Intriguing Properties of Nanographenes-
From Carbon Nanoribbons to Their Inorganic Cousins

Dr. Zhongfang Chen

Abstract: Page 104
Where is Puerto Rico (1)
How Big is Puerto Rico

The maximum length 110 miles (180 km)
the maximum width 40 miles (64 km)

Larger than Delaware and Rhode Island combined, but slightly smaller than Connecticut.

Population: 4M
What is Puerto Rico Like?
Outline

• Carbon graphene nanoribbons and band structure engineering by chemical modifications

• Inorganic Nanoribbons
  BN
  SiC
  MoS$_2$

• Acknowledgement
  Excellent collaborators are our treasure
Smalley’s Prediction

Carbon has this genius of making a chemically stable two-dimensional, one-atom-thick-membrane in a three-dimensional world. And that, I believe, is going to be very important in the future of chemistry and technology in general.

from 1996 Nobel lecture

so insightful that it predicted the exploding interest in graphene research today
Graphene- the 1st 2D Crystal Lattice
Super Hot Graphene

23 packed sessions on graphene in the recent APS meeting in Pittsburgh, Pennsylvania

Graphitic materials session of ACS fall meeting
Mechanical Cleavage to Realize the Impossible
- A “Simple” Breakthrough

In 2004, graphene (up to 100 micrometer in size) was obtained via adhesive tapes!

Ca. 1300 citations!
Many Methods to Get Graphenes…
Another “Simple” One

High-Quality Graphenes via a Facile Quenching Method for Field-Effect Transistors


1. Repeatedly bend highly ordered pyrolytic graphite (HOPG) to introduce tiny mechanical cracks

2. Rapidly heated to 1000 °C within 5 min

3. Quickly quench to room temperature in a bath of cool water containing 1.0 wt % ammonium hydrogen carbonate (NH₄HCO₃)
Why Graphene

- the strongest material ever measured, but flexible
- chemically stable and inert
- conducts electricity better than any other known material at room temperature
- Top down-bottom up possibility for all graphene ballistic electronic (spintronic) device at room temperature
- .......

New applications have a promise to fundamentally transform information technology, materials science, energy, and biotechnology in the 21st century, with impacts as profound as the silicon revolution of the 20th century.
Graphene Nanoribbons: Zigzag Edge vs. Armchair Edge
Armmchair and Zigzag Edges Are Favored

STM image (14.8 x 13.4 nm²) of a graphene edge

Armchair edges are most favored (most stable)
followed by zigzag edge
chiral edges are least favored

Electronic Properties of Armchair GNRs

All $N_a$-AGNRs are semiconductors with three distinct families of gap size.

Gap hierarchy:
$\Delta_{3p+1} > \Delta_{3p} > \Delta_{3p+2} (\neq 0)$

c.f. TB study
$\Delta_{3p} \geq \Delta_{3p+1} > \Delta_{3p+2} (=0)$

The zigzag edge possesses a unique localized state near the Fermi level, while the armchair edge does not.

Zigzag State Leads to *Magnetic Ground State*

Antiferromagnetic (AFM) phase most stable


Zigzag Edge Effect Holds True for Others with six or more edge atoms

Oligoacenes

Cyclacenes

H-terminated zigzag nanotubes

Bendikov, M. et al.

CNRs with Fewer Zigzag Edge Atoms Can also be Antiferromagnetic (open-shell singlet)!

Only four zigzag edge atoms, but antiferromagnetic!
How to Stabilize the Kinetically Unstable Zigzag GNRs

Two ways that transfer a long zigzag edge into armchair type

Four examplar chemical modifications
Confirmations of Our Proposed Procedure

1 (1.89 eV)
CNG[4,9]H_8

2 (1.76 eV)

CNG [4,9] (0.29 eV)

3 (1.37 eV)

4 (1.51 eV)
Edge-shape dependent electronic ground state, stability, and chemical reactivity of carbon nanographene.

Carbon nanographenes (CNGs) with long zigzag edges and their boron nitride analogues have different electronic ground states.

Chemical modifications that change the long zigzag edge into armchair type can efficiently stabilize the kinetically unstable CNGs (with open-shell singlet ground states) and modify their energy gaps.

Band Gap Engineering in N-doped Graphene Nanoribbons

Martins et al. Nano Lett. 2008, 8, 2293
Graphitic N: Structure and Energy Bands

Spin Gapless Semiconductor!

