Soft Electronic Organic Materials

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Outline

Introduction to electronic materials (nano/bio)

Biomedical applications using electronic materials

What is a nano-material?

A material consisting of a substance or structure which exhibits at least one dimension < 100 nm.

For comparison, a human hair is ~50,000 nm; visible light, ~ 400 - 700 nm.

Selected Examples of Technological Applications of Nano-structured Materials

- Light-Emitting Devices (LEDs)
- Anti-static coating on photographic film
- Corrosion prevention of metals
- Energy Storage (batteries, capacitors)
- Electromagnetic interference (EMI) shielding
- Anti-static floor tiles, carpets, shoe soles, etc.
- Hydrogen storage
- Transparent electrodes in liquid crystal displays
- Non-linear (NLO) devices
- Stealth (e.g., radar) avoidance systems
- Gas separation membranes
- Biochemical sensors (e.g., for glucose)
- Sensors for volatile organics (VOCs)
- Solar cells
- Drug releasing polymers
- “Plastic chips”
- Inexpensive, “throw-away” electronic devices (with possibly smaller efficiency, precision, lifetime, etc.) than conventional electronic devices
- All-plastic electronic motors

Electronic Organic Polymers (plastics that conduct electricity)

Carbon Nanotubes

Graphene

Endotoxin detector

Introduction to Plastics that Conduct Electricity

Synthetic Metals
Intrinsically conducting polymers
Electronic organic polymers
Inherently conductive polymers
Electronic plastics
‘Dirty metals’

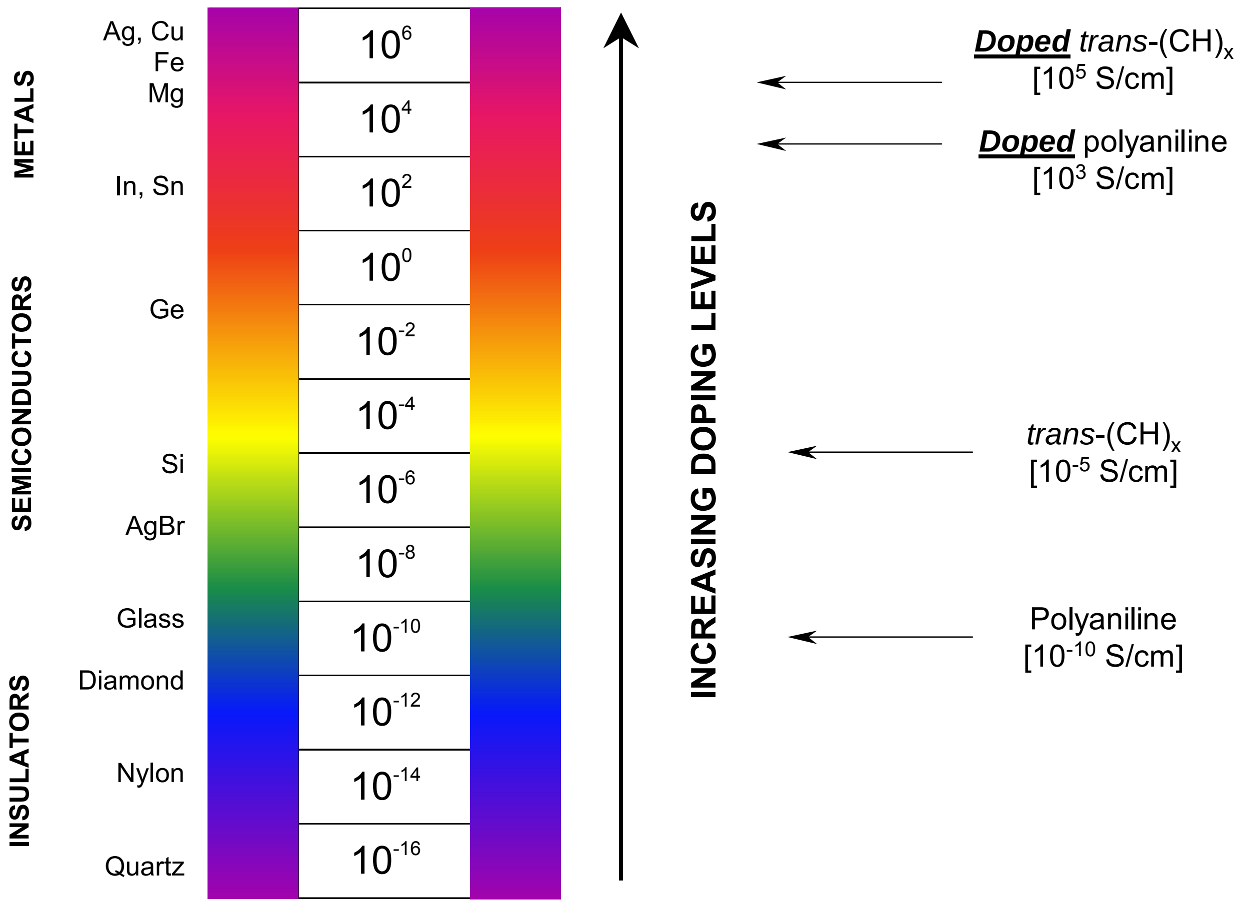
Conducting Polymers

"Synthetic Metals"

- Electronic, Magnetic, Optical Properties of a Metal.

- Mechanical Properties, Processability, etc., of a conventional polymer.

Conductivity increases with increased doping



What is Conductivity?

Conductivity is the Flow of Charge

It depends on:

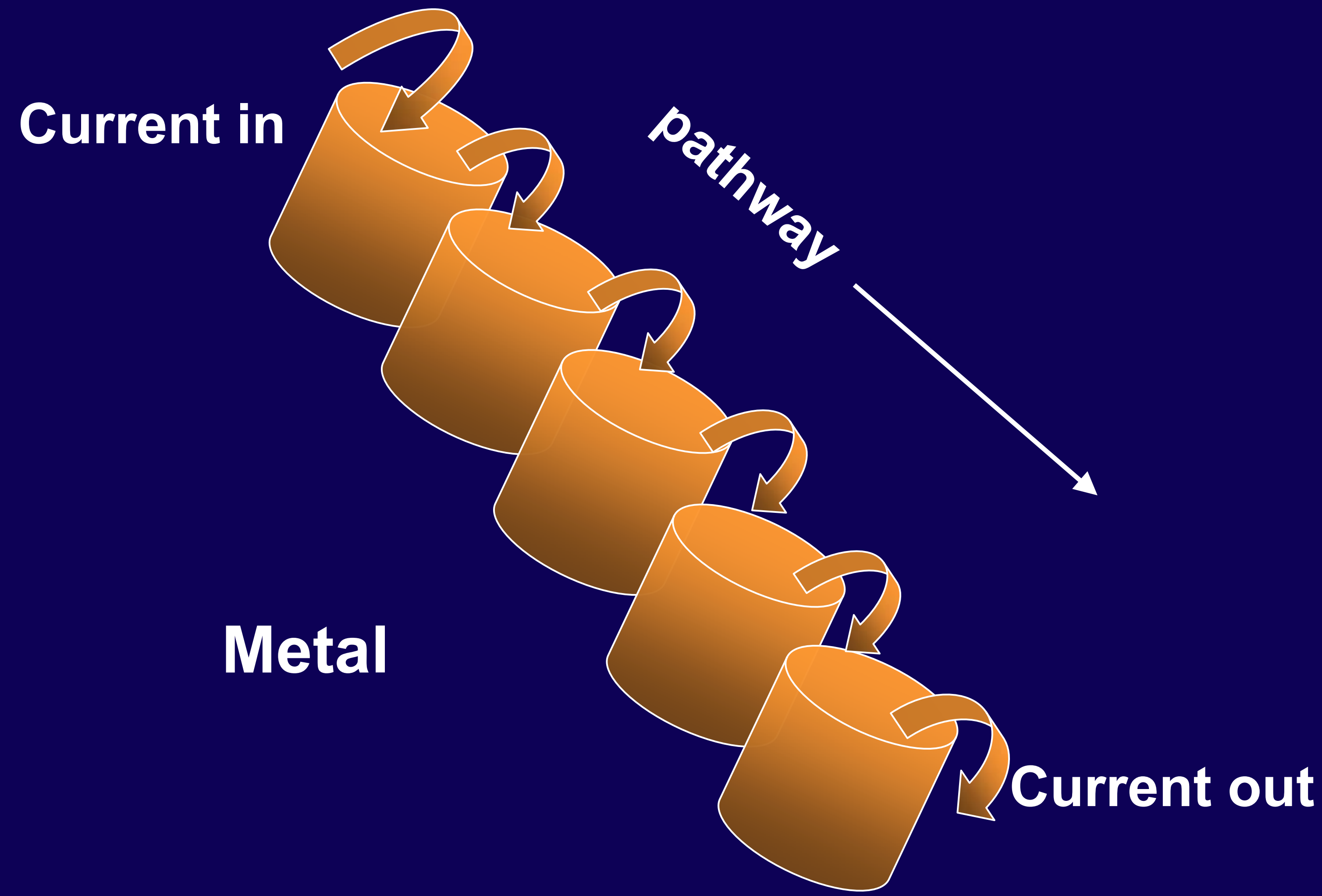
- **what is flowing ?** — charge
- **how many ?** — flow
- **how easily ?** — flow

$$\sigma = e \times N \times \mu$$

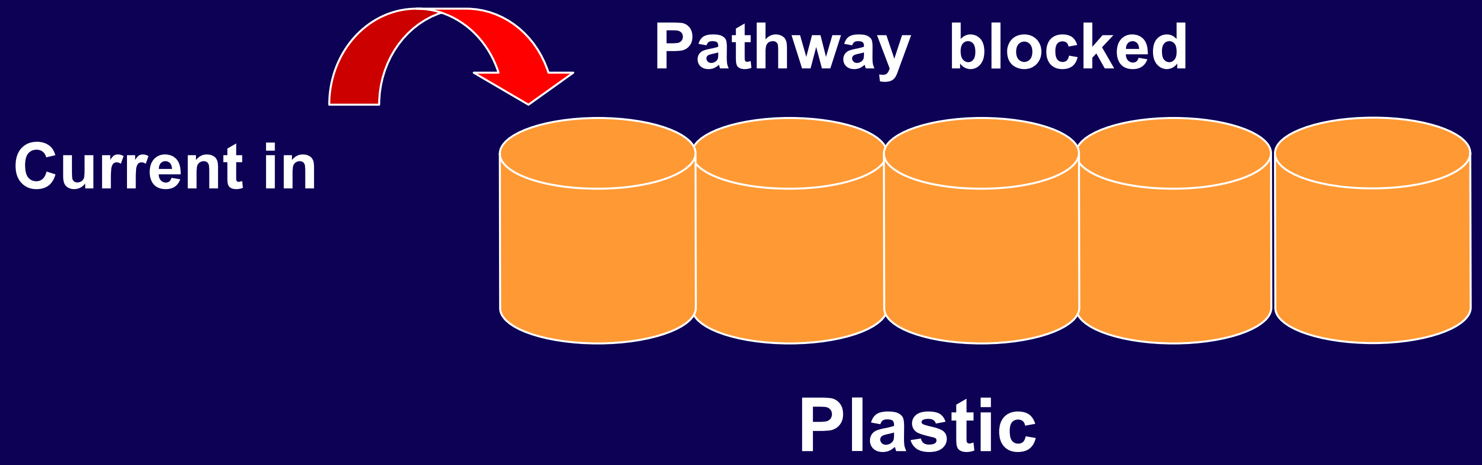
- e: Electron Charge
- N: Number of charge carriers (flow)
- μ: Carrier mobility (flow)

Metals are good conductors

Simple model for metal conduction



Plastics as Insulators



Why are plastics good insulators?

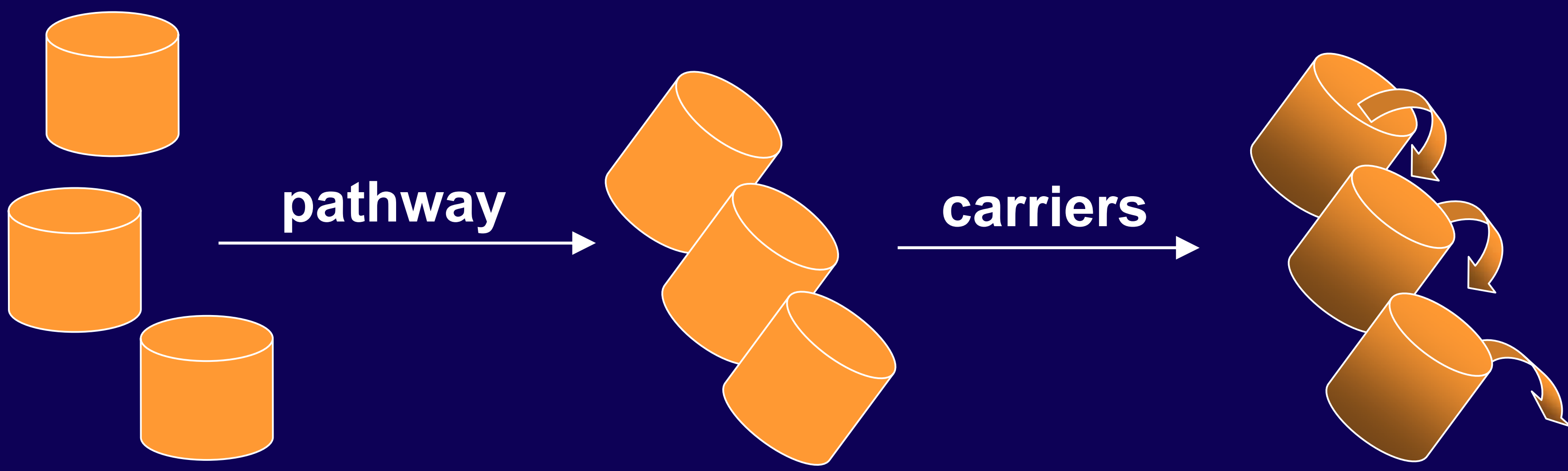
1. They don’t have a pathway to carry current.

