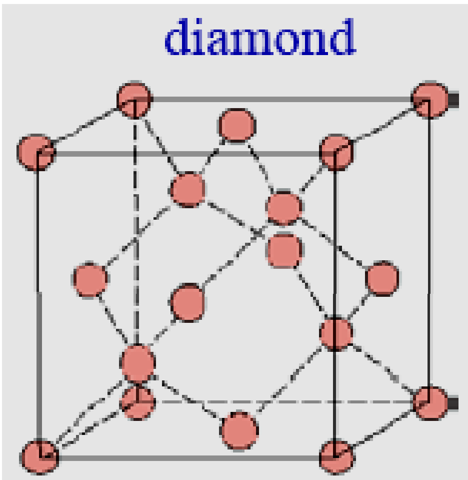
Section II:

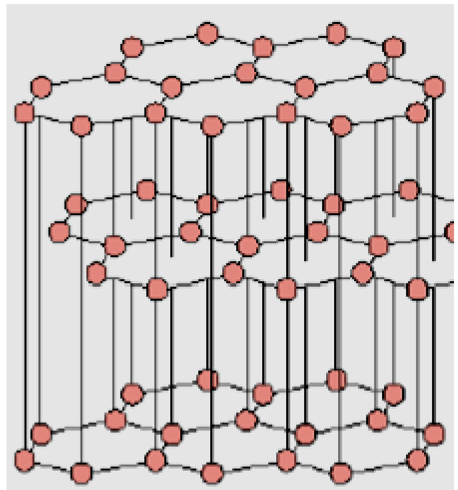
Synthesis of Carbon Nanotubes

Carbon Nanotube: A Form of Carbon

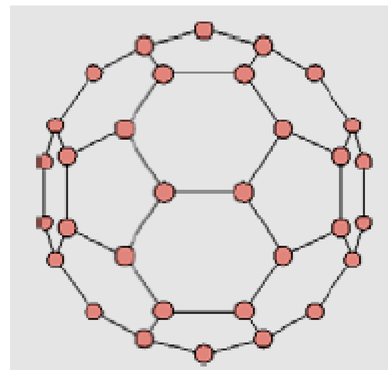
(metastable)



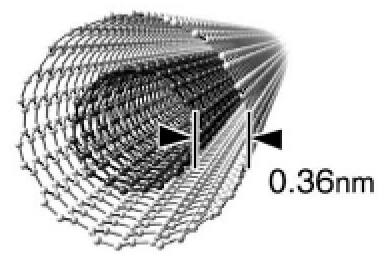
Graphite (stable)



Bucky ball
(metastable)



Nanotube = rolled sheet
of graphite

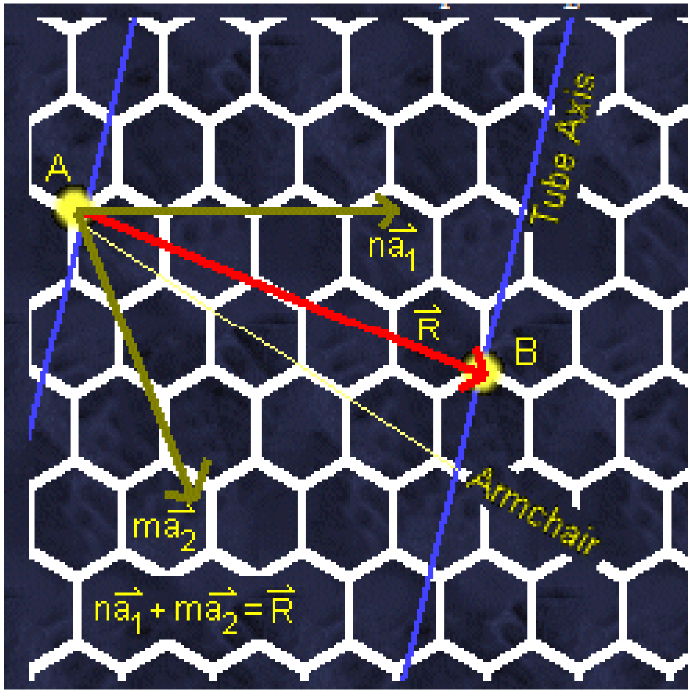


Smalley & Kroto, 1997 Nobel

Helical Microtubules of graphitic Carbon, Ijima, S, Nature, 354 (6348): 56-58 NOV 7 1991
Cited: >4000 times