Graphitic N: Structure and Energy Bands

Two single N atom substitution transform N-doped graphenenes into metals.
Pyridinic N: the Lowest Energy Configurations

Three-nitrogen vacancy (3NV) defect and four-nitrogen divacancy (4ND) defect) prefer the ribbon edge
Various Magnetic Orderings in Solids

- **Density of States**
  - **Ferromagnetic metal**
  - **Antiferromagnetic Insulator**
  - “Half-metal”
$P_{\text{N-edge}}$

$3\text{NV}$

$4\text{ND}$
Achieving Various Electronic States by Defect Engineering

SGS  Metal  SGS

SGS  Metal  SGS

Half-metal  Half-metal
Inorganic Nanotubes

BN nanotube
Wide-gap (5eV) semiconductor independent of chirality
*Science* 1995, 269, 966

SiC nanotube
Semiconducting independent of the helicity

The first inorganic nanotube
molybdenum disulfide (MoS$_2$)
*Nature* 1992, 360, 444

'Morning, Raven. What're you doing?

Scientists discovered how to make stable, atom-thin sheets of graphite by peeling sticky tape off of larger graphite fragments.

They're called graphene, and they're the most efficient room-temperature electrical conductors in nature. My dad's really excited about them.
O-okay...

So I was thinking, what if you applied that technique to other materials?

And then it hit me—CUPCAKES! Super-thin sheets of cupcake would be the most efficient room-temperature deliciousness conductors in nature!
I give you: CUPCAKENE. Here, try one.
Atomically Thin Boron Nitride Membranes Just Synthesized

Meyer, Chuvilin, Algara-Siller, Biskupek, Kaiser
_Nano Lett._ **2009**, *9*, 2683
Publication Date (Web): May 29, 2009 (Letter)
The Electronic State of BN Nanographenes

HOMO-LUMO gaps energies of BN nanographenes

BN nanographenes are all closed-shell singlets!

Gao, X.; Zhou, Z.; Zhao, Y.; Nagase, S.; Zhang, S., Chen, Z.
The H-terminated BNNRs are Non-magnetic

Wide gap of ca. 4 eV
Not So Robust Band Structures of BNNRs

All of BNNRs with SW defects still remain semiconductor character.

May be feasible to engineer the band structure by edge modification (ongoing)
Half-metallic Graphene Nanoribbons
- various magnetic orderings in solids

Energy

Density of States

Ferromagnetic metal

Antiferromagnetic Insulator

“Half-metal”
Two Methods to Realize Half-metallicity

Apply external transverse electric field to a zigzag graphene nanoribbon (ZGNR)

Edge-Modified Zigzag Graphene Nanoribbons

Kan, E. J.; Li, Z.; Yang, J.; Hou, J. G.
25 citations now!

Son, Y.; Cohen, M. L.; Louie, S. G.
266 citations
Armchair SiC NRs
Nonmagnetic Semiconductor

SiC sheet
direct energy gap of 2.55 eV

Armchair SiC NRs
semiconducting with direct band gap

Sun, L.; Li, Y.; Li, Z.; Li, Q.; Zhou, Z. Chen, Z.; Yang, J.; Hou, J. G.
The zigzag SiC NR with $W=7$ is **half-metallic** even **without** external electric field and chemical modification!

Spin-polarized band structures of the zigzag SiC NRs with $W=7$, 20, and 40.

Thanks to Ping Lou and Jin Yong Lee, *J. Phys. Chem. C* 2009, 113, 126
Structures of MoS$_2$ Nanoribbons

8-ZMoS$_2$NR

15-AMoS$_2$NR.
Armchair MoS$_2$ NRs
Nonmagnetic Semiconductor

Band structure of 15-AMoS$_2$NR

Variation of energy band gaps vs. ribbon width.
Zigzag MoS$_2$ NRs
Ferromagnetic and Metallic

Spatial spin distribution (up-down)
of 8-ZMoS$_2$ NR.
Zigzag MoS$_2$ NRs
Ferromagnetic and Metallic

Computed spin-polarized band structure for 8-ZMoS$_2$NR

Total density of states (TDOS) and local density of states (LDOS) for 8-ZMoS$_2$NR
High Stability of MoS$_2$ NRs

Triangular single-layer MoS$_2$ nanocluster of different size in the range $n = 6-8$.
(a)-(c) Mo edge with 100% S coverage; (d)-(f) S edge with 100% S coverage.
Summary

- Electronic structures of CNRs can be engineered by chemical modification.

- BNNRs are always nonmagnetic semiconductor, but the band structures are not as robust as BNNTs, and may be altered significantly by edge modifications.

- Armchair SiC and MoS$_2$ NRs are nonmagnetic semiconductor.

- Zigzag SiC and MoS$_2$ NRs are ferromagnetic and metallic, especially SiCNRs narrower than $\sim$4 nm are half-metallic. *Edge effects are super important!*

There is a also BIG space for Inorganic Nanoribbons!
Acknowledgement

Major Collaborators

Mr. Yafei Li
Nankai University

Dr. Xingfa Gao
IMS, Japan

Prof. Zhenyu Li
USTC

Prof. Zhen Zhou
Nankai University

Dr. De-en Jiang
ORNL

New Members

Dr. Wei Chen
UPR

Dr. Guangtao Yu
Jinlin University
Thank for your attention!

Collaborations are welcome!