2. They don’t have any charge to carry current

Modification of Plastics

Make a pathway

Create current carriers

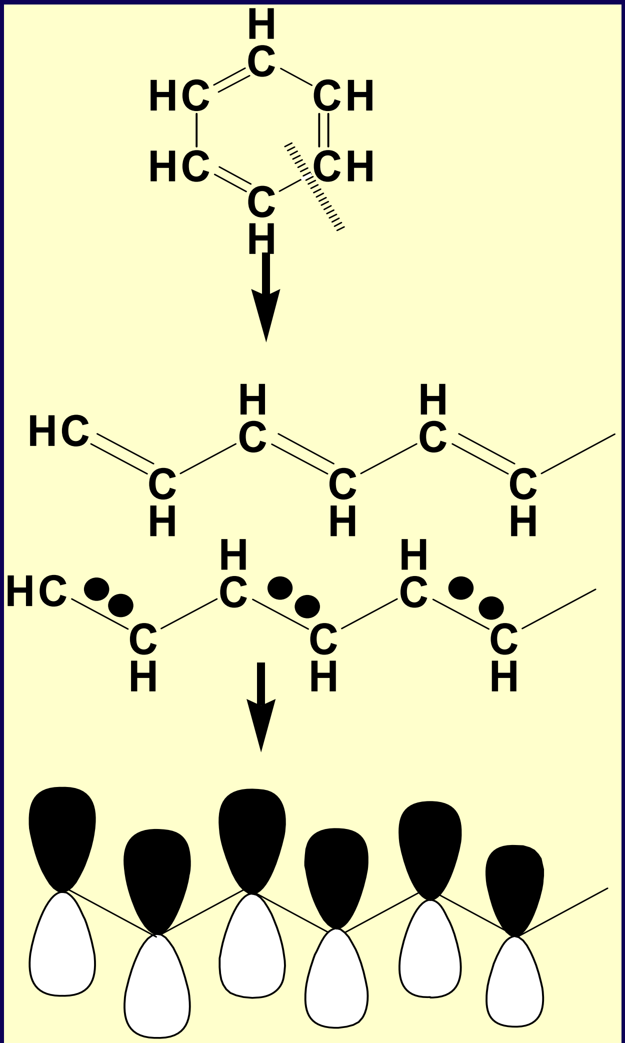


no pathway
no carriers

pathway
no carriers

pathway
carriers

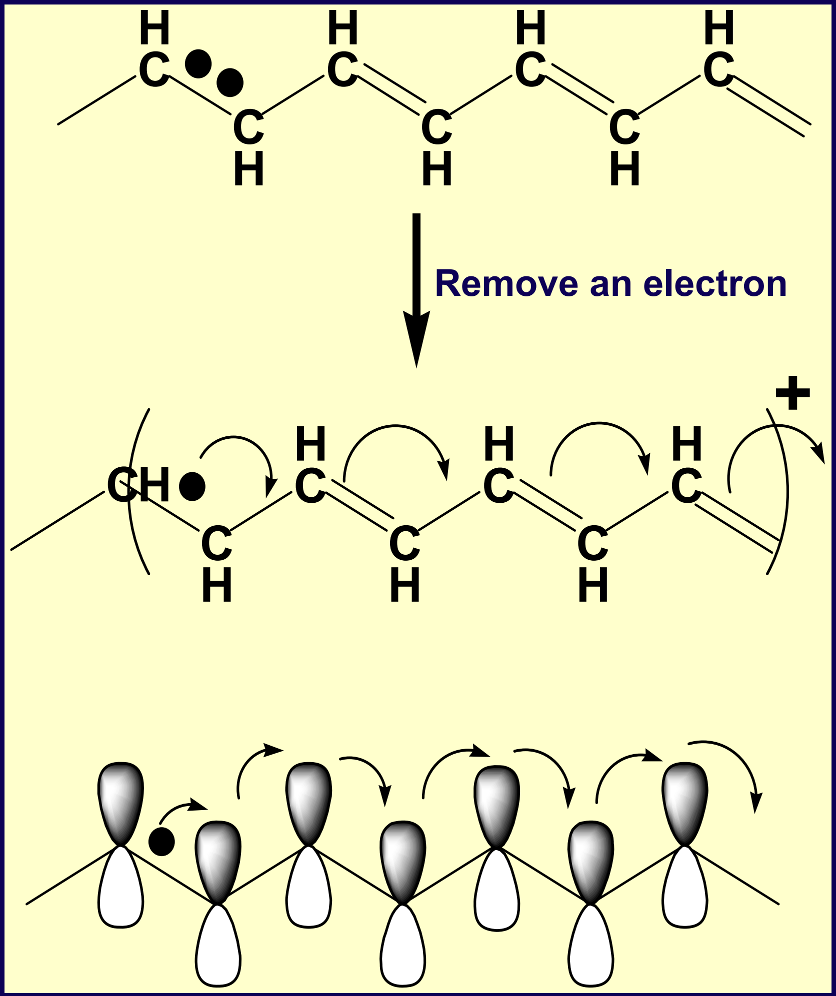
The Idea



Benzene
3 single bonds
3 double bonds

Now, how do you introduce charge?

Idea…creating charge in the plastic



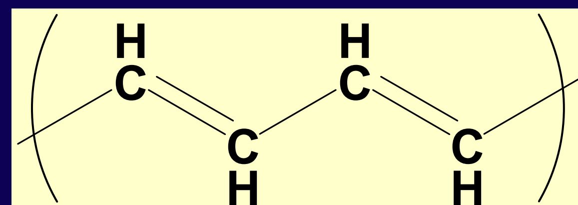
Electricity travels along the chain

World's first conductive plastic! 1977

$HC \equiv CH$

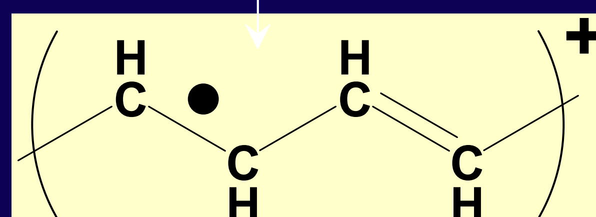
Welding gas, acetylene

↓ **Flow, or pathway**



"Poly" acetylene insulating

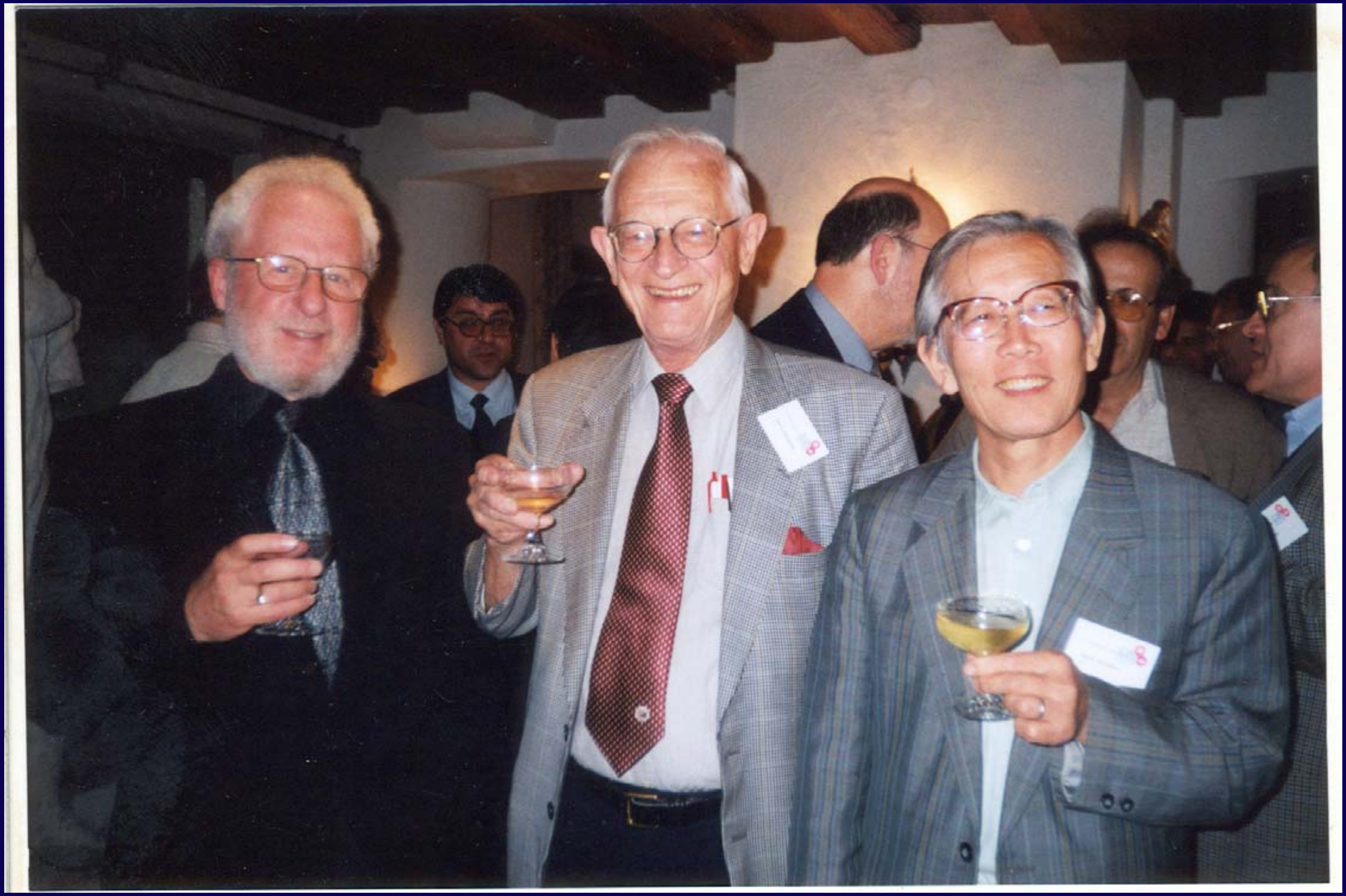
↓ **charge**



"Poly" acetylene…. conducting

Conductivity: 34 S/cm (1977); 150,0000 S/cm (2004)

Y2K Nobel Prize in Chemistry



Alan Heeger   Alan MacDiarmid   Hideki Shirakawa

Electronic (Organic) Polymers

Non-Doped: Semiconductors/Insulators

dope” ⇅ ***“de-dope”***

Doped: “Metals”

(Conducting Polymers: “Synthetic Metals”)

- **Organic Polymers**

  - **Electrically Insulating**
  - **Electrically conducting**

- **The Concept of Doping of an Organic Polymer**
  (to increase its conductivity to the metallic regime)

- **Redox Doping**

  - **p-doping**
    - **-- chemical**
    - **--electrochemical**

  - **n-doping**
    - **-- chemical**
    - **-- electrochemical**

- **Non-redox Doping: *The Polyanilines***

- **Technological Applications**

Concept of Doping of Organic Polymers

- **Doping:**
  - The unique, central, underlying and unifying theme in conducting polymers

- **Controlled addition of known, small (<10%), non-stochiometric quantities of chemical species results in dramatic changes in electronic, optical, and structural properties of the polymer**

- **Doping is reversible (No degradation of the polymer "backbone")**

- **Doping and undoping by either chemical or electrochemical methods**

- **ALSO:**

  •"Photo-doping" ***(Transitory: no chemical species added)***
  •"Charge Injection Doping" ***(Transitory: no chemical species added)***

Polyacetylene*
"The Prototype Conducting Polymer"

0.5x $HC\equiv CH$ → *cis*- **$(CH)_x$**
Silvery films
(semiconductor)

↓ **~150 ^{o}C**

trans- **$(CH)_x$**
Silvery films
(semiconductor)

* H. Shirakawa and S. Ikada, *Polym. J.*, **2**, 231 (1971).

Redox Doping*

(Increase or decrease number of electrons on the polymer backbone)

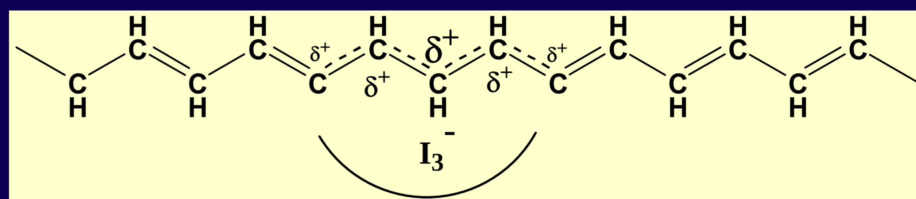
***p*-Doping** *(partial oxidation of the π-system)*

Polyacetylene *(The prototype conducting polymer)*

Chemical Doping

trans- $(CH)_x$ + 3/2(*xy*) I_2 ⟶ $[(CH^{+y})(I_3^-)_y]_x$ $y \leqslant \sim 0.1$

$\sigma \sim 10^{-5}$ S/cm $\sigma \sim 10^{5}$ S/cm



A positive soliton *(~15 CH units)*

Electrochemical Doping

Anode

trans- $(CH)_x$ + (*xy*) $(ClO_4)^-$ ⟶ $[(CH^{+y})(ClO_4)_y^-]$ + (*xy*) e^- $y \leqslant \sim 0.1$

$\sigma \sim 10^{-5}$ S/cm $\sigma \sim 10^{3}$ S/cm

*Shirakawa, *et al*., *J. Chem Soc., Chem. Comm.*, 578 (1977); *Phys.\ Rev. Lett.*, 39, 1098 (1977).