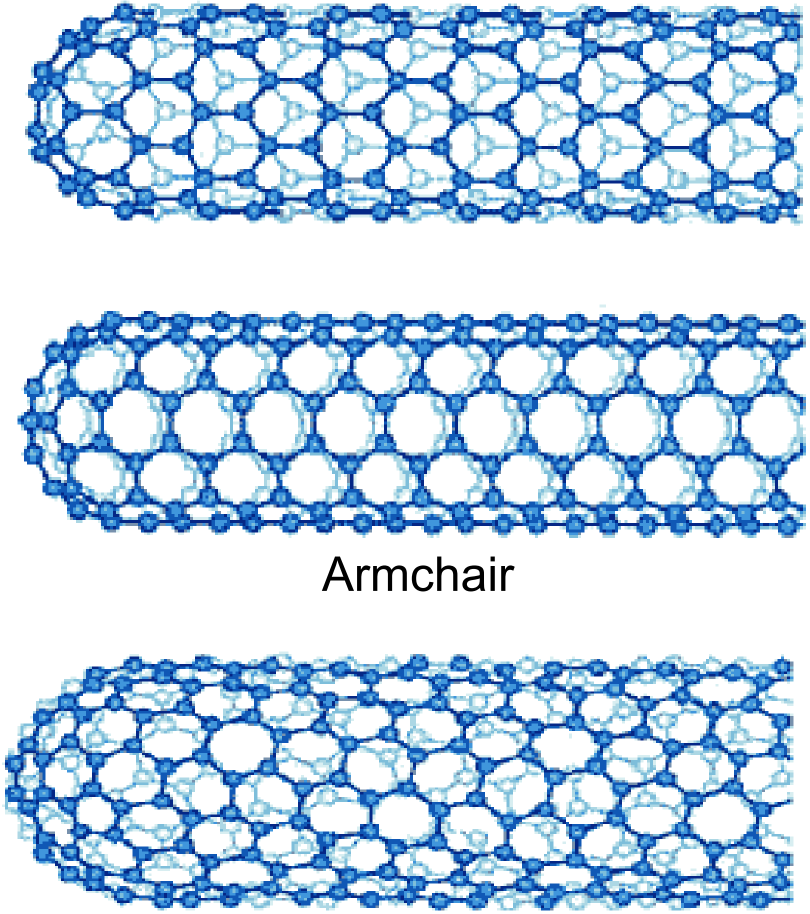
Review on Nanotubes:
Accounts of Chemical Research (2002), 35(12). Entire issue is based on Nanotubes.
Dai, Hongjie. Carbon nanotubes: opportunities and challenges. Surface Science (2002), 500(1-3), 218-241.

