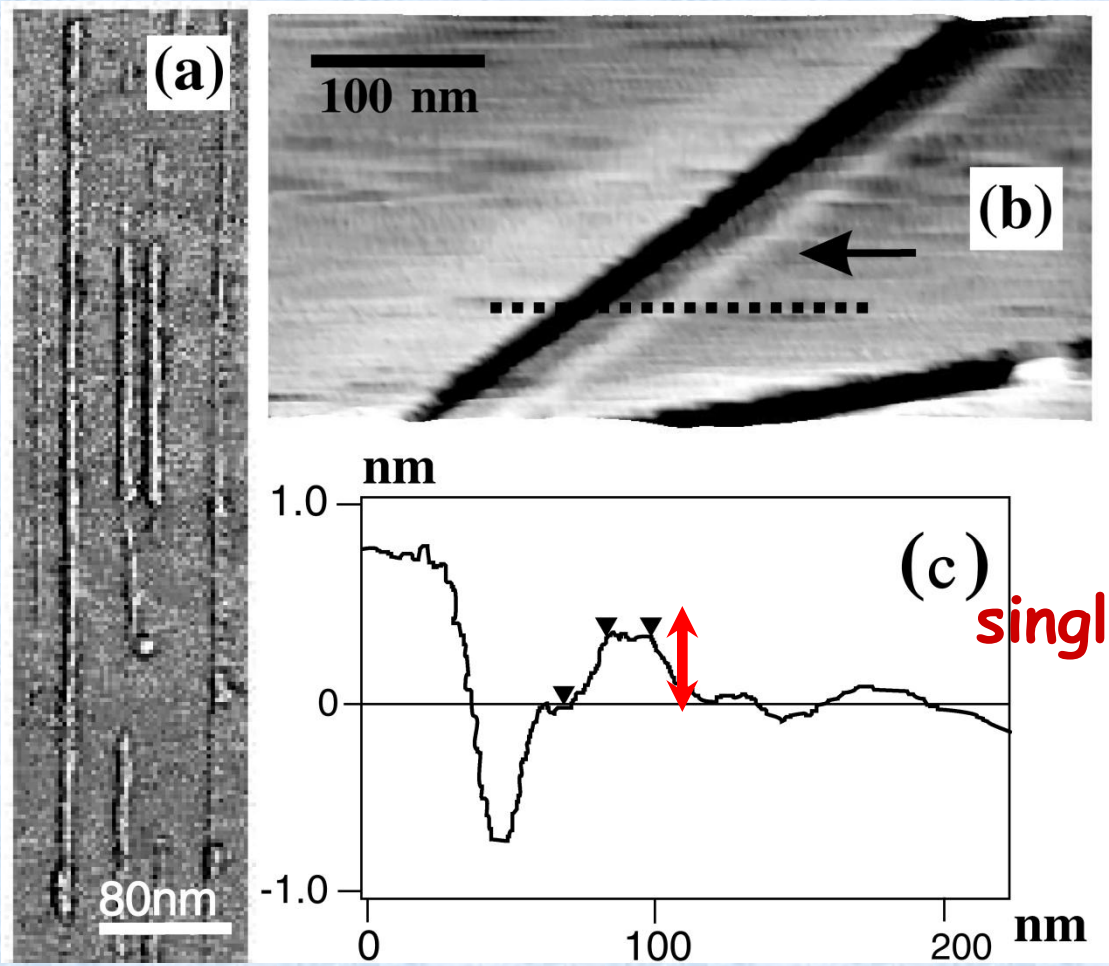
no standing wave

armchair-edged graphene nanoribbon observed by resonance Raman experiments

Cançado, Kobayashi, Pimenta, Enoki, et al., *Phys. Rev. Lett.* **93**, 047403 (2004)
Sasaki, Saito, Wakabayashi, Enoki, *J. Phys. Soc. Jpn.* **79**, 64082 (2010)
Sasaki, Saito, Wakabayashi, Enoki, *J. Phys. Soc. Jpn.* **80**, 044710 (2011)