Redox Doping *(cont'd)*

***n*-Doping** *(partial reduction of the π-system)*

Polyacetylene

Chemical Doping

trans- $(CH)_x$ + *(xy)* Na/Hg ⟶ $[Na_y^+(CH^{-y})]_x$ $y \leqslant \sim 0.1$

$\sigma \sim 10^{-5}$ S/cm $\sigma \sim 10^{3}$ S/cm

Cathode

Electrochemical Doping

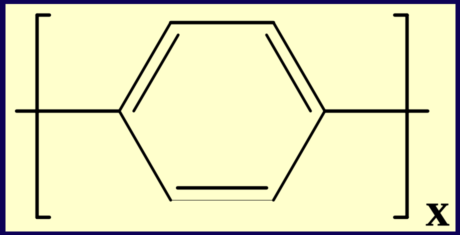
trans- $(CH)_x$ + *(xy)* Li^+ + *(xy)* e^- ⟶ $[(CH^{+y})(ClO_4)_y^-]$ $y \leqslant \sim 0.1$

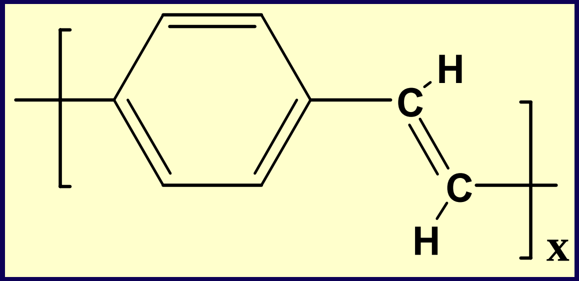
$\sigma \sim 10^{-5}$ S/cm $\sigma \sim 10^{3}$ S/cm

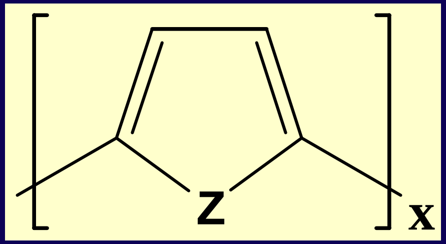
Redox Doping *(cont'd)*

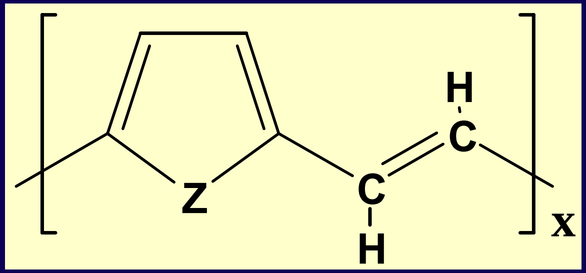
Other examples of redox-dopable polymers

(chemical and/or electrochemical)





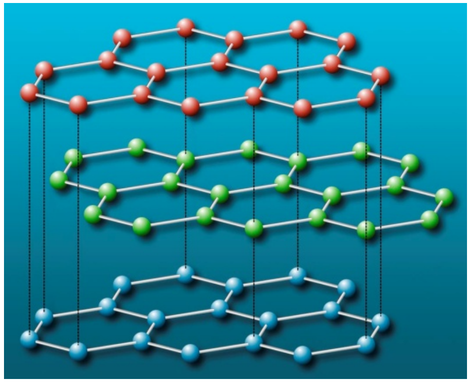




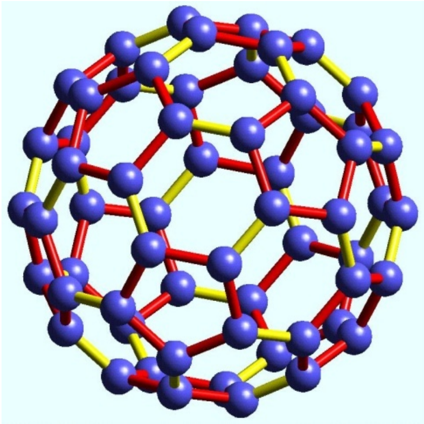
Z = NH, NR, S, O, etc.

Carbon Nanotubes

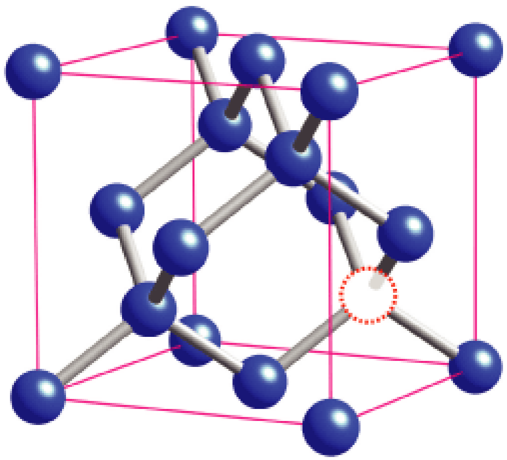
What are Carbon Nanotubes?



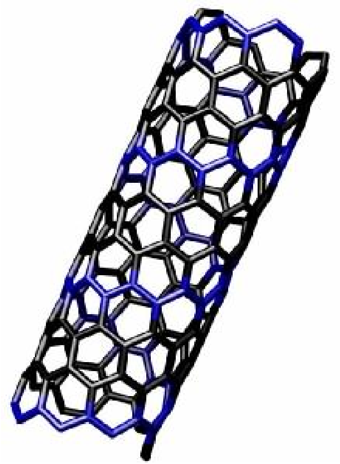
Graphite, sp^2



Fullerene, C_{60}, sp^2



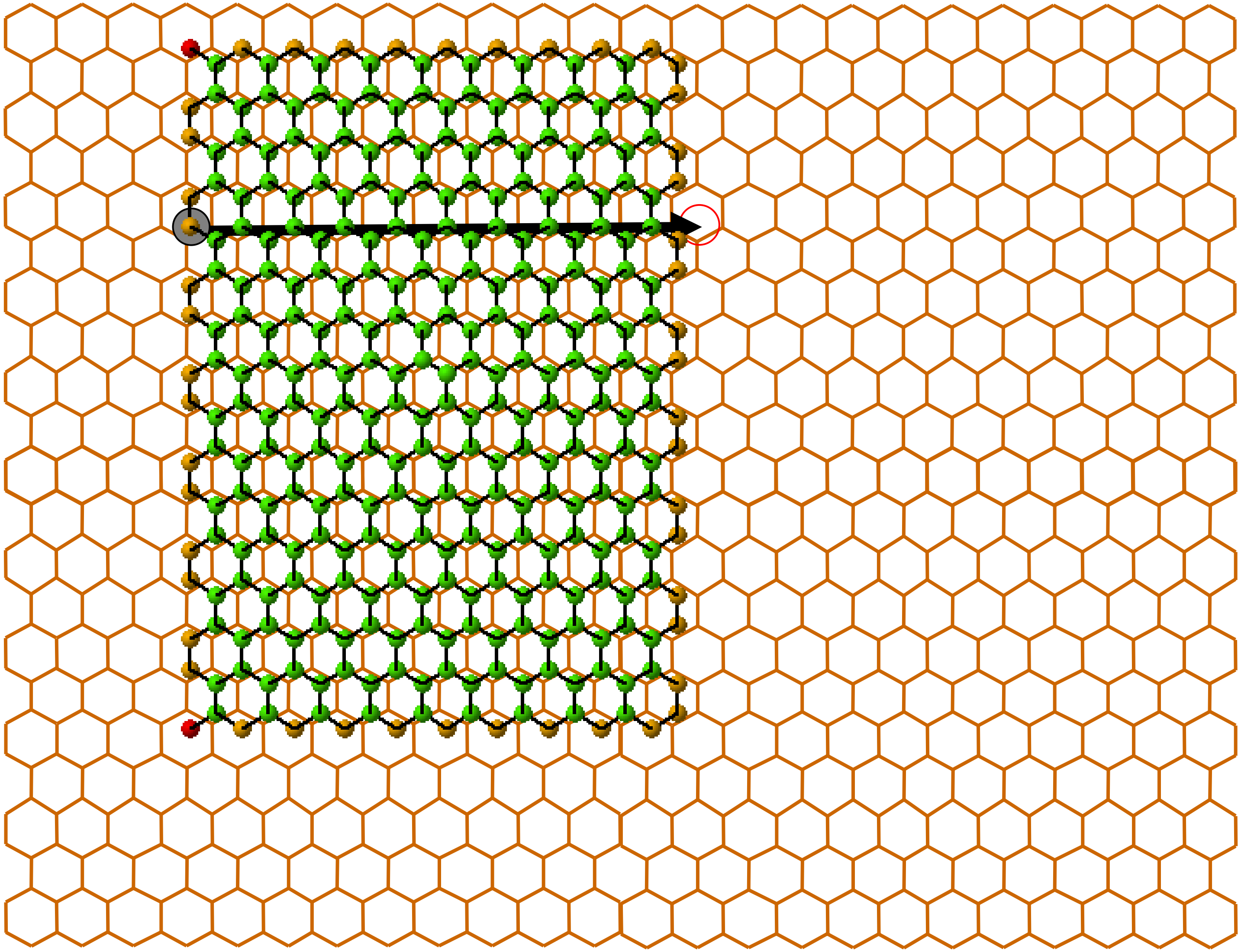
Diamond, sp^3



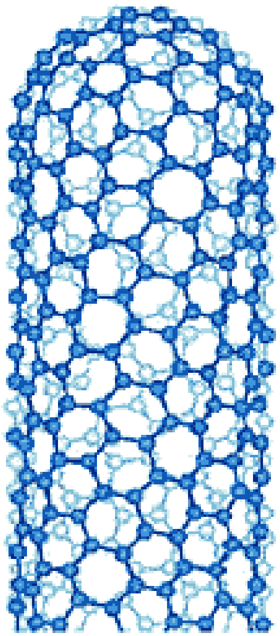
Nanotubes, sp^2

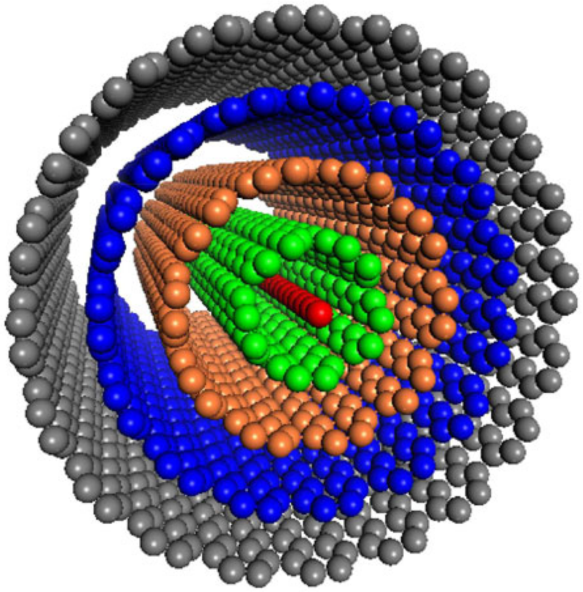
What are Carbon Nanotubes?

- A graphene sheet rolled up into a cylinder…..



Single vs. Multi Walled Carbon Nanotubes

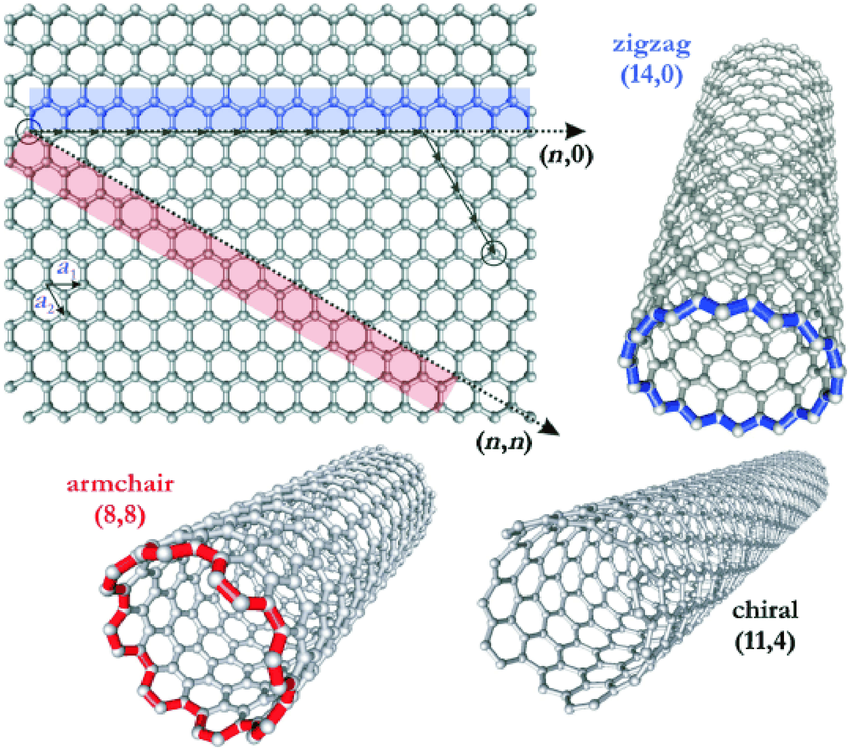




- Single-wall carbon nanotube: Tubes closed at the ends by half-fullerenes

- Multi-walled carbon nanotube: A concentric arrangement of many tubes

Metallic and Semiconducting SWNTs



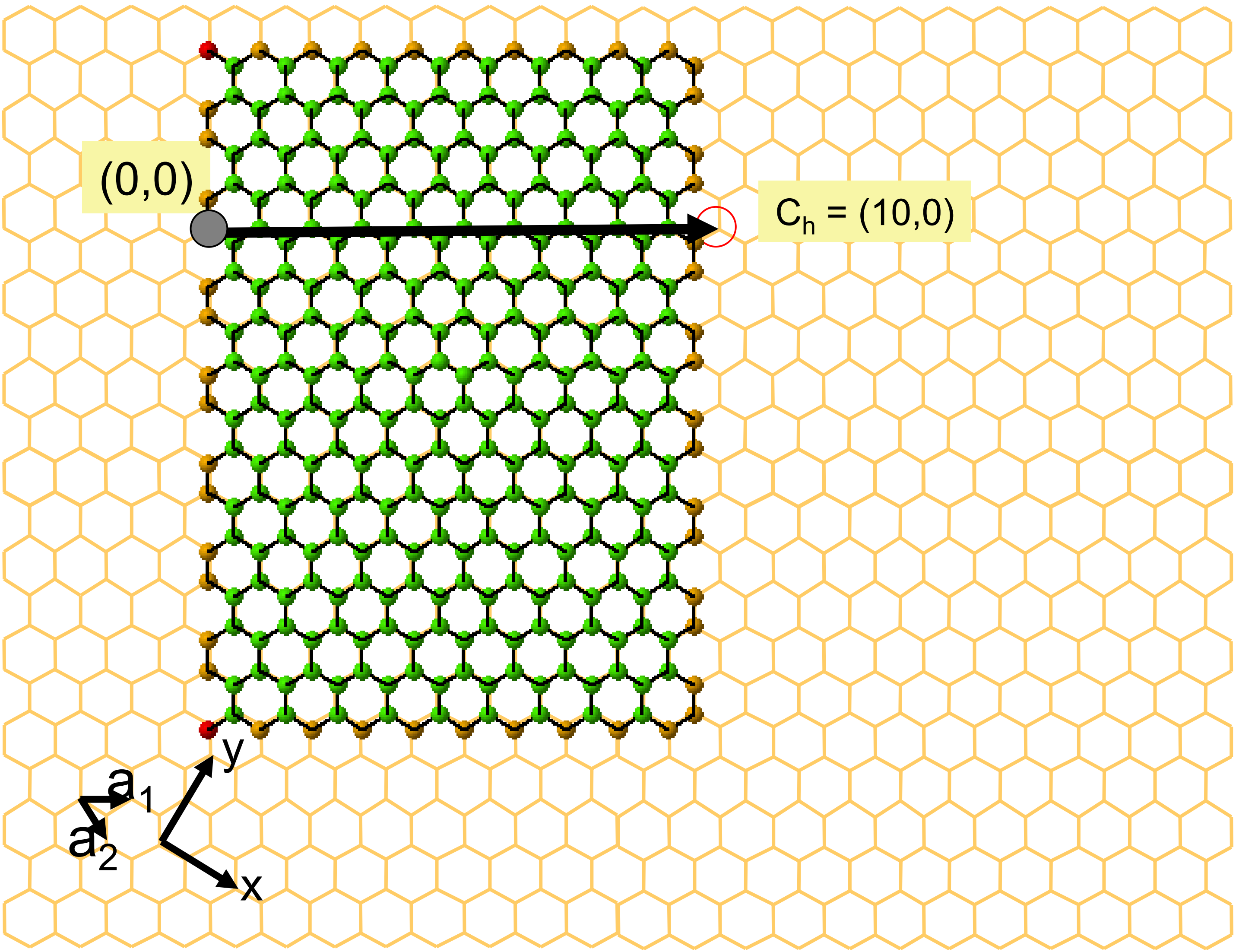
$n - m = 3q$ (q: integer): metallic
$n - m \neq 3q$ (q: integer): semiconductor