Different Types of Nanotubes



a1 zig zag vector
a2 reflection over armchair line

Zig-Zag



Armchair

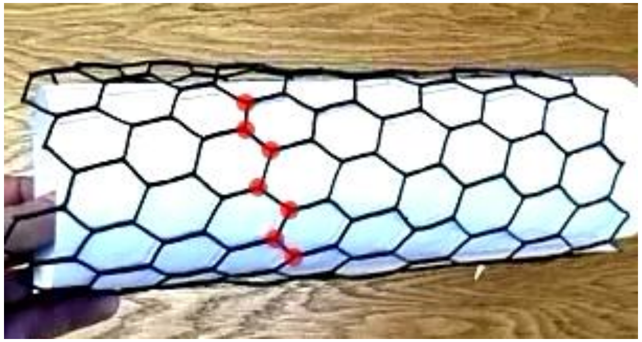
Chiral

Self-assembly and Nanotechnology

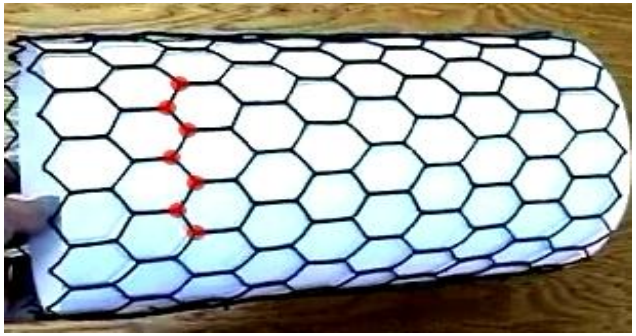
nano manufacturing center at UML

Types of carbon nanotubes

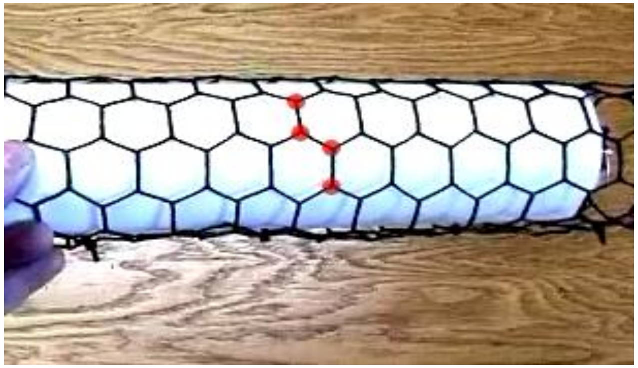
1) A "chiral" carbon nanotube.