AFM image of single nanographene ribbon

single sheet of nanographene ribbon at a step edge

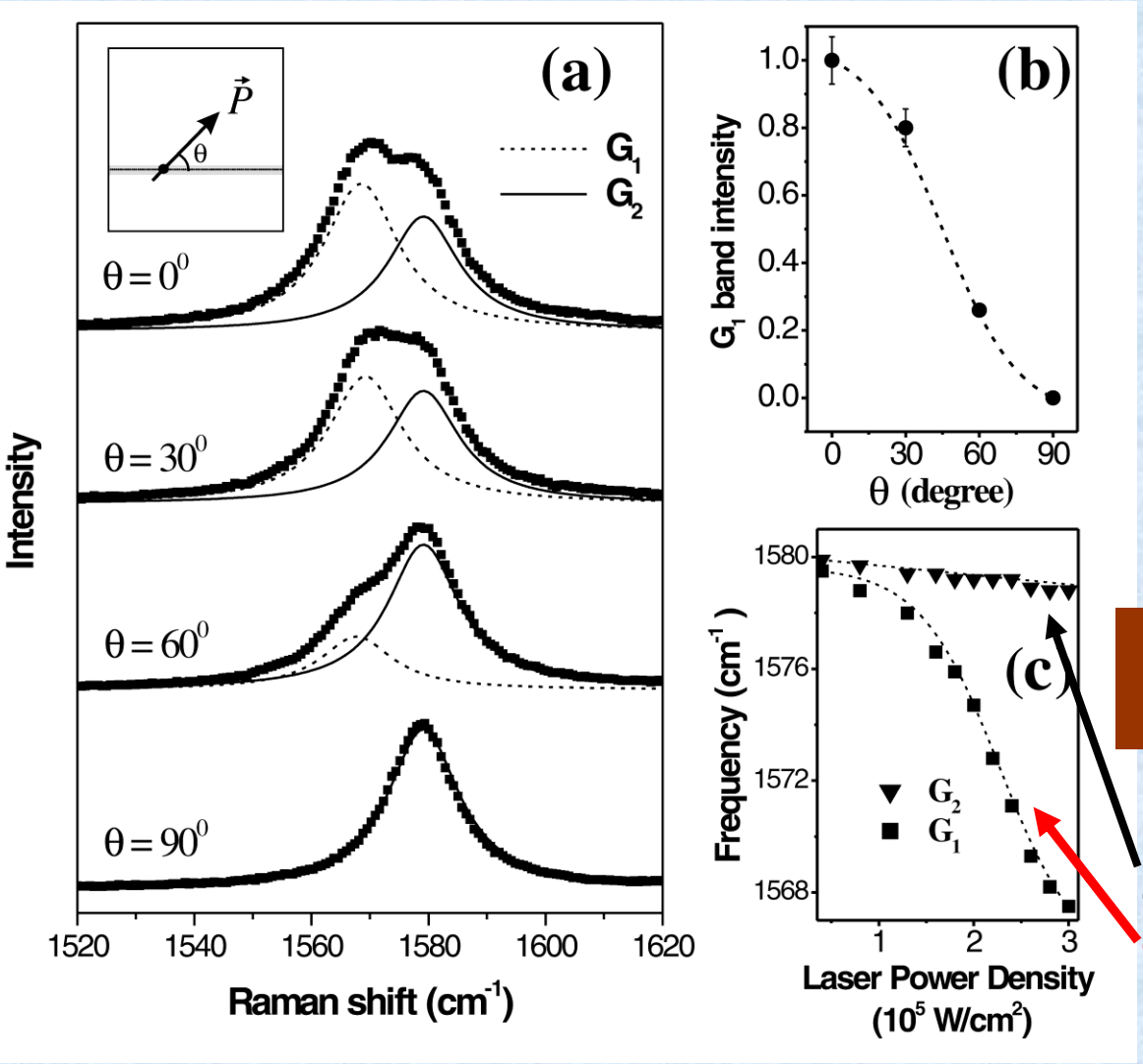


single sheet

ribbon size

8 nm x >1 μm

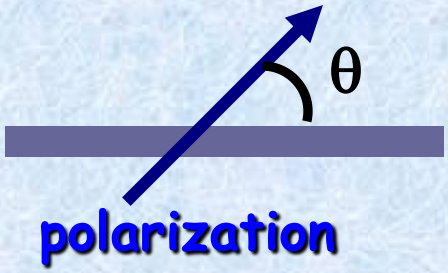
Resonance Raman experiments with polarized light



G band

G2: substrate HOPG

G1: nanographene ribbon



alignments of individual ribbons are determined

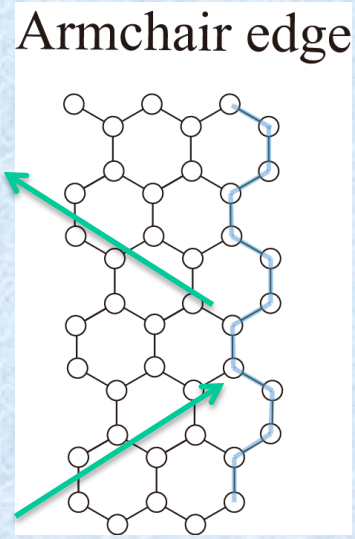
G2

G1

small nanographene ribbon can be easily heated by light

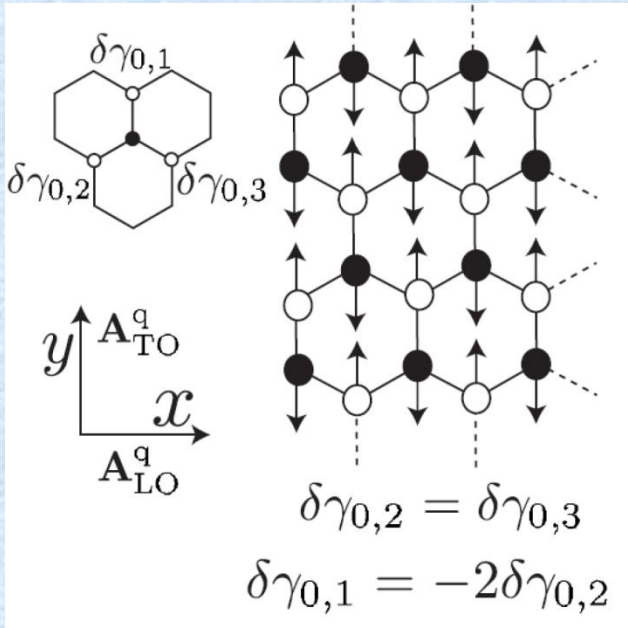
G-band intensity (armchair edge) theoretical analysis

Sasaki, Saito, Wakabayashi, Enoki, *J. Phys. Soc. Jpn. 79,* 64082 (2010)



inter-valley scattering

$k_x \longrightarrow -k_x$



lattice deformation for active LO mode

transfer integral γ_0 modified

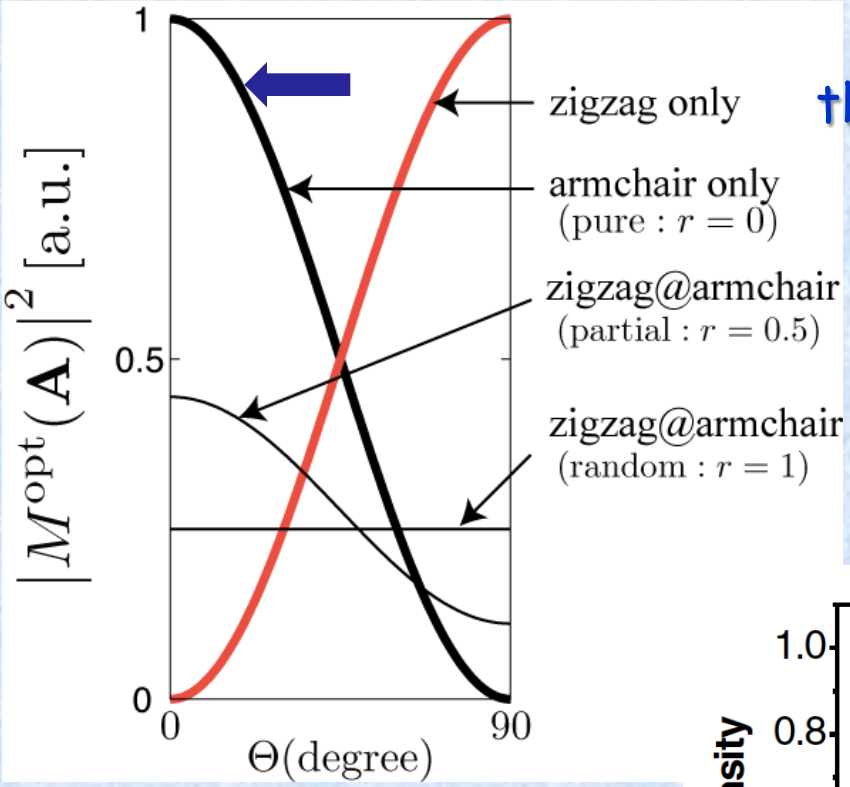
$$\mathbf{p} \rightarrow \mathbf{p} + \mathbf{A}^q - e\mathbf{A} \qquad \hat{H} = v_{\mathrm{F}}\sigma\left(\mathbf{p} + \mathbf{A}^q - e\mathbf{A}\right)$$