- **Metallic tubes**: Optoelectronic displays, transparent conductors, and chemiresistors

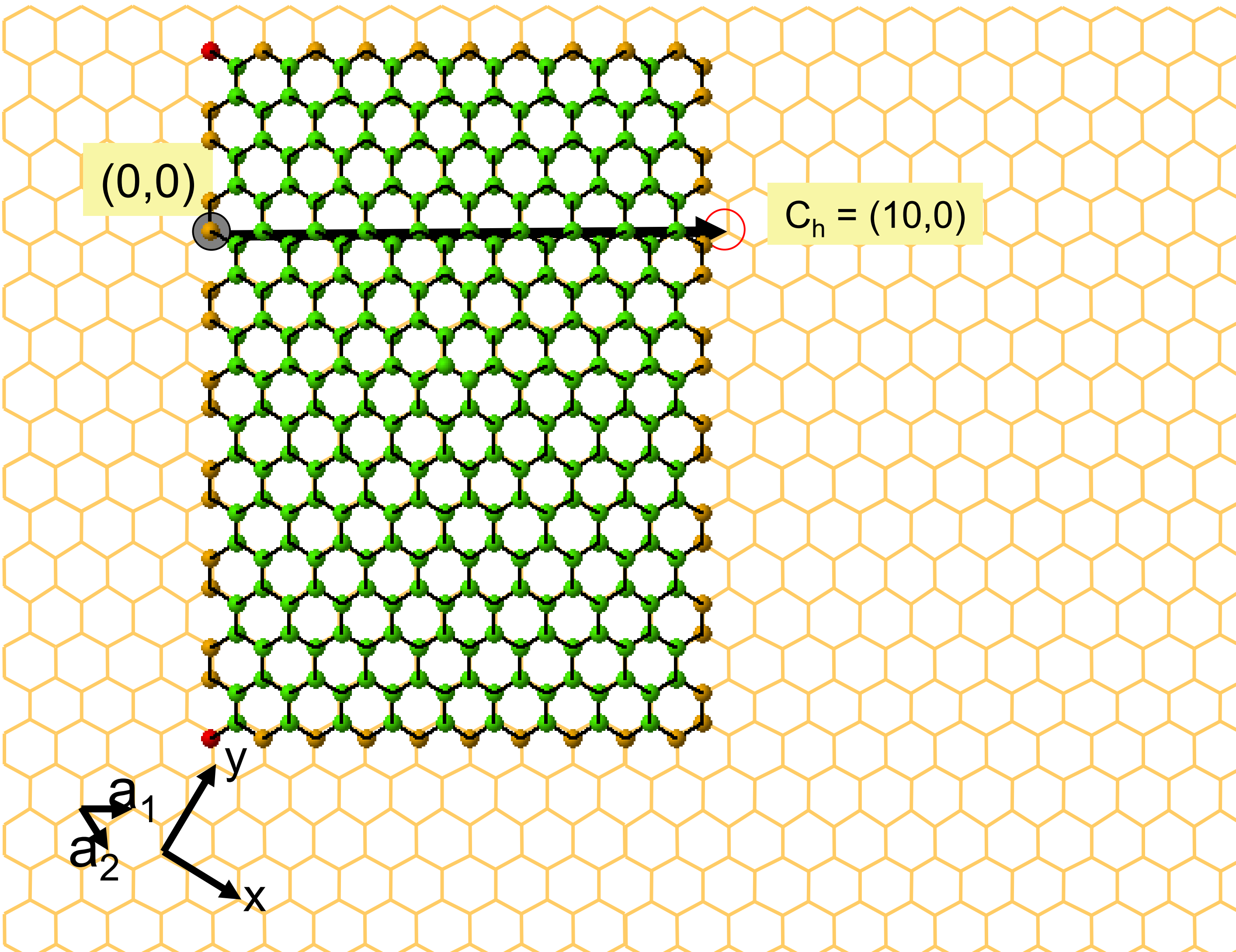
- **Semiconducting tubes**: Switching devices like transistors, diodes and sensors (chem-FETs)

Burghard, M. *et al., Small;* **2005**; 2; 180-192

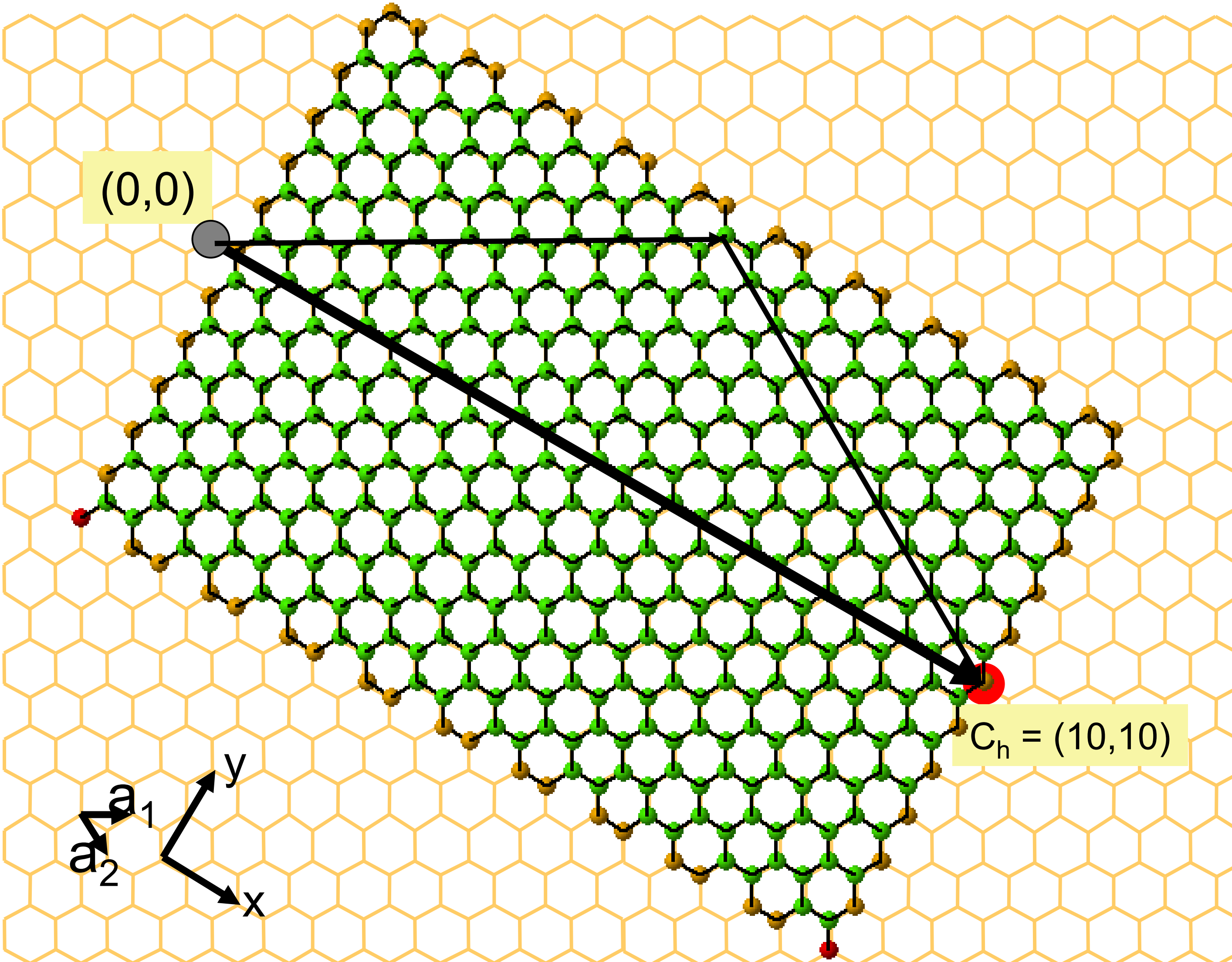
Wrapping (10,0) SWNT (zigzag)



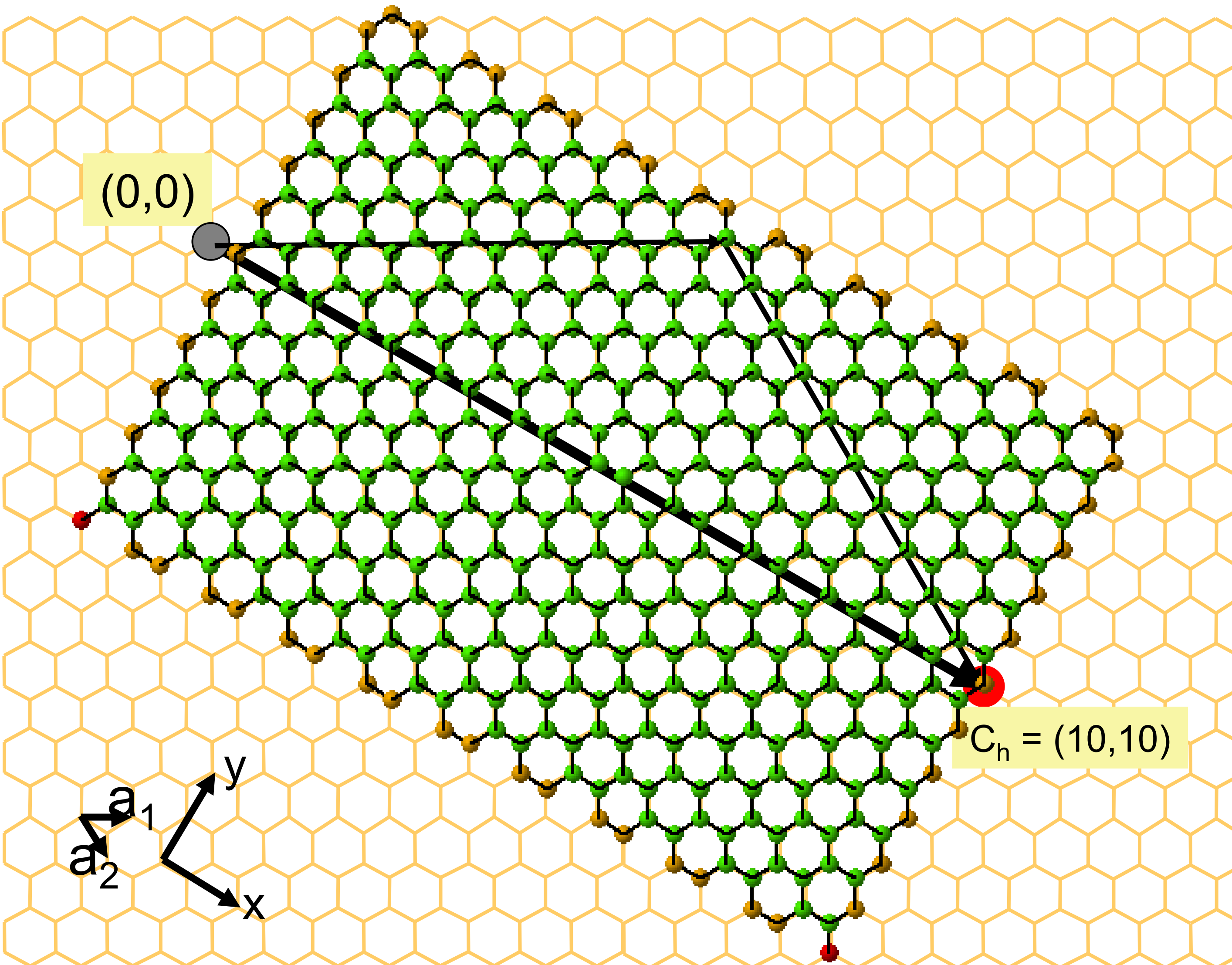
Wrapping (10,0) SWNT (zigzag)