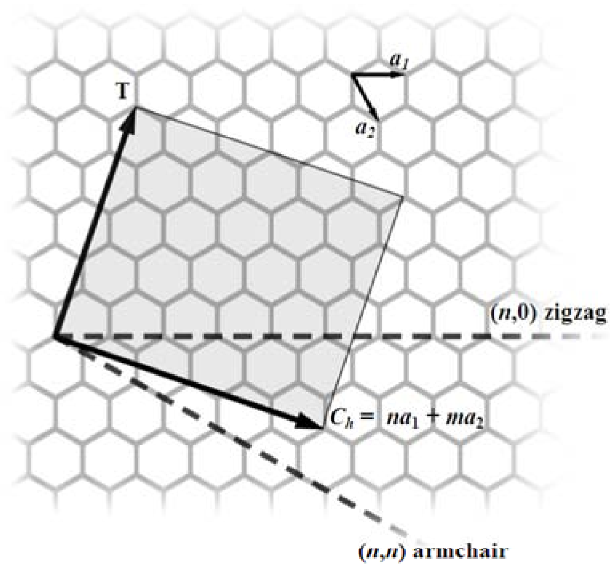
2) A "zig-zag" carbon nanotube



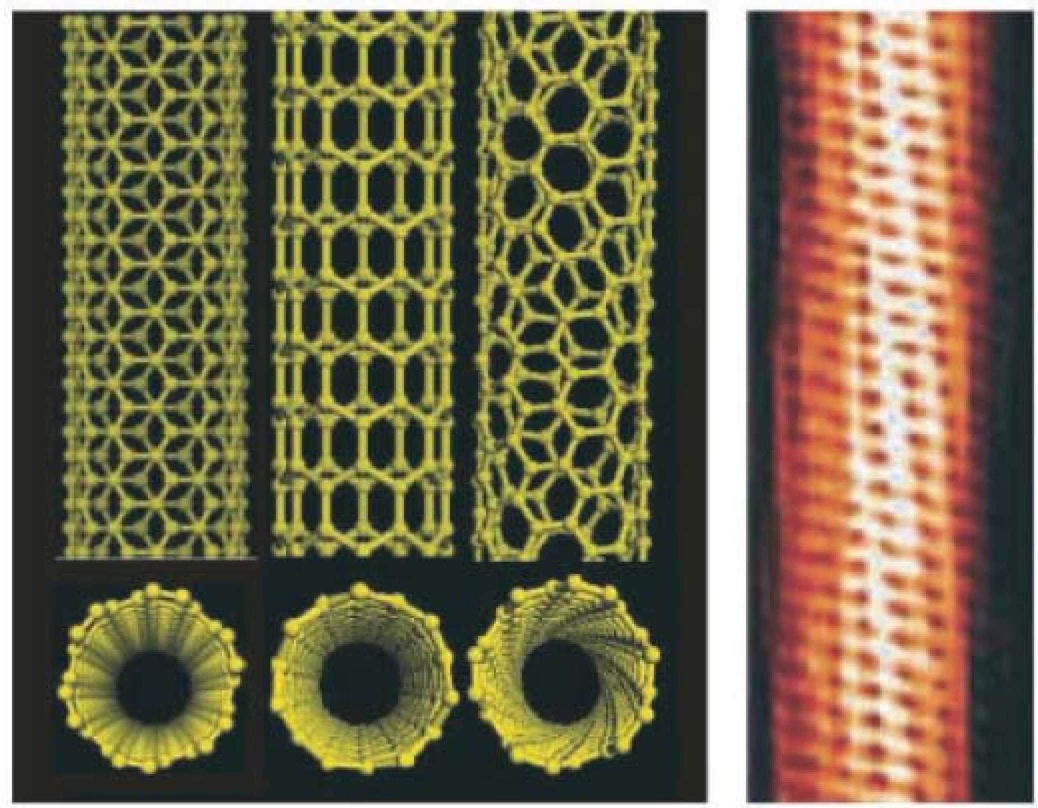
3) An "armchair" carbon nanotube.



Different Types of Nanotubes



The (n,m) nanotube naming scheme can be thought of as a vector (Ch) in an infinite graphene sheet that describes how to 'roll up' to graphene sheet to make the nanotube. T denotes the tube axis, and