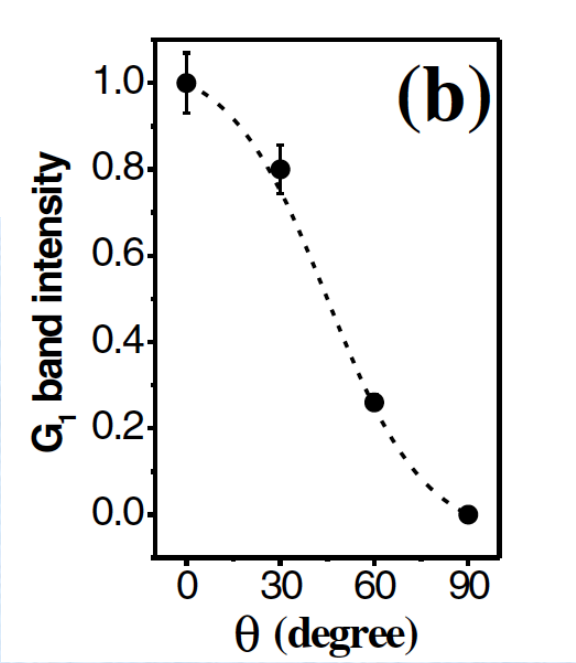
$$\mathbf{A}^q\left(\delta\gamma_{0,1}, \delta\gamma_{0,2}, \delta\gamma_{0,3}\right) = \left(A^q_x, A^q_y\right)$$ deformation-induced gauge field

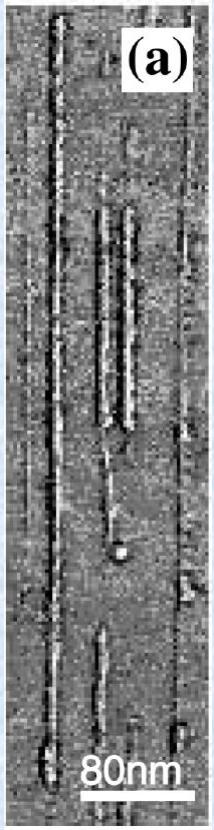
$\mathbf{A}$: gauge field of the laser beam

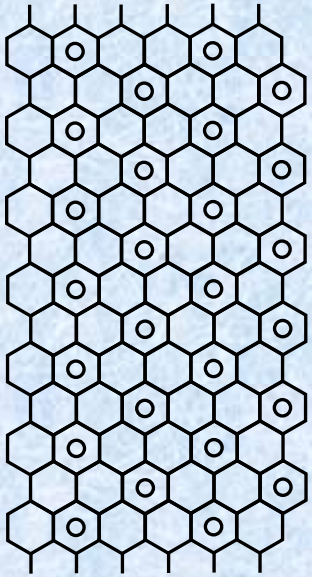
G-band intensity $$\left|M^{\mathrm{opt}}(\mathbf{A})\right|^2 \propto \cos^2\theta$$

theoretical results of the G-band intensity









100 % armchair nanographene ribbon

STM superlattice and its fine structure

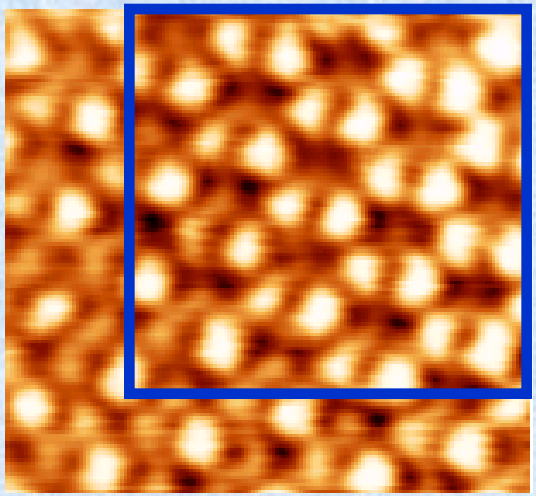
Sakai, Takai, Fukui, Enoki, Nakanishi, *Phys. Rev.* **B81**, 235417 (2010)

low temp.-STM measurement near an armchair edge

Sakai, Takai, Fukui, Enoki, Nakanishi, *Phys. Rev. B* (2010)

$\sqrt{3} \times \sqrt{3}$
honeycomb

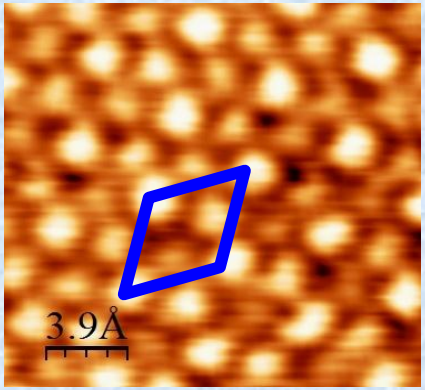
a = 4.26 Å



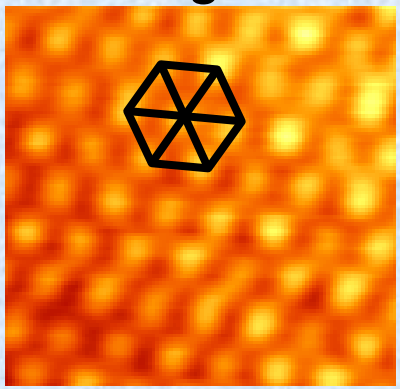
1.5 × 1.2 nm^2

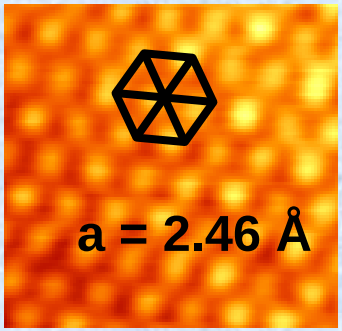
(V = 20 mV, I = 0.32 nA, 5.5 × 1.2 nm^2, 9 K)