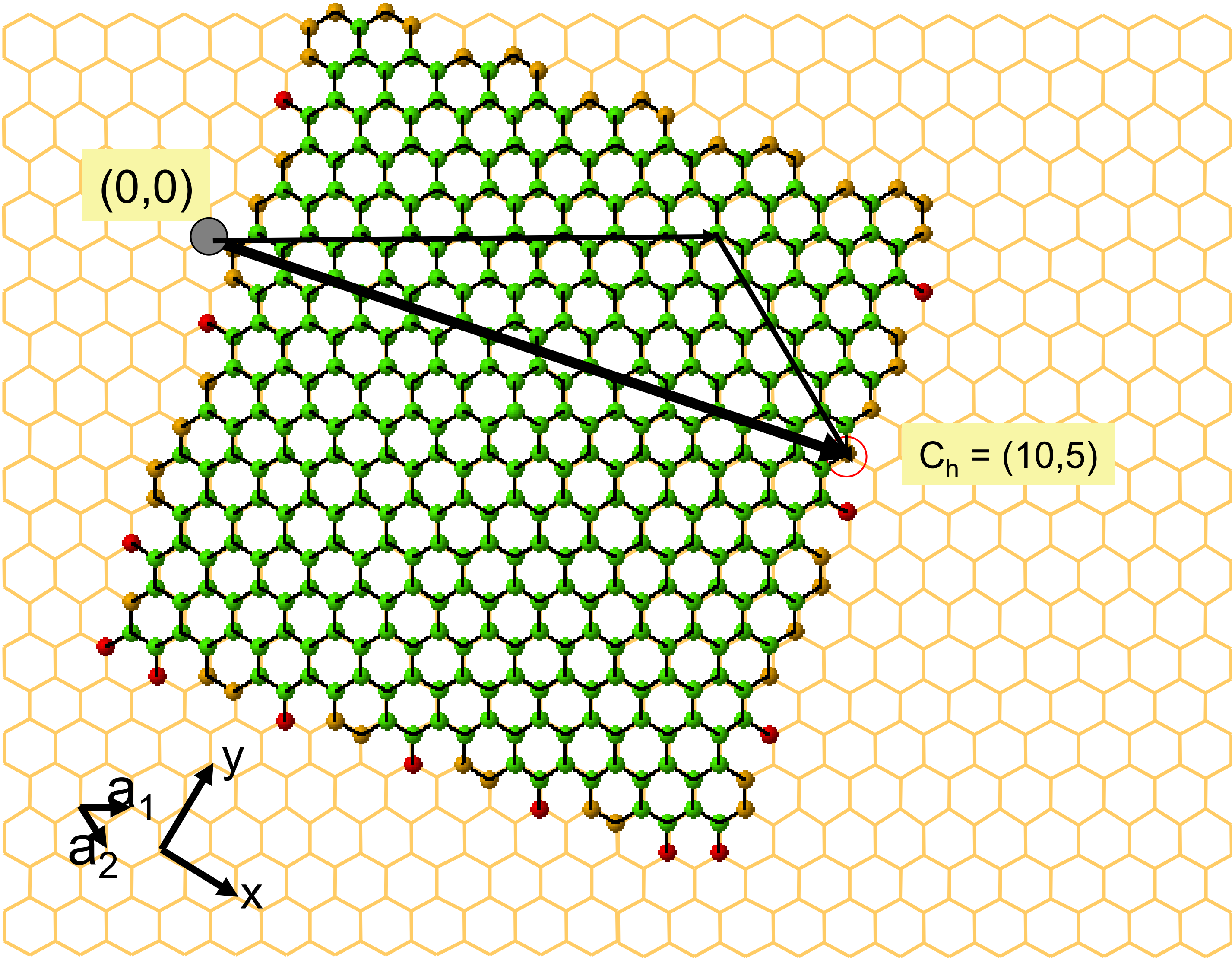
Wrapping (10,10) SWNT (armchair)



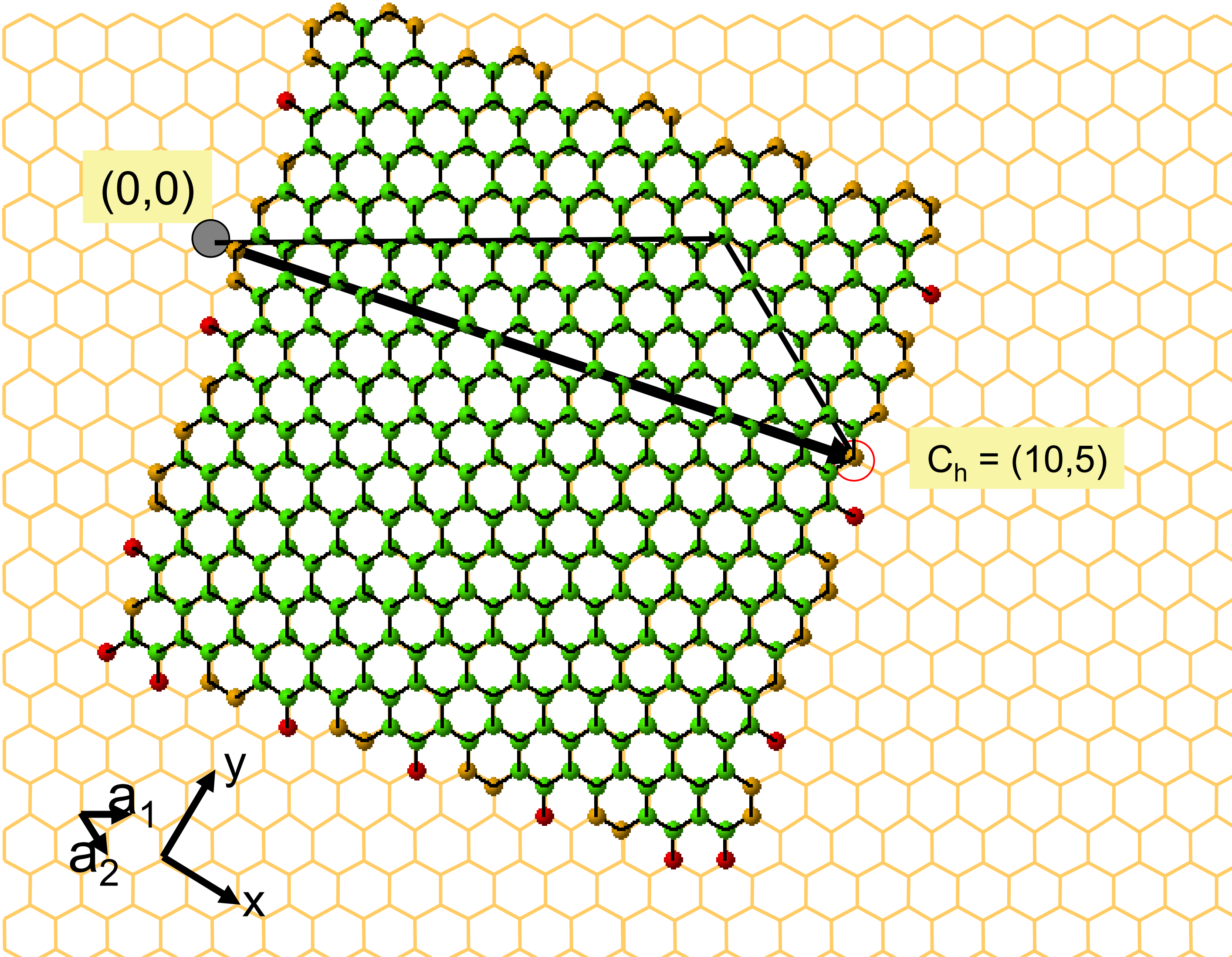
Wrapping (10,10) SWNT (armchair)



Wrapping (10,5) SWNT (chiral)



Wrapping (10,5) SWNT (chiral)

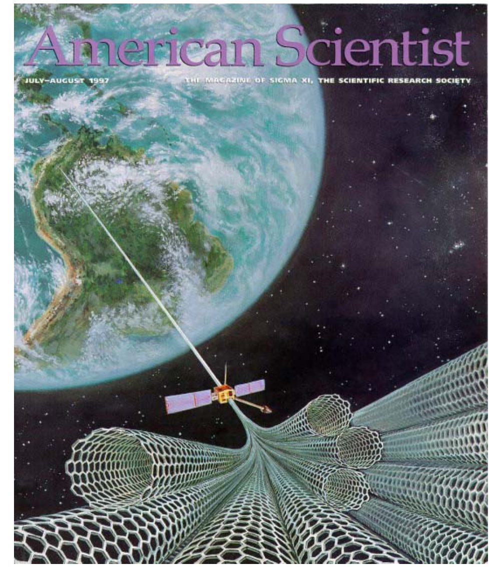


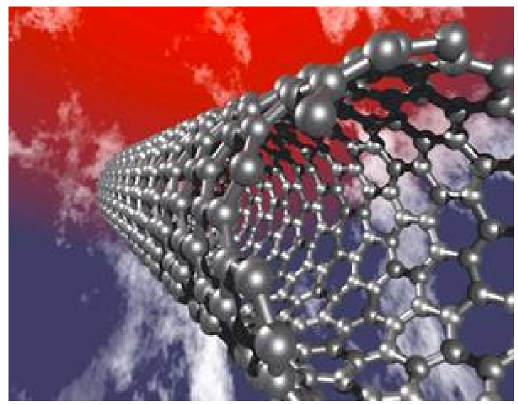
Interesting Properties of Carbon Nanotubes

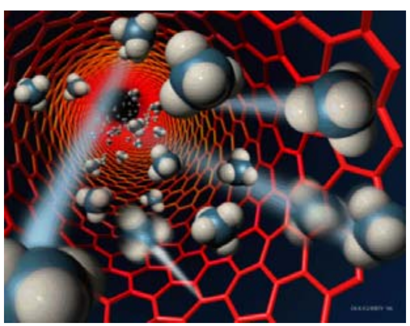
- 1nm in diameter, up to 1cm in length, aspect ratio of 10^7
- 1 defect in 10^{12} C atoms => ballistic conduction
- High melting point ~3800^{o}C
- High young's modulus 1TPa (10^3 times diamond)
- High electronic current carrying capacity (10^9A/cm^2) ~10^3 times higher than that of the noble metals
- Thermal conductivity 6600W/mK at room temperature is twice the maximum known bulk thermal conductor, isotropically pure diamond = 3320W/mK

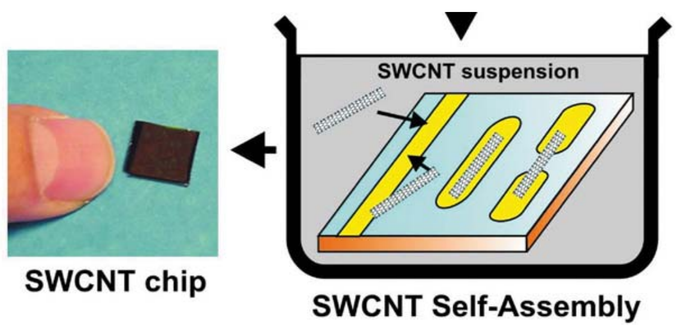
Ajayan M *et al.*, *Chem.. Rev.;* **1999**; 2; 180

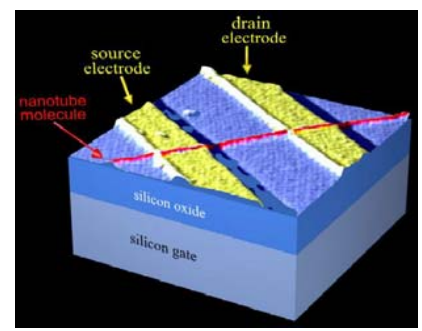
Potential Applications of Carbon Nanotubes





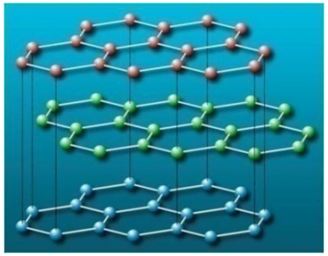




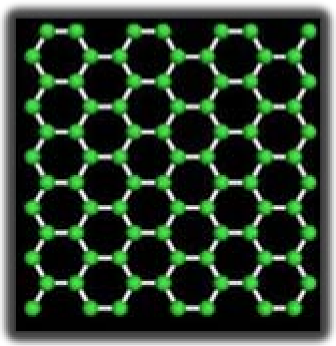


Graphene oxide and reduced graphene oxide

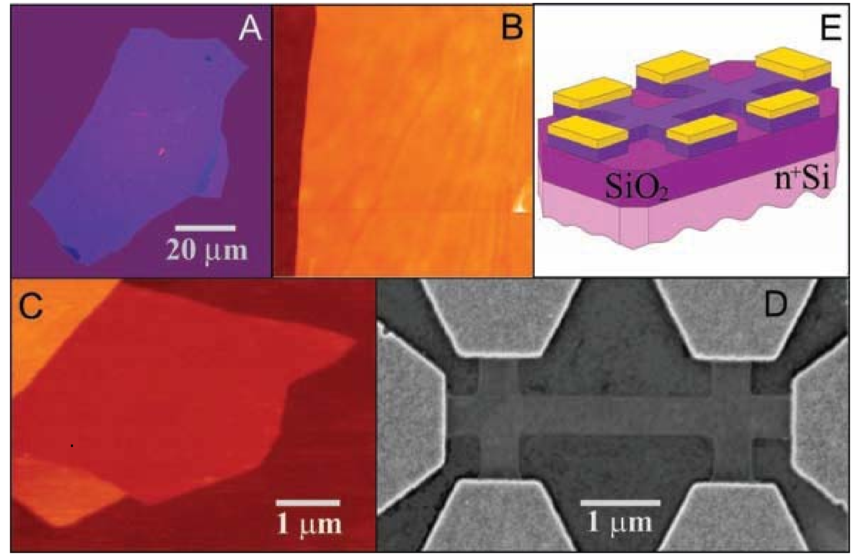
Isolation of single layer graphene sheet (2004)



Graphite (3D)



Graphene (2D) (2004)



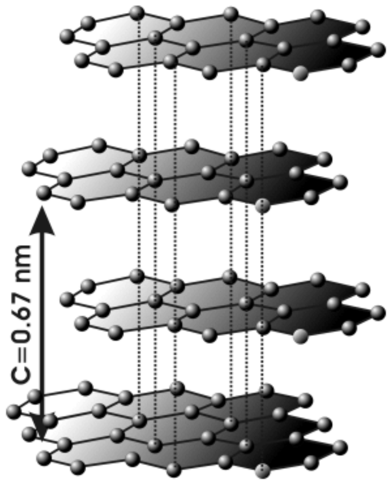
Mechanical exfoliation - (repeated peeling) of highly ordered graphite using scotch tape

Limited yield……

Chemical methods……..