a1 and a2 are the unit vectors of graphene in real space. It is based upon similar diagrams found in the literature (for instance, Odom et al. Topics Appl. Phys., 2001, 80, 173).



armchair Zig-Zag Chiral TEM Chiral

Science, 297, 2 Aug 2002

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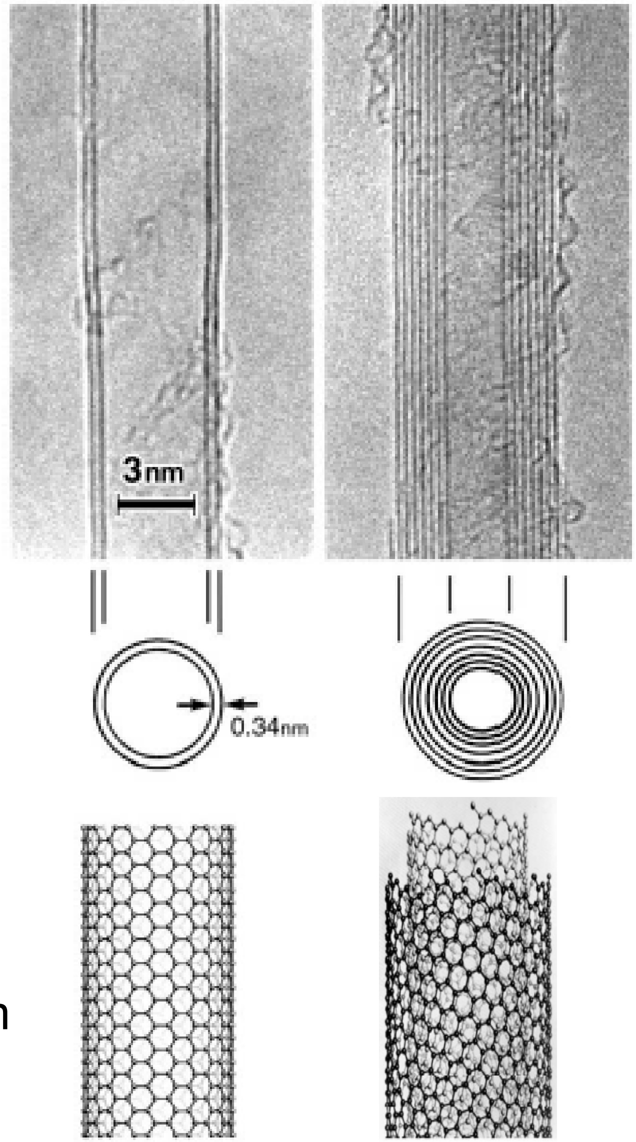
Single Wall and Multi Wall Nanotubes