$\sqrt{3} \times \sqrt{3}$

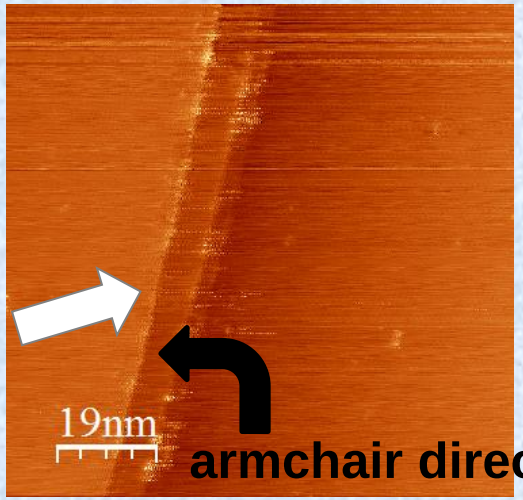


triangle





← interior of terrace

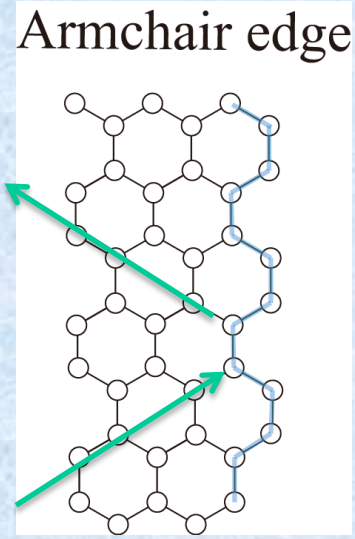


armchair direction

two types of superperiodic patterns: honeycomb and $\sqrt{3} \times \sqrt{3}$

appearance of 3-fold symmetric fine structure in the honeycomb area

tight binding analysis:
electronic structure of graphene with armchair edge



$k_x \rightarrow -k_x$

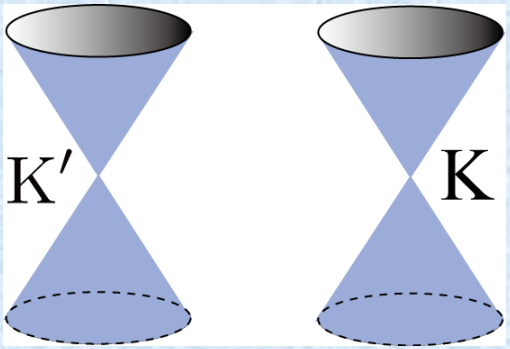
$\mathbf{K} \rightarrow \mathbf{K}'$

interference between K and K′

$$\psi_A(\mathbf{R}_A) \approx 0$$

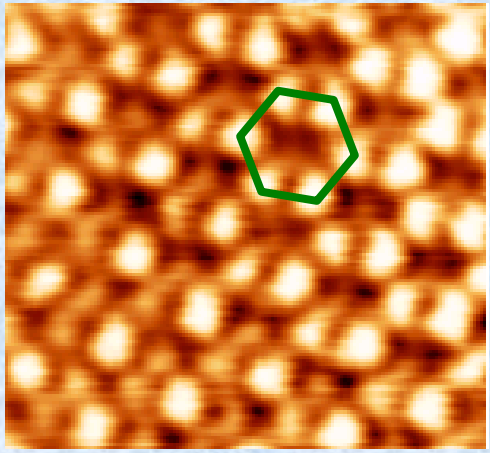
$$\psi_B(\mathbf{R}_B) \propto \left(-\exp(-i\mathbf{K}\mathbf{R}_B) + \exp(i\mathbf{K}'\mathbf{R}_B)\right)$$

inter-valley scattering



two Dirac cones

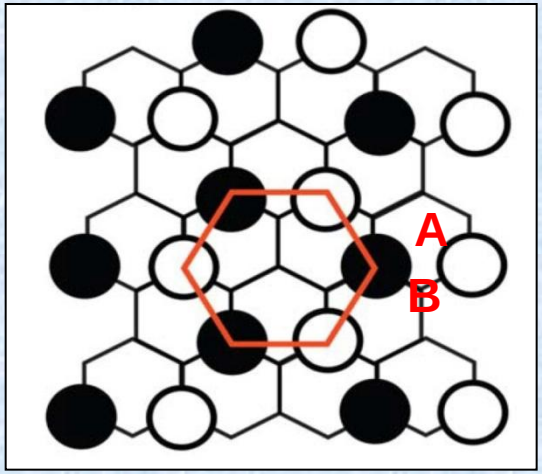
honeycomb superperiodic reproduced



anti-phase coupling

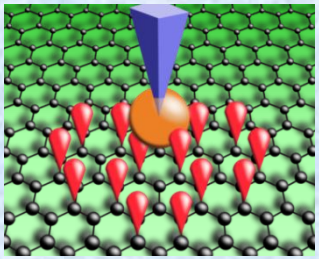
+phase: ○

-phase : ●

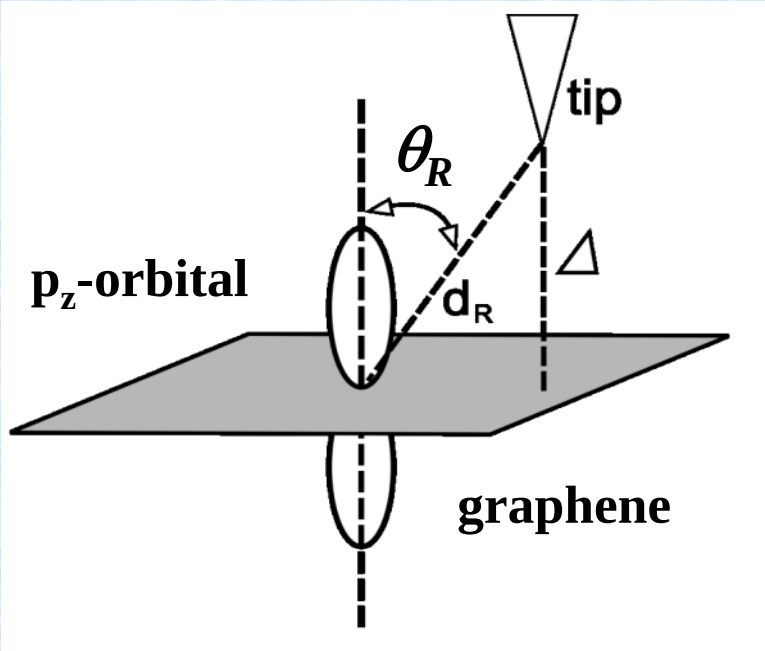


2D mapping of squared amplitude of the wave function

theoretical analysis for the 3-fold fine structure: simulation of STM image



calculation model for tunneling current



matrix element

$$t_R = t_0 w_R \exp\left(-\frac{d_R}{\lambda}\right)\cos\theta_R$$

$$w_R = \exp\left(-\alpha^2 d_R{}^2\right)\left[\sum_{R'}\exp(-\alpha^2 d_{R'}{}^2)\right]^{-1}$$

t_0: scaling factor

α^{-1} ~ 0.13 nm (visual optimization)

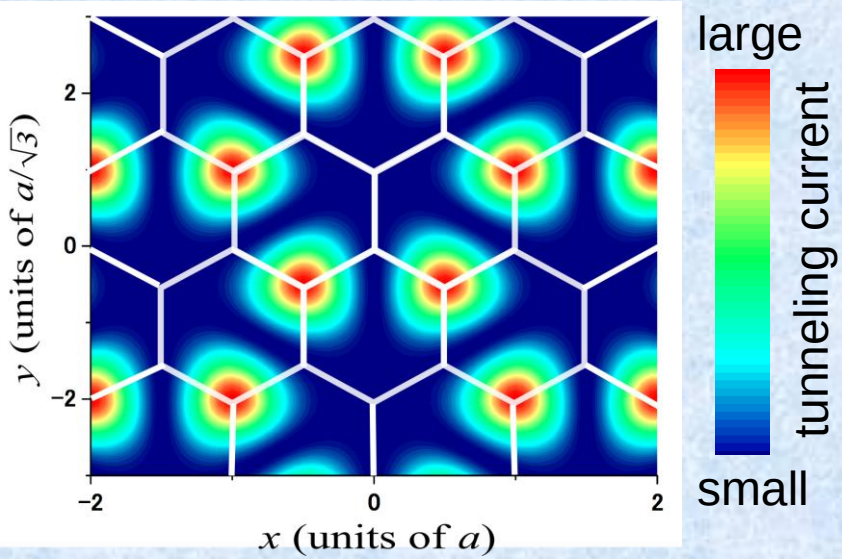
λ= 0.085 nm

Δ = 0.5 nm

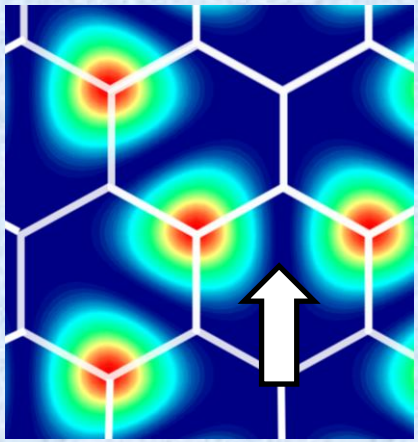
wave function of tip-end atom: s-orbital