Novoselov, K. S.; Geim, A. K.; Morozov, S. V.; Jiang, D.; Zhang, Y.; Dubonos, S. V.; Grigorieva, I. V.; Firsov, A. A., Electric Field Effect in Atomically Thin Carbon Films. *Science* **2004**, *306*, 666-69

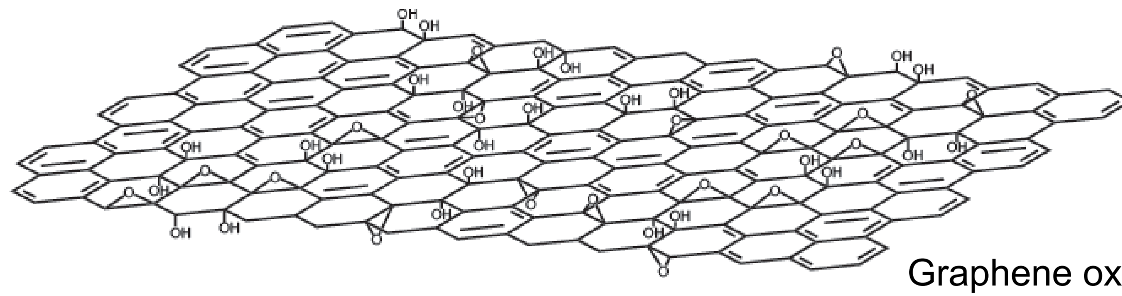
Synthesis of reduced graphene oxide from graphite



Graphite

Oxidation

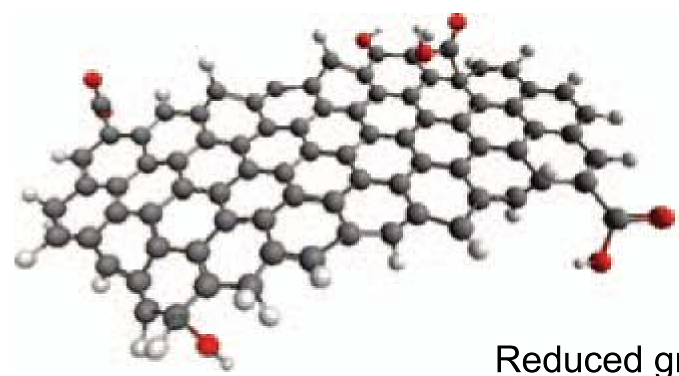
1) Hummers
2) Brodie
3) Staudenmaier



Graphene oxide

1) N_2H_4, $NaBH_4$
2) Thermal
3) Radiation

Reduction



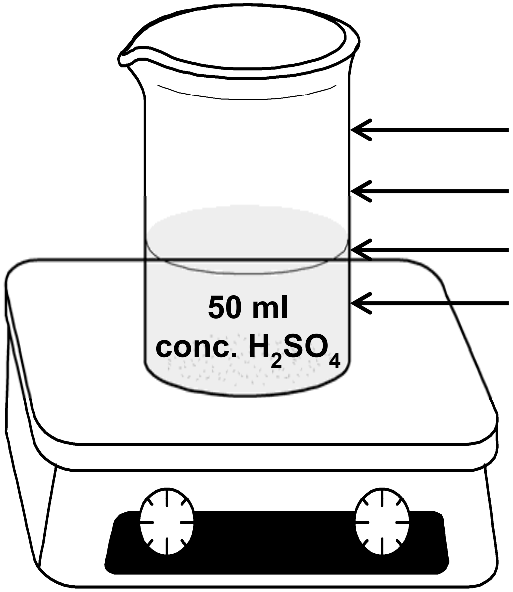
Reduced graphene oxide

Park, S.; Ruoff, R. S., Chemical Methods for the Production of Graphenes. *Nature Nanotechnology* **2009**, *4*, 217-24

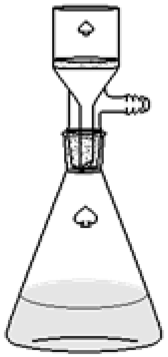
Hummers, W. S., Jr.; Offeman, R. E., Preparation of Graphitic Oxide. *Journal of the American Chemical Society* **1958**, *80*, 1339

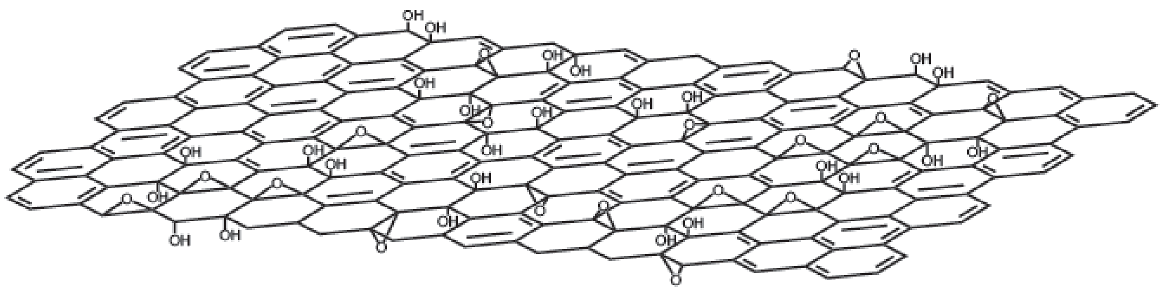
Staudenmaier, L., Preparation of Graphitic Acid. *Berichte der Deutschen Chemischen Gesellschaft* **1898**, *31*, 1481-70

Synthesis of graphene oxide (Hummers method)*



Graphite Nanoplatelets (2g)
$NaNO_3$ (1g)
$KMnO_4$ (6g)
5 ml H_2O_2





Graphene Oxide

Strong acids and oxidants!

H_2O
Sonication

Graphene oxide dispersion

*Hummers, W. S., Jr.; Offeman, R. E., Preparation of Graphitic Oxide. *Journal of the American Chemical Society* **1958**, *80*, 1339

Graphene oxide is readily inkjet printed on PET, paper, etc., using commercial printers

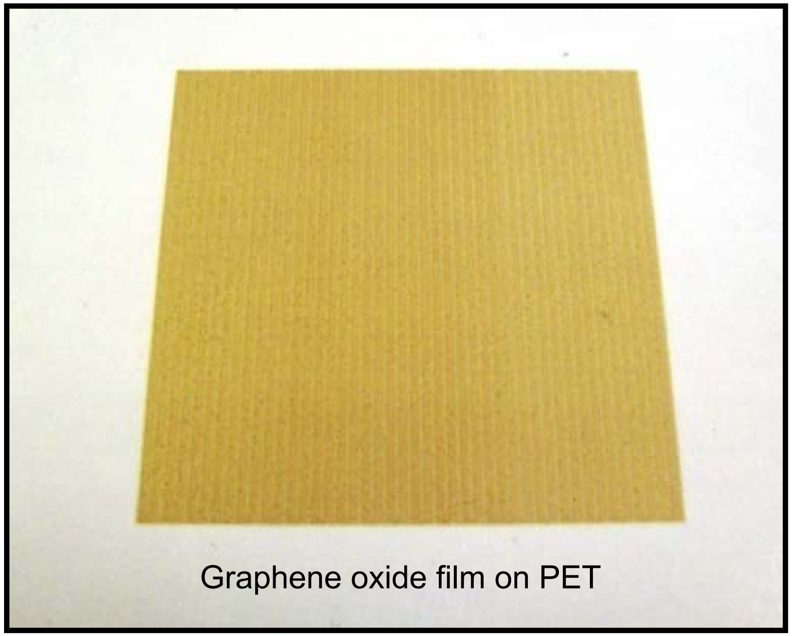
Graphene oxide dispersion in water

1. Empty inkjet commercial cartridge
2. Fill cartridge with graphene oxide dispersion

Inkjet print using commercial printer on paper or plastic

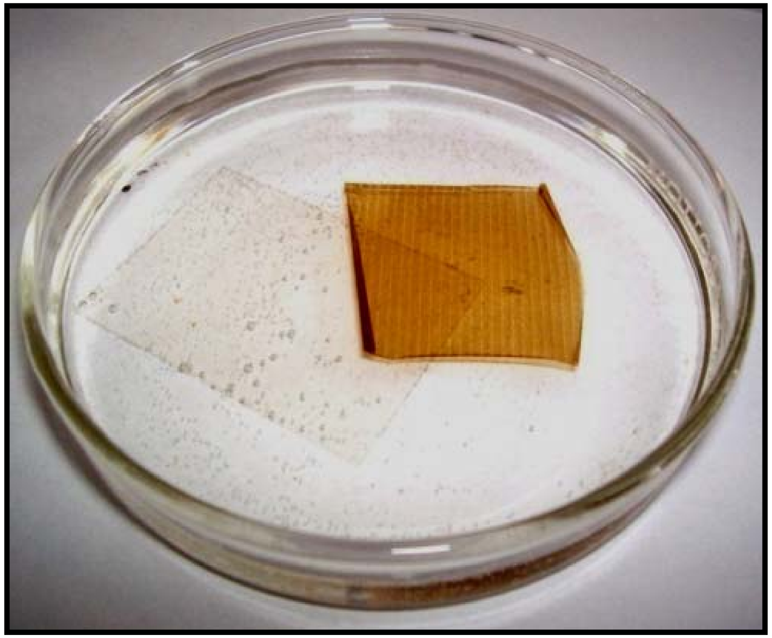
Graphene oxide film on PET

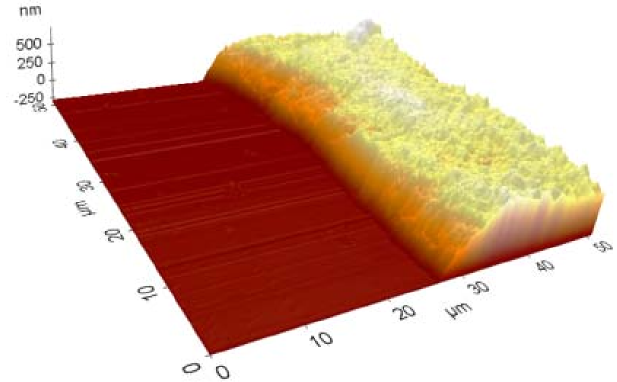
Free-standing films of inkjet printed graphene oxide lift off a PET substrate