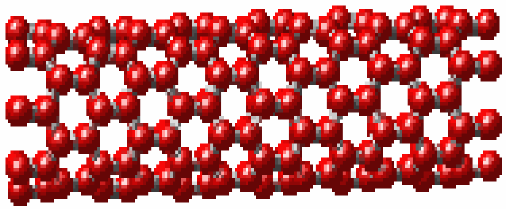
Up to cm long

SWNT
(single
Wall nanotube)
Diameter ~ 1.4 nm

MWNT
(multiwall)
Diameter 10-20 nm

Must read Paper:
Iijima, Sumio. Carbon nanotubes: past, present, and future. Physica B: Condensed Matter (2002), 323, 1-5.

Nanotubes(NTs)

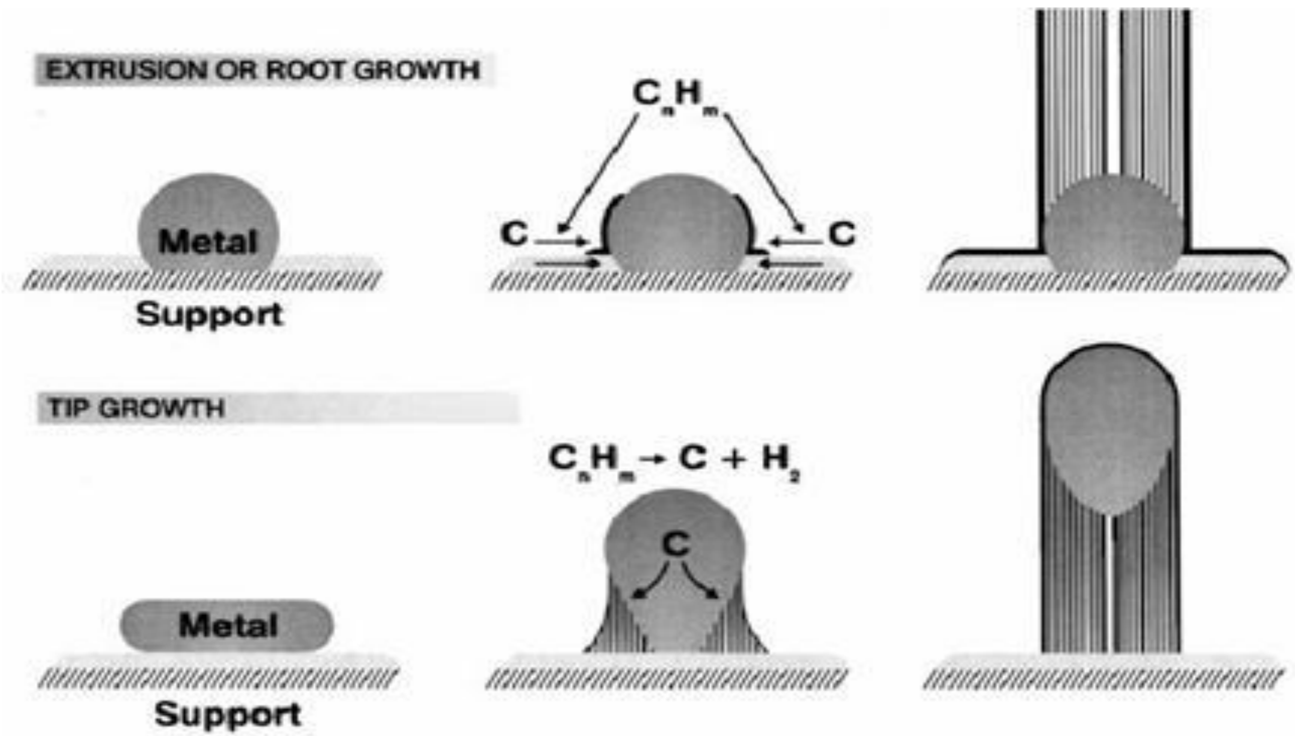


- Can be either electrically conductive or semiconductive, depending on their magnetic helicity.
- Exhibit electrical conductivity as high as copper.
- Have thermal conductivity as high as diamond.
- Strength 100 times greater than steel at one sixth the weight and high strain to failure.

Growth mechanism

- The way in which nanotubes are formed is not exactly known.

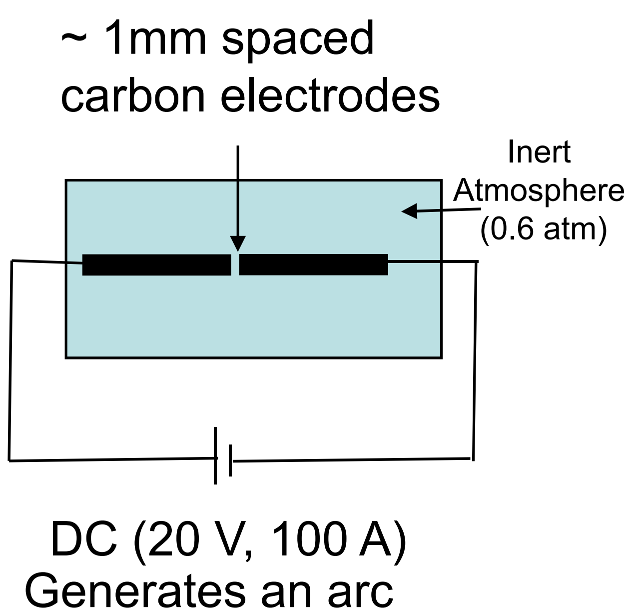
- More than one mechanism might be operative during the formation of CNTs



Methods for Fabricating Nanotubes

- Arc Vaporization
- Laser Vaporization
- CVD
- Flame

Arc Discharge



Metal doped electrodes (Fe, Co, Ni, Mo): SWNT

Pure Graphitic electrodes: MWNT (other fullerenes etc)

During this process, the carbon contained in the negative electrode sublimates because of the high temperatures caused by the discharge. Because nanotubes were initially discovered using this technique, it has been the most widely used method of nanotube synthesis.

The yield for this method is up to 30 percent by weight and it produces both single- and multiwall nanotubes, however they are quite short (50 microns)

Production of SWNTs

- **a) Inert Gas:** Argon with lower diffusion coefficient and thermal conductivity smaller diameter (1.2nm)

- **b)Optical Plasma Control:**distance between anode and cathode is increases, anode vaporization increases, The nanotubes diameter ranges from 1.27 to 1.37 nanometer.

- **c) Catalyst:** By changing metal catalyst, the nanotubes with a diameter of 0.6 to 1.2nm are produced. Catalysts used are Co and Mo.

- **d)Open Air Synthesis with Welding Arc Torch:** Steel based electrode, torch arc aimed at the edge of target and soot is deposited on substrate.