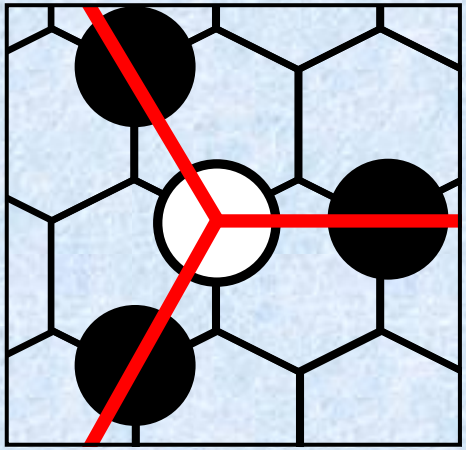
V. Meunier and Ph. Rambin, *Phys. Rev. Lett.* **81**, 5588 (1998).
T. Nakanishi and T. Ando, *J. Phys. Soc. Jpn.* **77**, 024703 (2008).

current image (three fold symmetry)



the electronic structure in the vicinity of the armchair graphene edge, information about the phase of the wave function





anti-bonding coupling with a node between the nearest neighbor sites mediated by tip-end atom

3-fold symmetric LDOS distribution in honeycomb superperiodic pattern

Outline

1. Edge state at zigzag edge and the magnetic structure of edge-state spins
   # spin-polarized edge state
   from theoretical and experimental understandings
   # what is the difference in the magnetic structure between the edge-state spins of π-electron origin and the σ-dangling bond spins
   nanographene (π) and fluorinated nanogrphene ($\pi+\sigma$)

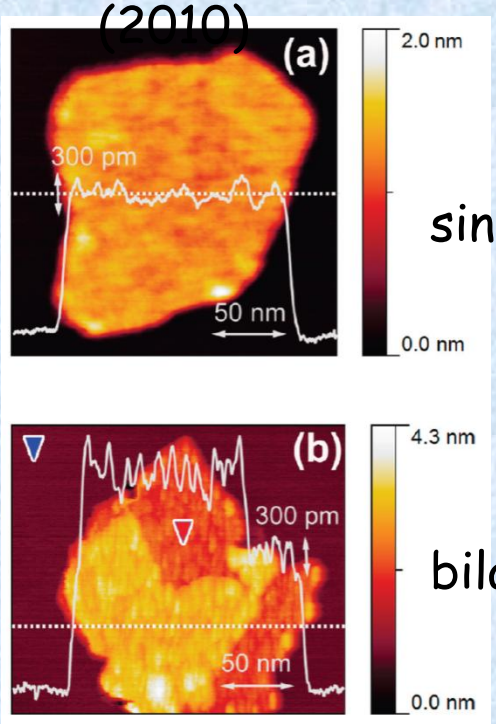
2. Electron wave interference at armchair edge
   # resonance Raman G-band of armichair-edged graphene nanoribbons
   # STM superlattice and its fine structure in the vicinity of edge

3. Nanofabrication
   # graphene oxide, AFM tip **zigzag-edged** graphene nanoribbons

4. Conclusion

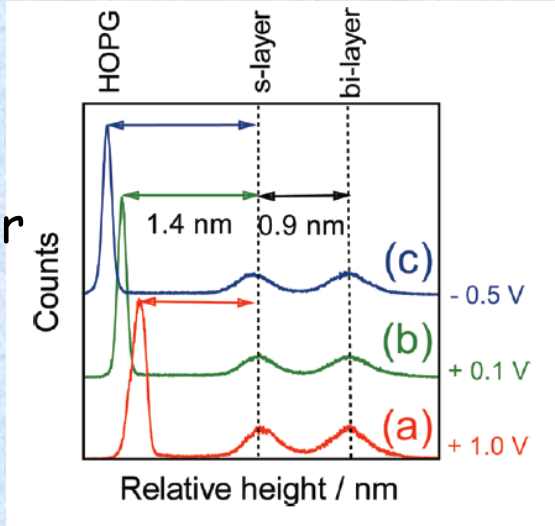
nanographene oxide

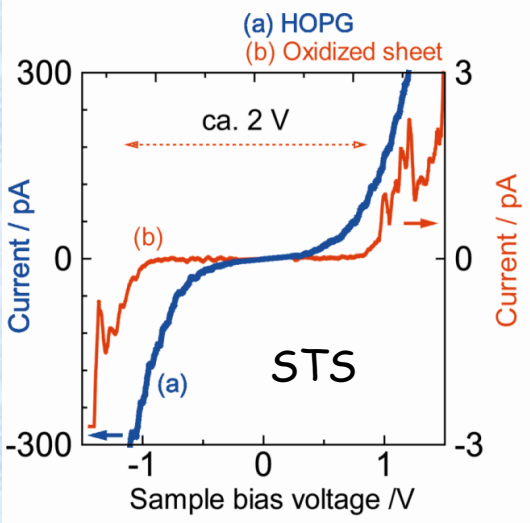
Fujii & Enoki, *JACS* 132, 10034 (2010)