Graphene oxide film on PET

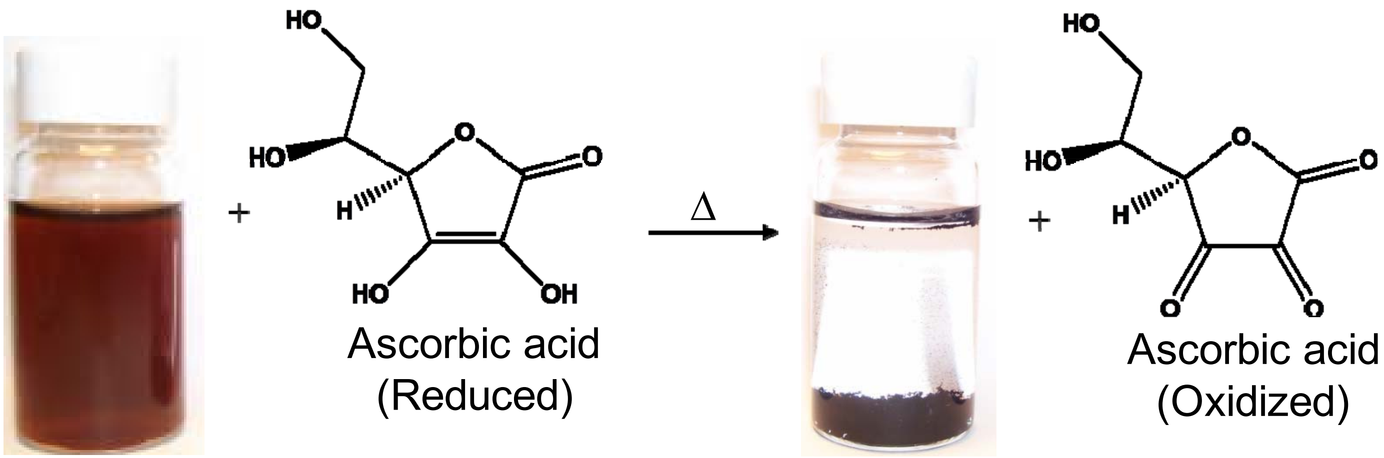
Immerse in water →





~700 nm

Ascorbic acid readily converts graphene oxide to reduced graphene oxide

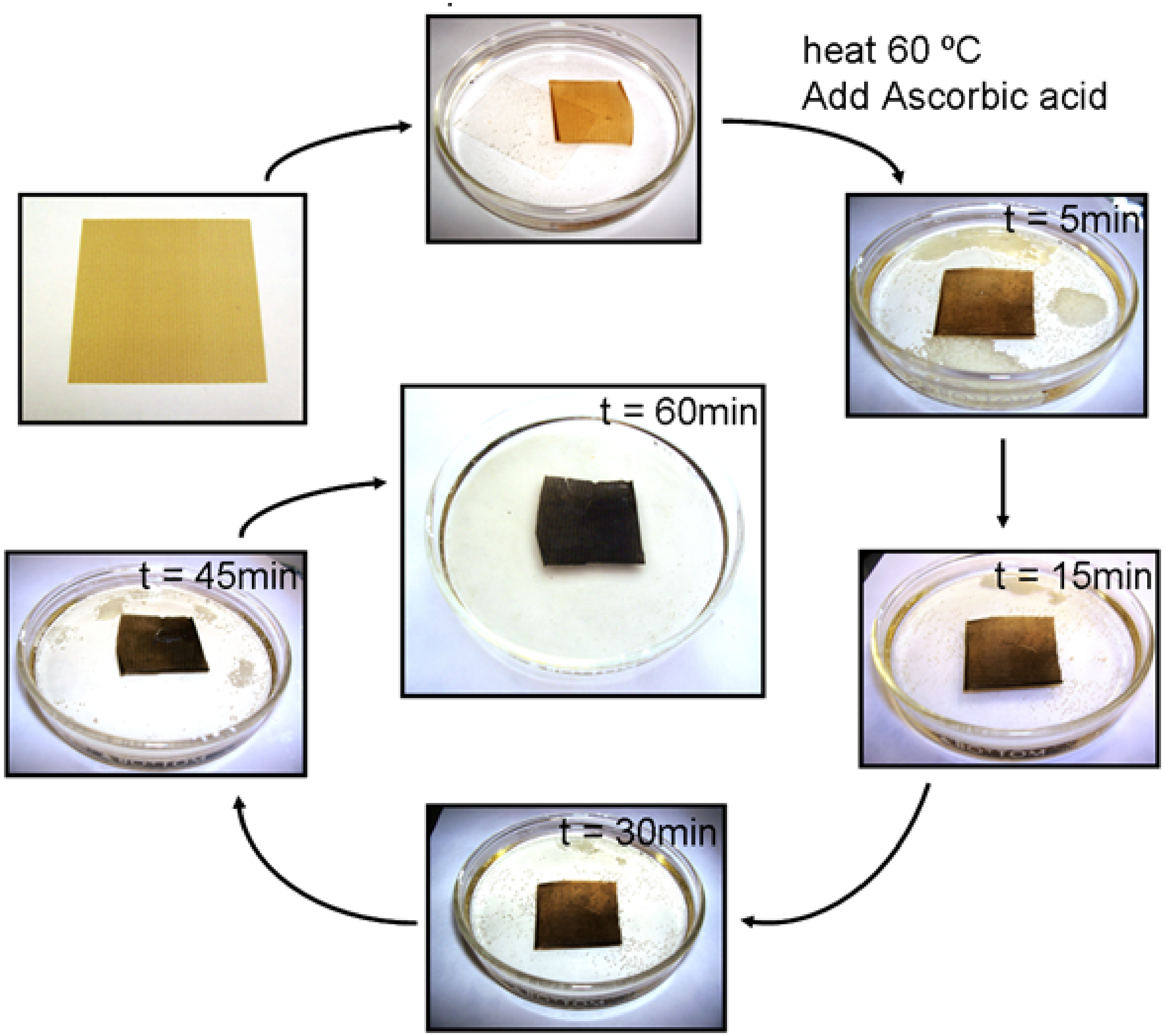


Graphene oxide

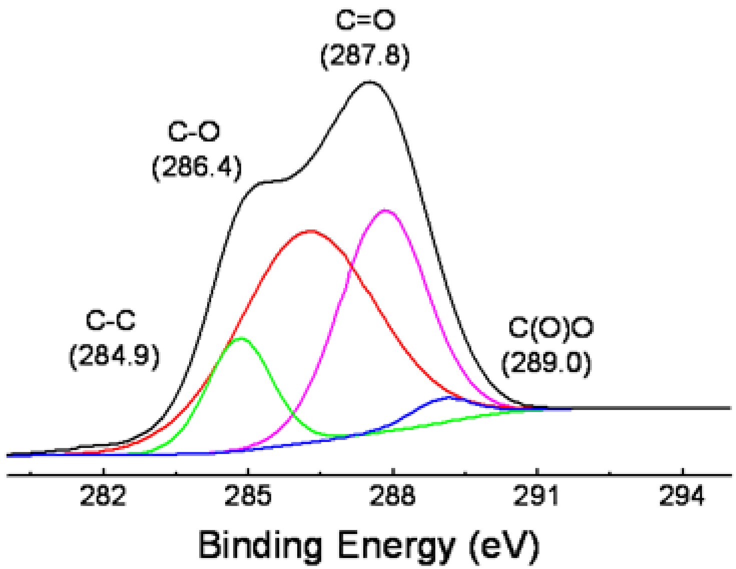
Reduced graphene oxide

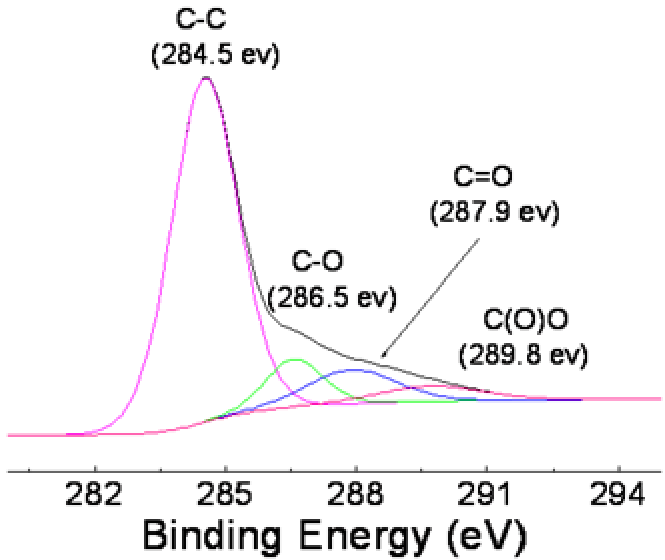
Pressed pellet conductivity 15 S/cm
Vitamin C reduced is similar to hydrazine reduced graphene

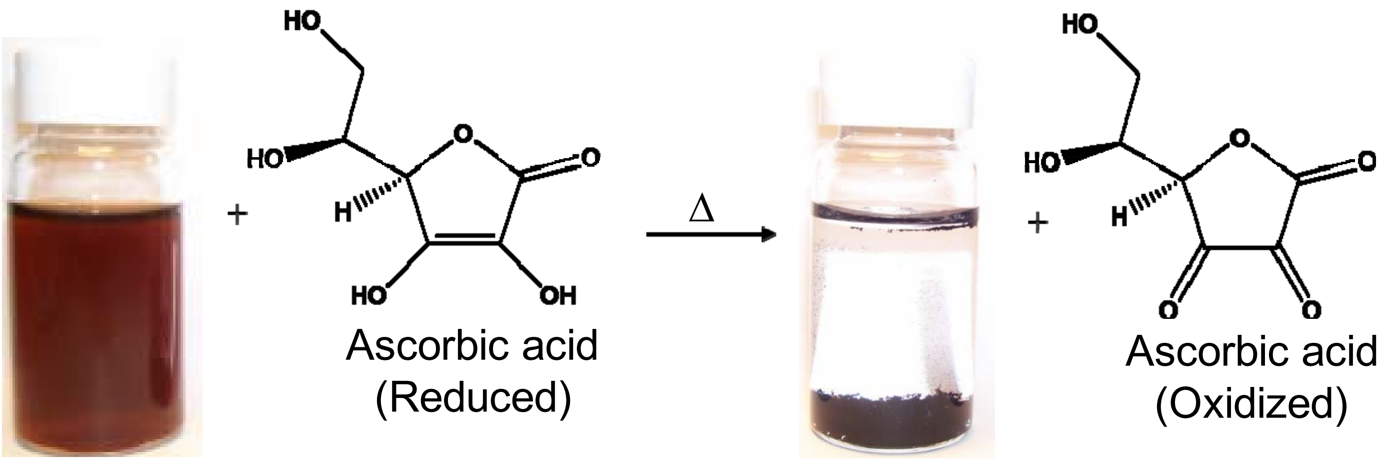
Free-standing film of reduced graphene oxide readily obtained by ascorbic acid treatment



XPS: Fewer defects observed using ascorbic acid as the reducing agent



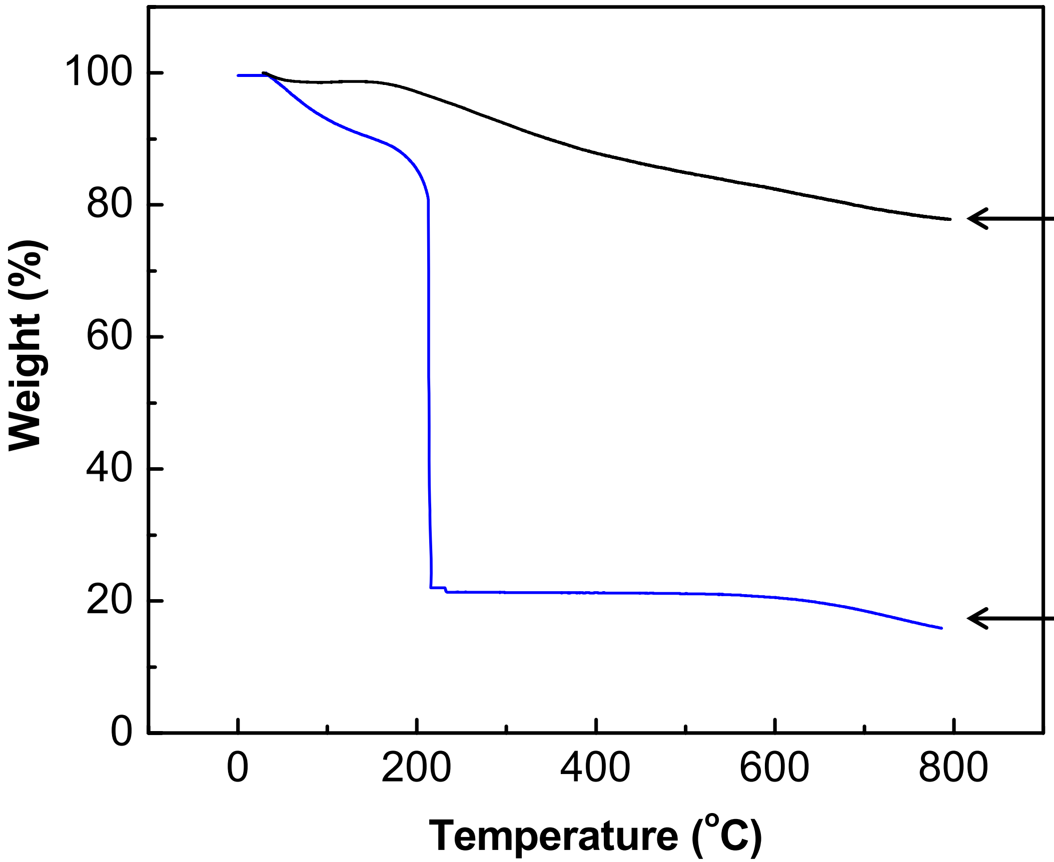




Graphene oxide

Reduced graphene oxide

TGA: Reduced graphene oxide powder obtained by ascorbic acid and hydrazine reduction are similar

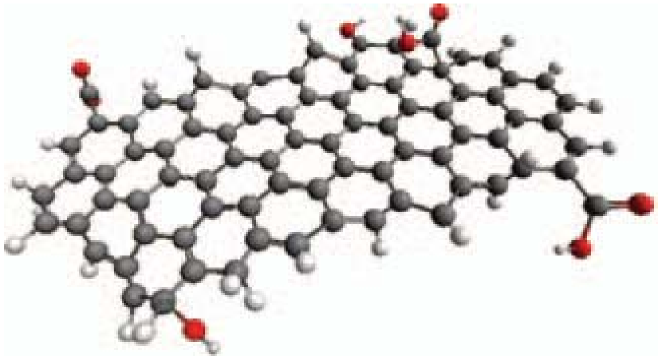


Reduced graphene oxide

Graphene oxide

Vitamin C reduced graphene is similar to hydrazine reduced graphene

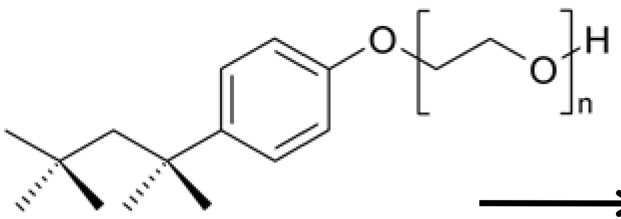
An electronic ink of reduced graphene oxide is readily obtained as an aqueous surfactant supported dispersion



Reduced graphene oxide (10 mg) in water

Reduced graphene oxide

+



Triton-X-100; n = 9-10

→

Reduced graphene oxide dispersion

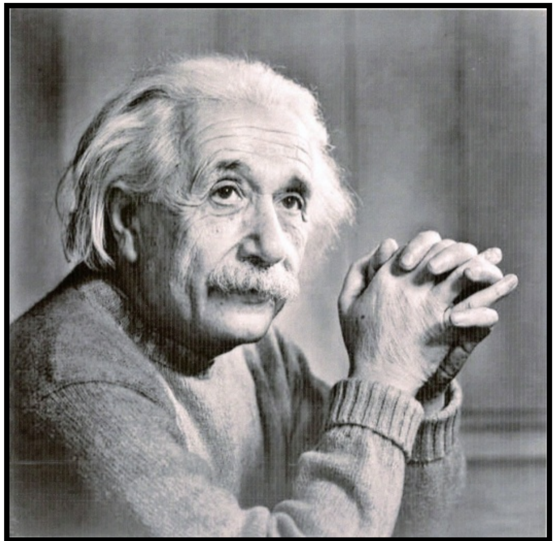
- Bath sonicate (20 min)
- Probe sonicate (5x5 min)

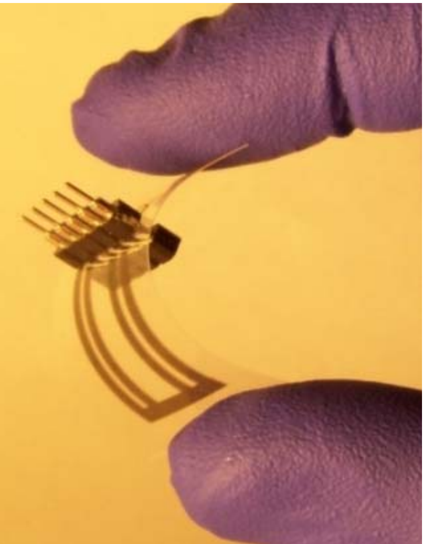
Reduced graphene oxide is readily inkjet printed on PET

Reduced graphene oxide dispersion

1. Empty inkjet commercial cartridge
2. Fill cartridge with graphene oxide dispersion

Inkjet print using commercial printer on paper or plastic





Rapid Endotoxin Detector for the Global Industrial Microbiological Market

VALUE PROPOSITION:

An inexpensive, easy-to-use, hand-held instantaneous endotoxin detection system for industrial and medical applications that requires little to no pre-treatment of samples

Urgent and unmet market need

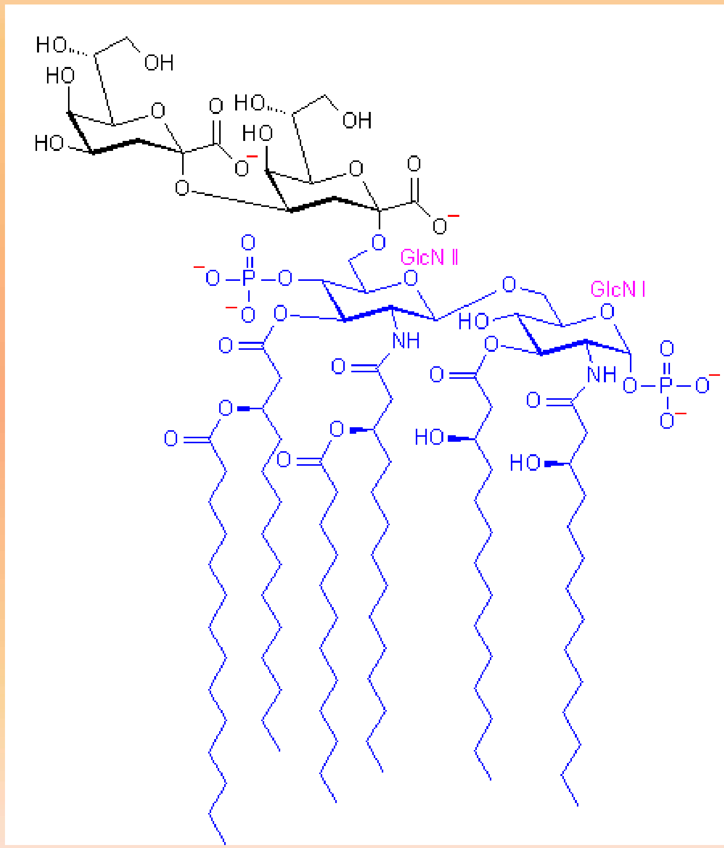
- ✓ Testing for endotoxins is now mandatory for every medical device
- ✓ Global industrial microbiological market - 1.5 B tests (~$4.5 B)
  - Beverage, food processing, pharma, personal care, industrial processes & environmental
- ✓ Endotoxins also cause septicemia (sepsis) –
  - ✓ 2 million/yr lives lost in the US - ~$17 billion
  - ✓ No direct test to detect endotoxins in blood
- ✓ Existing test is based on using blood from horseshoe crab (LAL test)
  - ✓ Slow, cumbersome (<u>takes days for a single test</u>)
  - ✓ Costly (1 quart of horseshoe crab blood ~$15,000, revenues ~$100 million)
  - ✓ Horseshoe crab blood population declining