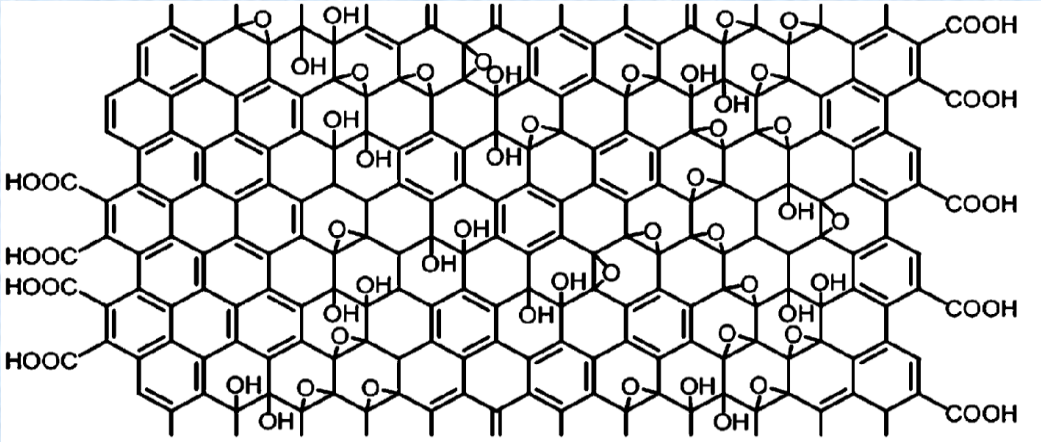
single layer

bilayer





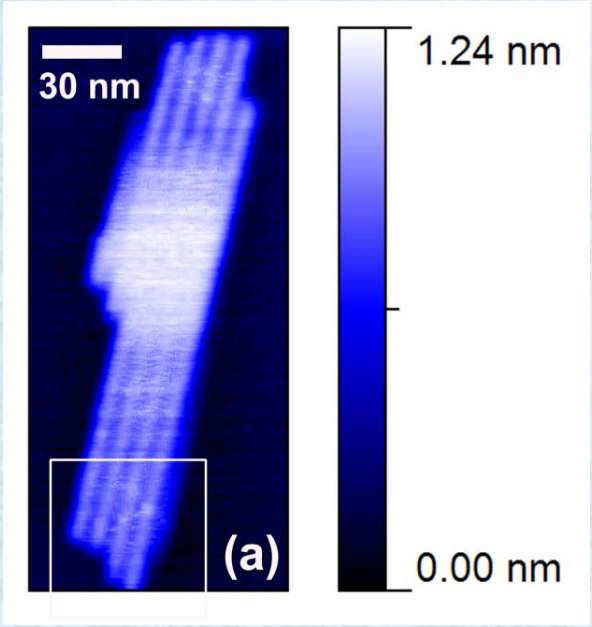
insulating
gap~ 2 eV
O/C= 0.20-0.25

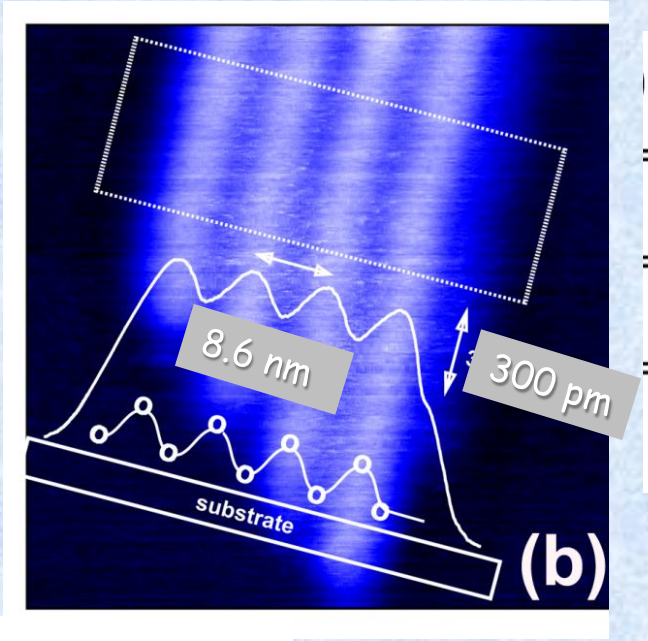


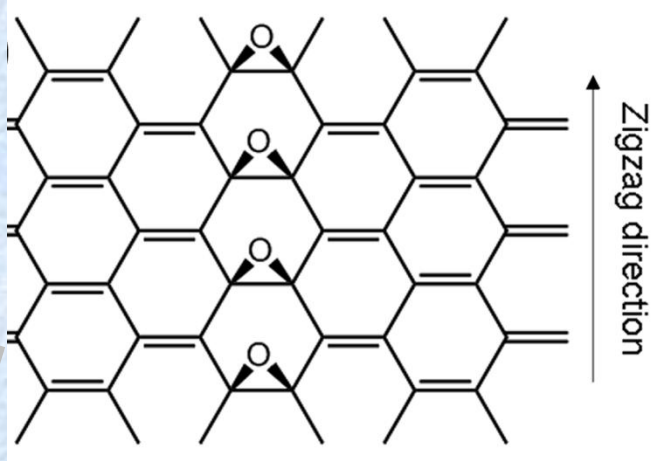
non-contact AFM

disordered structure

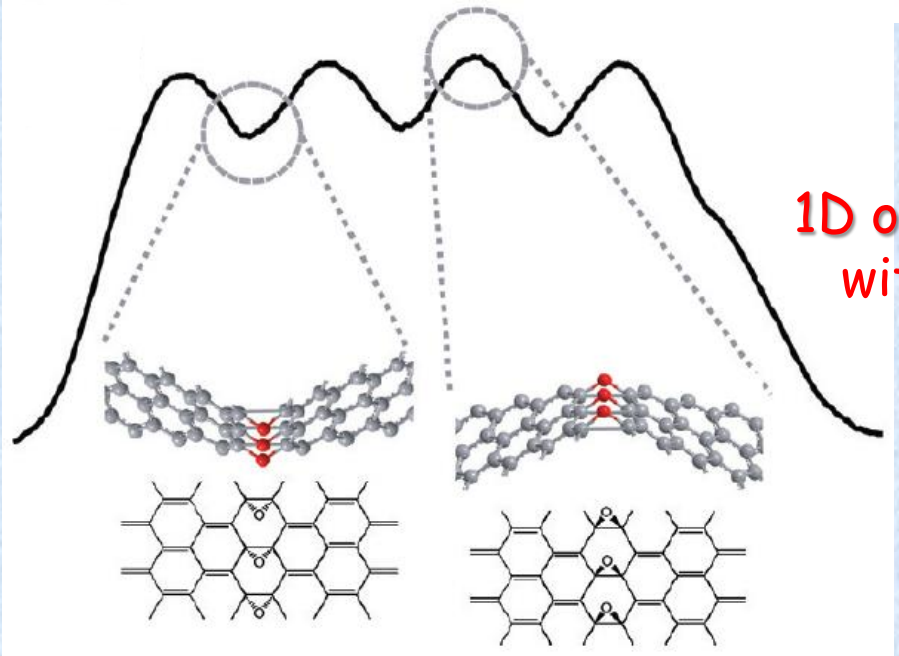
non-contact AFM







epoxide rings
arranged along
a zigzag direction

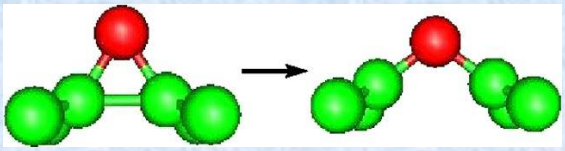


1D ordered wrinkles
with a regular width of ca. 9nm
zigzag nanographene ribbon (ca.4.5nm)