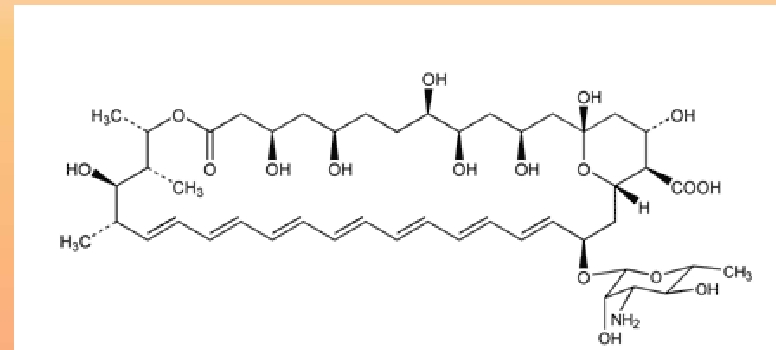
Urgent and unmet market need

- ✓ Urgent need for a fast, low cost, endotoxin detection system
  - ✓ Current revenues from rapid microbiology test systems ~$200 million/yr
- ✓ Customers- US Pharma (USP), US FDA, DHS and the entire industrial microbiological sector
- ✓ End-users - Amgen, Genentech, Genzyme, Biogen Idec (& others), Homeland Security, Hospitals
- ✓ Potential licensees - Lonza Group, Charles River, Bio Test, BioDtech (BDTI) and Associates of Cape Cod (ACC)

Our new technology

- ✓ Identified novel chemistry between endotoxins and antifungals:
  - ✓ Antifungals - large class of polyene macrolides
  - ✓ Instantaneous complex formed between endotoxins can antifungals



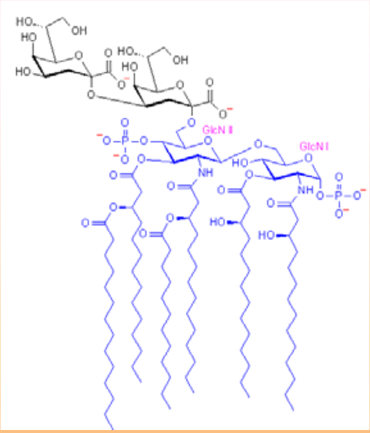


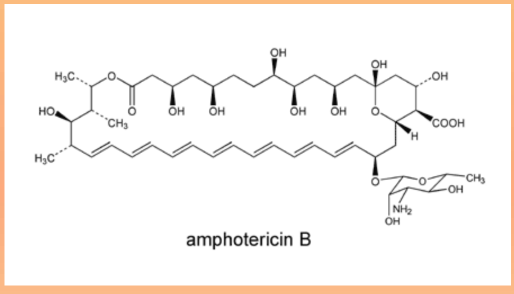
Antifungal – amphotericin-B

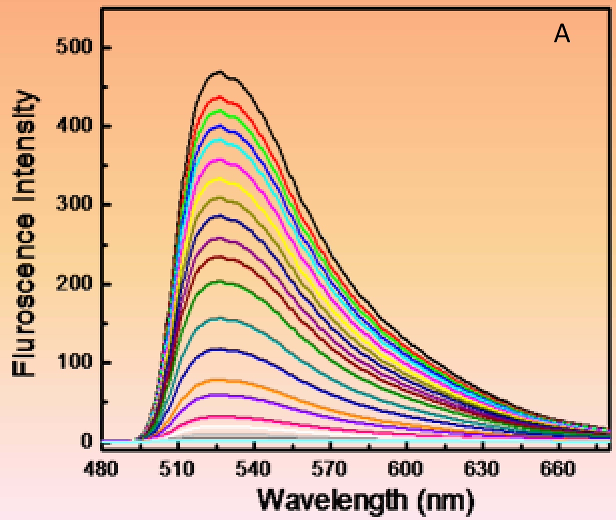
Endotoxins

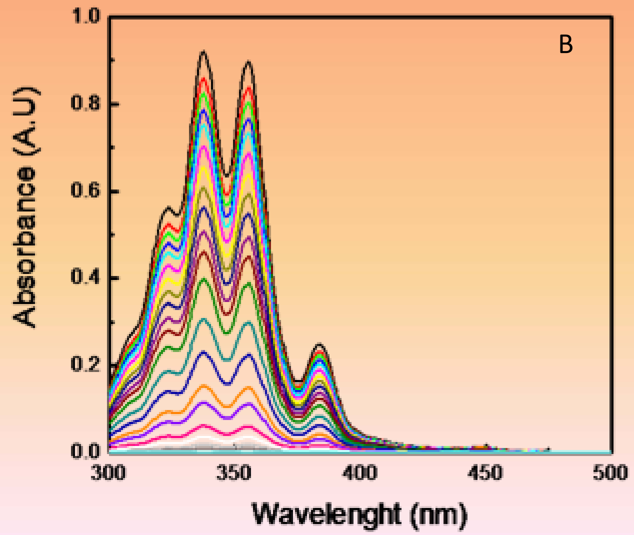
Our new technology....cont'd

- ✓ Interrogate this novel chemistry in 3 different ways:
  - ✓ Optical (instantaneous 1ppt level detection)
  - ✓ Electrical (using carbon nanotubes)
  - ✓ Electrochemical (using conducting polymers)
  - ✓ Provisional patent application filed 02/09/2011 covering all 3 detection methods









Our new technology….cont'd

- ✓ Signal change is near instantaneous (optical), or within 2-5 min - significant advantage vs. horseshoe crab blood test (takes days)
- ✓ Signal is very selective to endotoxins - significant advantage vs. horseshoe crab blood test (sensitive to interferents)
- ✓ Detection limit is at 0.001 EU/ml (parity with horseshoe crab blood test) with potential to be lowered even further

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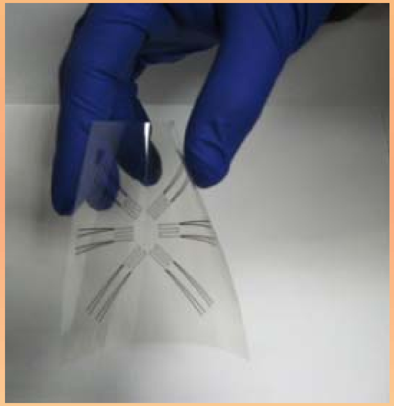
Maturity of our technology

- ✓ Validated in laboratory environment (all 3 detection methods)
- ✓ Both optical detection methods already at 0.001 EU/ml (best of class)
- ✓ Electrical detection using carbon nanotubes at 2-10 EU/ml (lower using UML's inkjet printing technology)
- ✓ Electrochemical detection using conducting polymers at 0.5 EU/ml (lower using UML's oligomer synthesis methodology)
- ✓ Tolerates a wide range of potential interferents



PROOF-OF CONCEPT:

Established. Need to lower detection limits further for electrical & electrochemical methods (use of seed fund)

Benchmarking *vs.* competition

Desired Properties	LAL[1]	Charles River[2]	Dimer-AmB Electrochemical	r-GO-AmB Chemiresistor	Optical
Toxin Response	● Excellent	● Excellent	● Good	● Excellent	● Excellent
Sensitivity[3]	● 0.005EU/ml	◉0.02EU/ml	○ 0.5EU/ml	◉ 0.05Eu/ml	● 0.001EU/ml
Interferents	○	◉	◉	◉	● Excellent
Response time	○ 72hrs	○ 15min	◉ 1 min	● 45 sec	●5min
Startup time	○ Poor	● <1min	◉ < 1 min	● <1min	● <1min
Portable	○ No	● Yes	○ Yes	● Yes	● Yes
Operator skills	○ High Skills	◉ On/Off	○ On/Off	◉ On/Off	◉ On/Off
Environments	○ Clean room	● Robust	○	● Robust	● Robust
Unit cost	○ Expensive	○ Expensive	◉ <$200	● <$20	◉

[1]Horseshoe crab assay, the industry standard. It is costly, time consuming and cumbersome (but very sensitive). [2]New fluorescence based commercial detector (2009). [3]1EU/ml=100 pg/ml.

Endotoxin detection platform technology

FIRST MARKET (INDUSTRIAL): Manufacturing Quality Control (1-3 Yrs)
Pharmaceutical, medical device, food, and beverage industries all require endotoxin testing for safety of their products.

UML Solution: Inexpensive, hand-held sensors that can be taken to the manufacturing site for instant readings without need for sterile procedure or sample preparation. In-line sensors for water supply systems with alarms

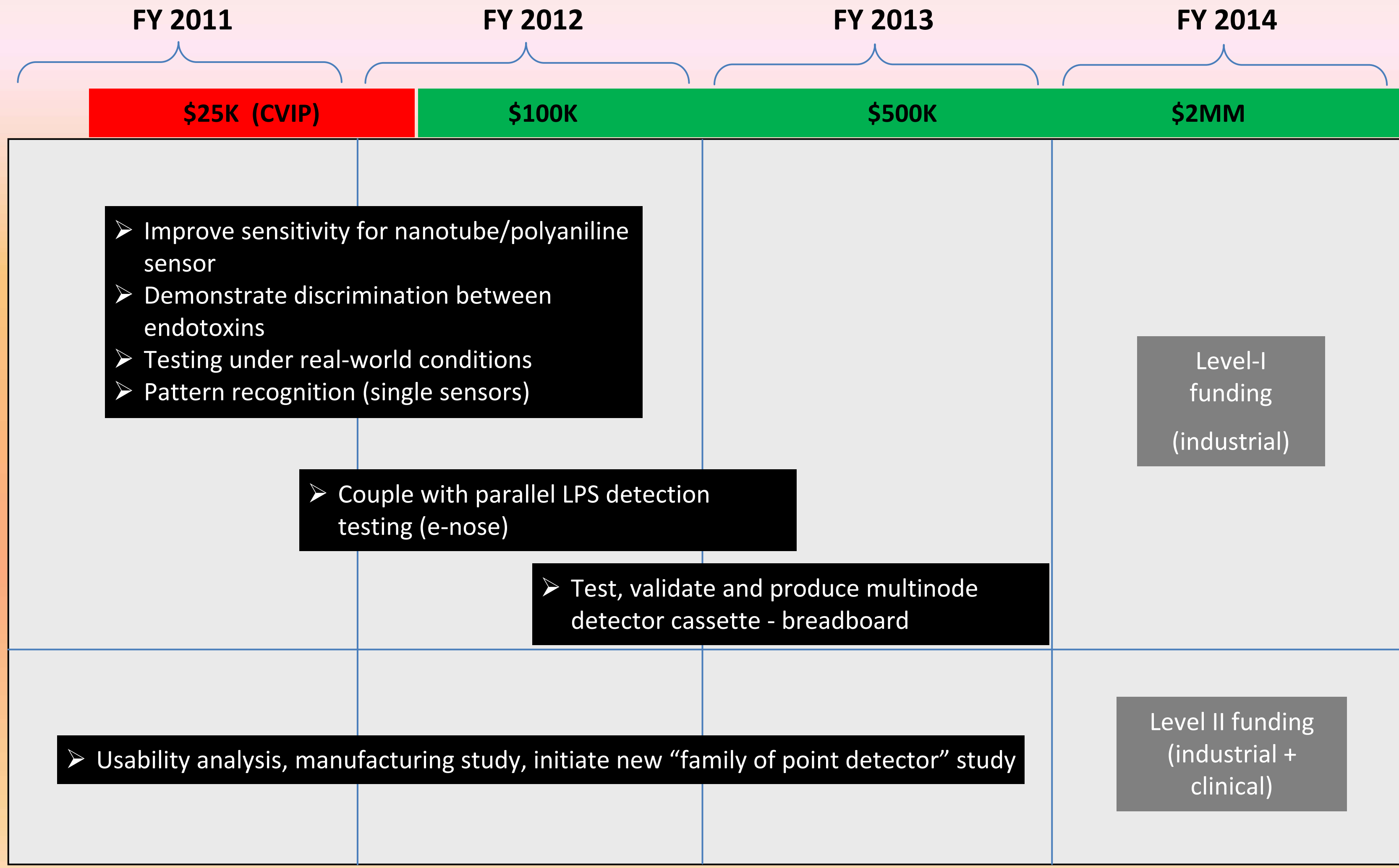
$25K SEED FUNDING WILL BE USED TO:

- **Increase the sensitivity of the 2 electrical methods**
- **Make a breadboard demonstrator**
- **Attract a licensee for industrial applications**
- **From the basis of a second product (clinical)**

SECOND MARKET (CLINICAL): Diagnostics (3-6 years)
There are over 750,000 cases of sepsis each year in the United States with 28-50% being fatal

UML Solution: Array detector that can detect sepsis-causing endotoxins in whole blood and determine organism responsible, allowing proper drugs to be administered

Technology transfer plan



Development team

Members	Affiliation	Function
Sanjeev K. Manohar	UMass Lowell Chemical Engineering	➢ Improve sensitivity of electrical and electrochem methods ➢ Improve selectivity using wider range of antifungals (sensor array)
Dr. Stephen Heard	UMass Medical Center Anesthesiology	➢ Validation under realistic conditions ➢ Test for detector fouling
Dr. Steve Tello	UMass Lowell College of Management	➢ Prepare the technology for the "Venture Project"

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Dr. Sanjeev K. Manohar
Associate Professor
Chemical Engineering
UMass Lowell

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