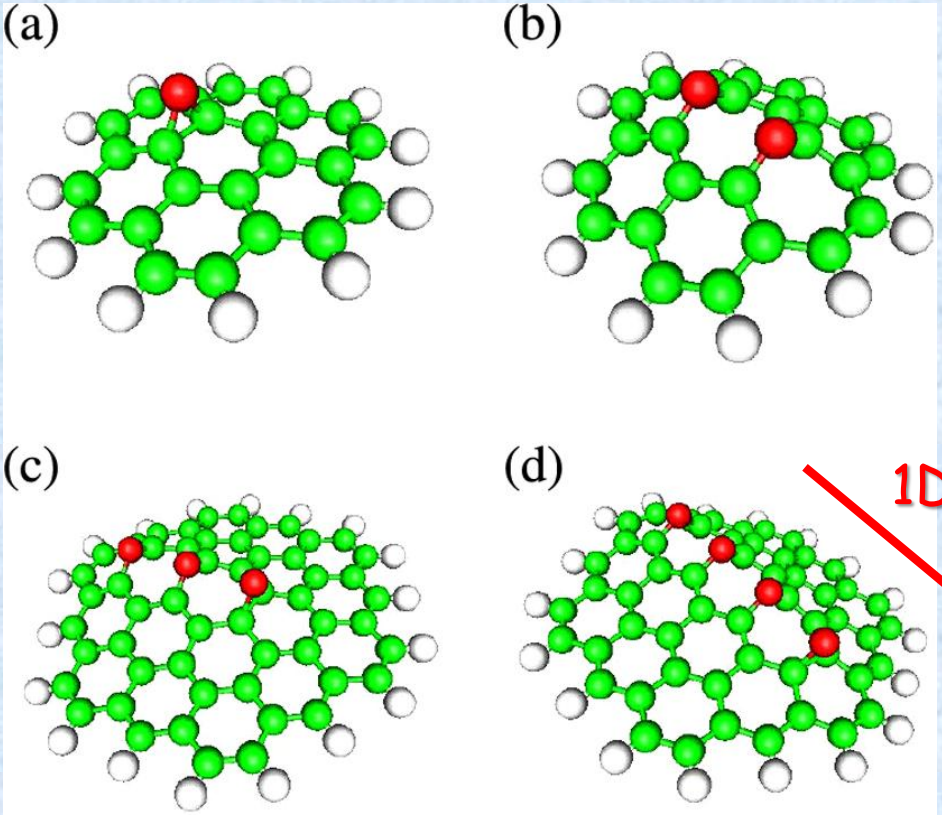
epoxy groups aligned → **unzipping process**

J.-L., Li et al. *Phys. ReV. Lett.* 96, 176101 (2006)

oxygen



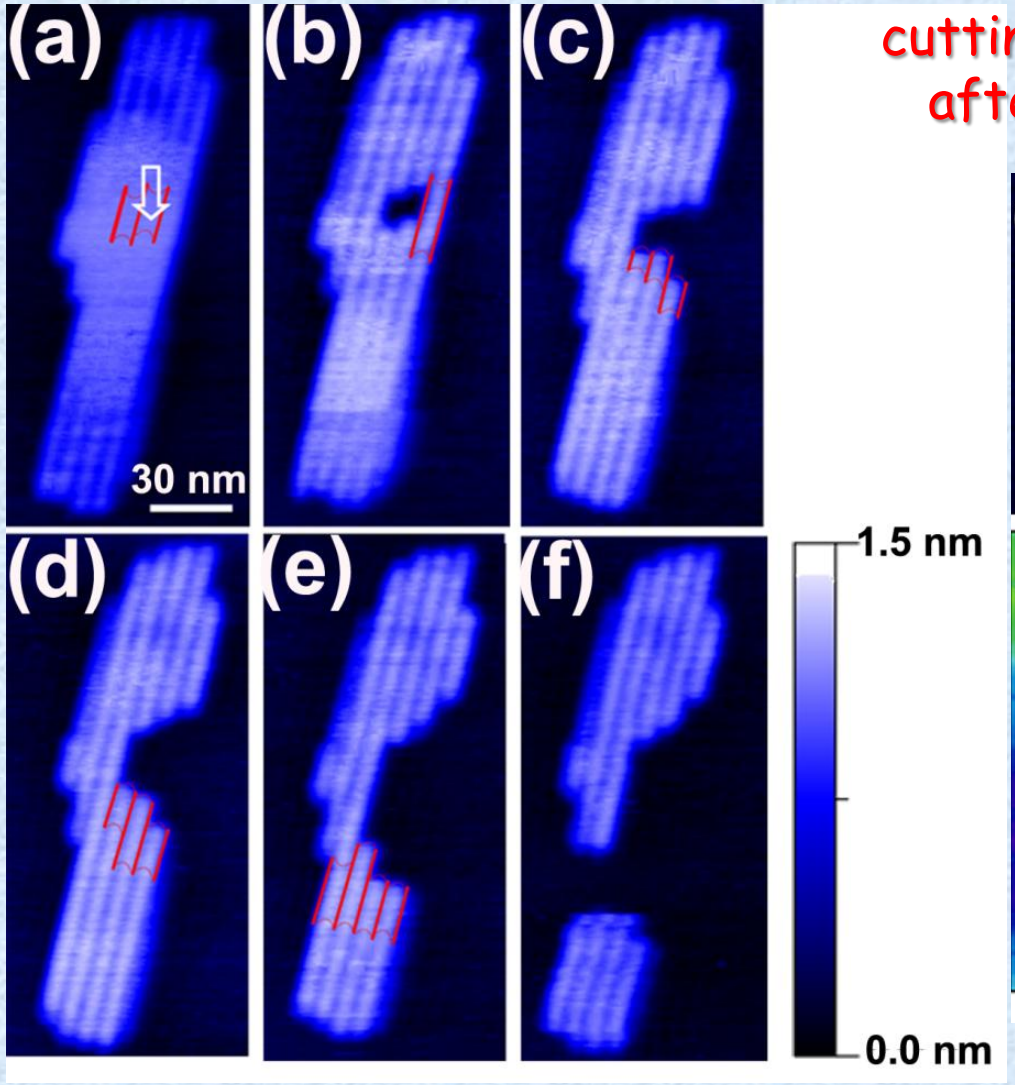
oxidation of graphene



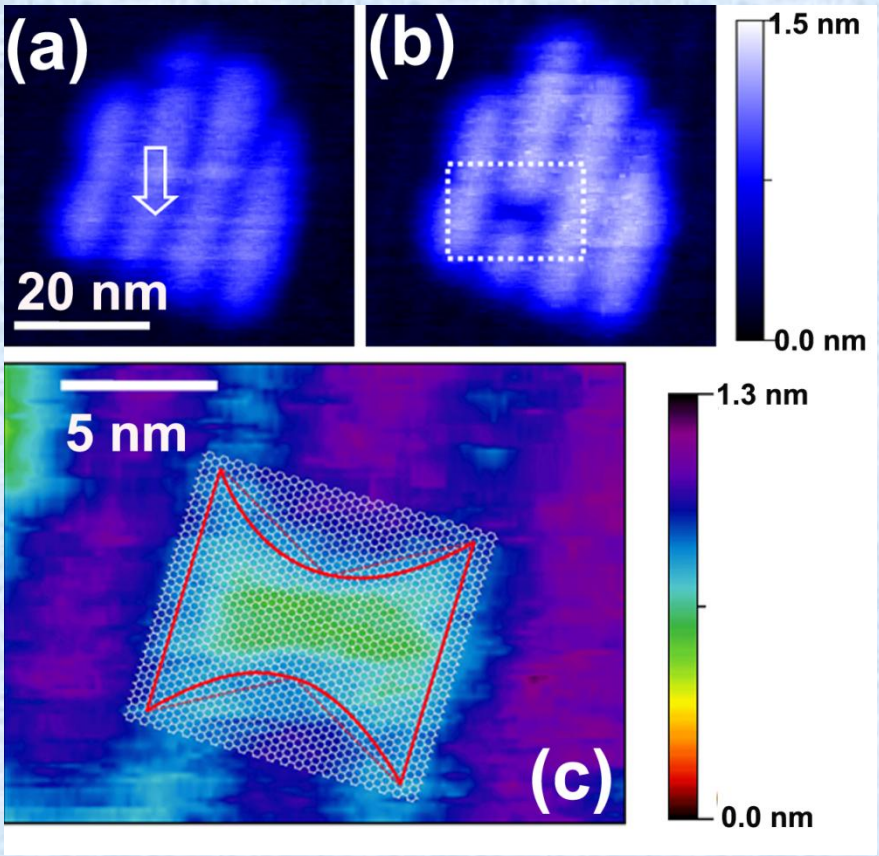
unzipping process

1D oxidation line
along the zigzag direction

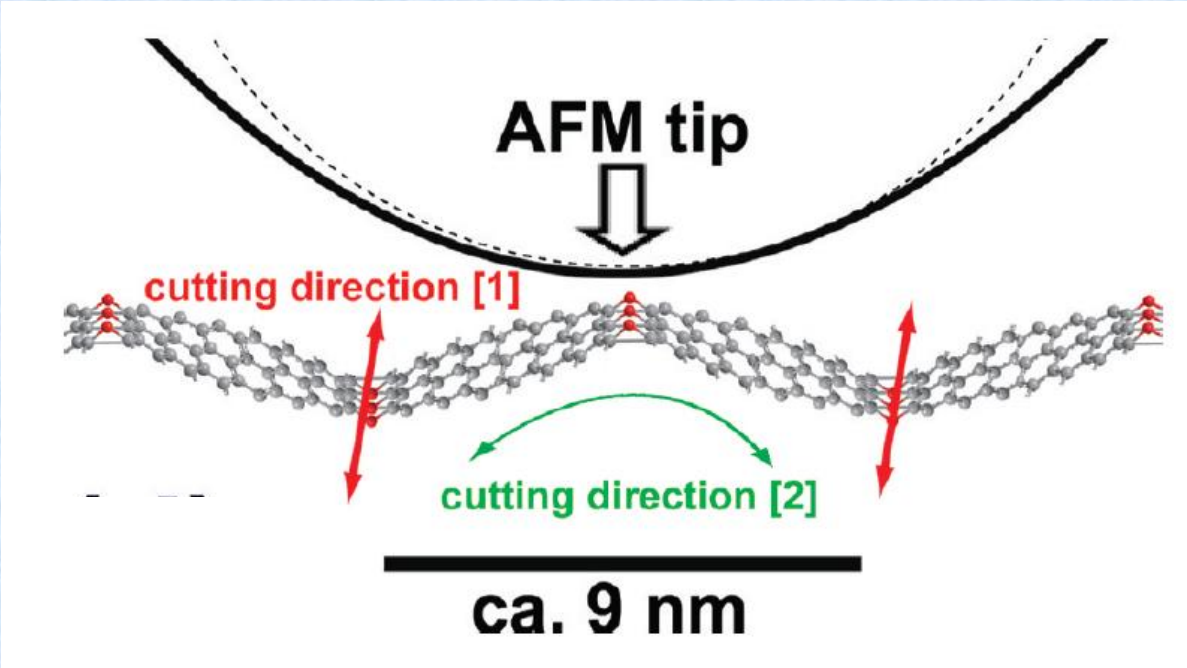
nanofabrication using an AFM tip

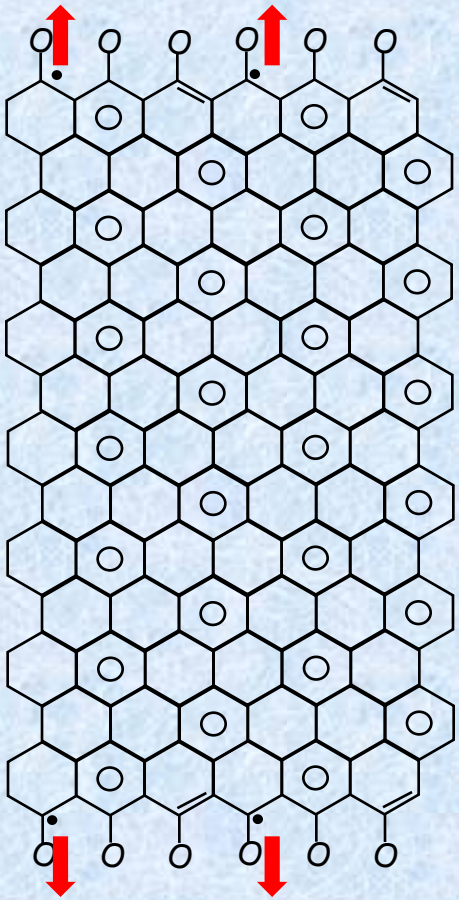


cutting by an AFM tip
after nanographene sheet is oxidized



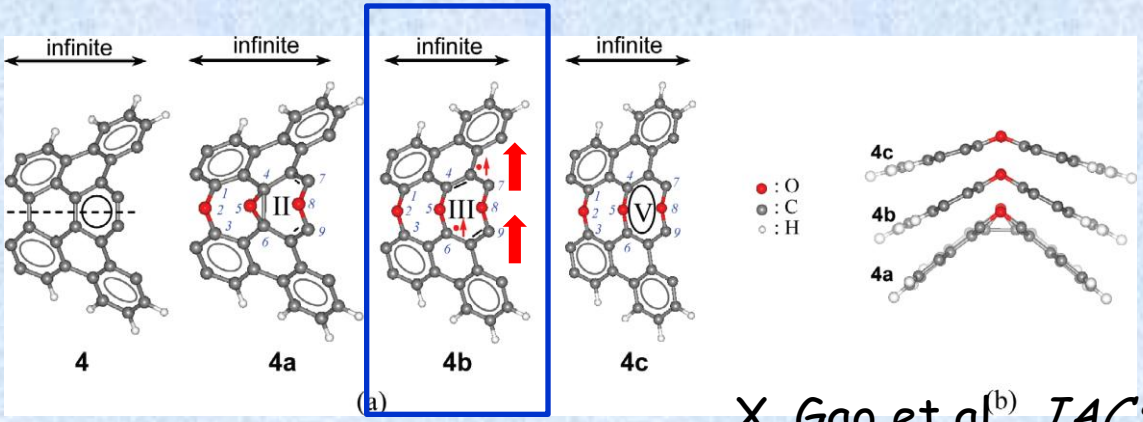
nanofabrication using an AFM tip





zigzag edge thermodynamically unstable

oxidation of graphene can create zigzag edges



ferromagnetic zigzag-edged nanographene ribbon

X. Gao et al., *JACS* 131, 9663 (2009)

Edges modiy the electronic structure of graphene

zigzag edge; nonbonding edge state
electronic, magnetic, chemical activities

armchair edge; electron wave interference

a variety of electronic properties & functions
basic science & applications

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SURFACE SCIENCE