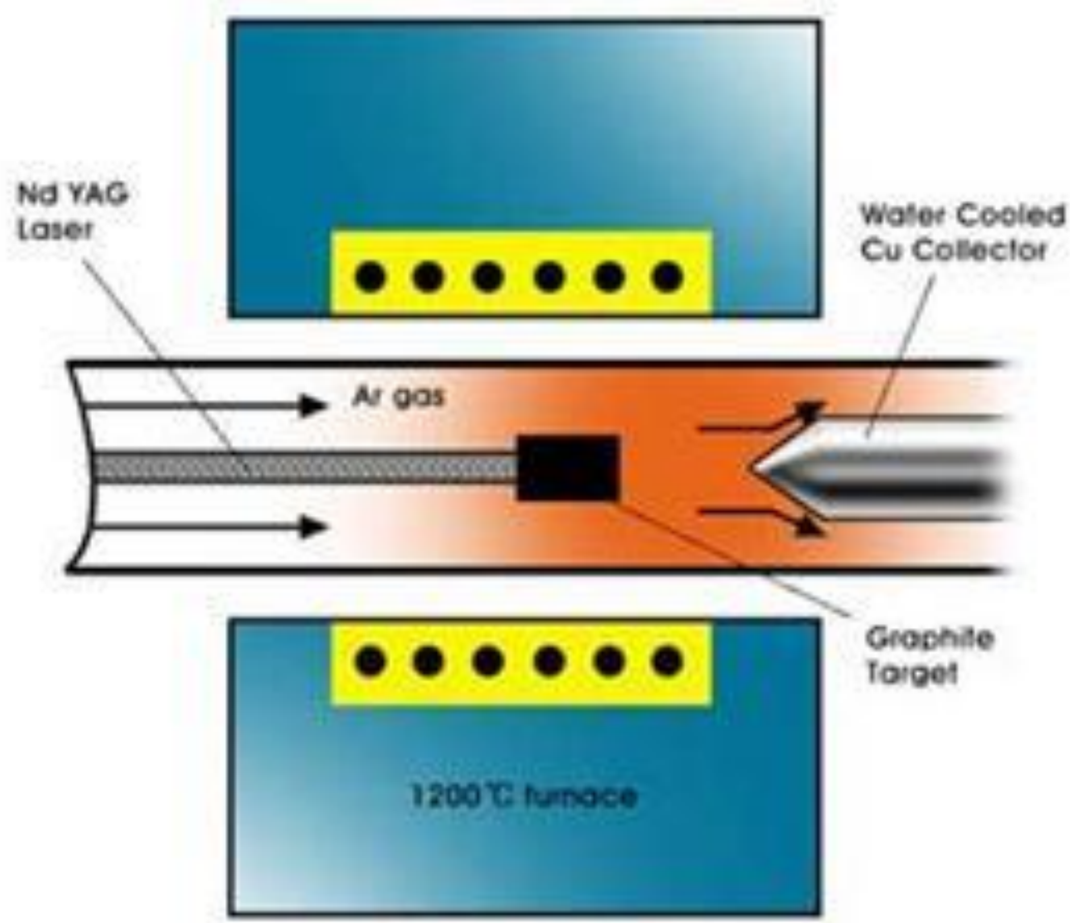
Production of MWNTs

- **a) Synthesis in Liquid Nitrogen**: Arc- discharge generated in liquid nitrogen. Yield is about 70% of reaction product.

- **b)Magnetic Field Synthesis** :Arc- discharge is controlled by a magnetic field around the arc plasma. Extremely pure graphite rods (purity > 99.999 %) are used as electrodes. Highly pure MWNTs (purity > 95 %) are obtained.

- **c) Plasma Rotating Arc Discharge**[14]: The centrifugal force caused by the rotation generates turbulence Plasma volume and the plasma temperature raises. The yield can be increased up to 90% after purification if the rotation speed(5000rpm)

2) Laser Ablation



Production of SWNTs

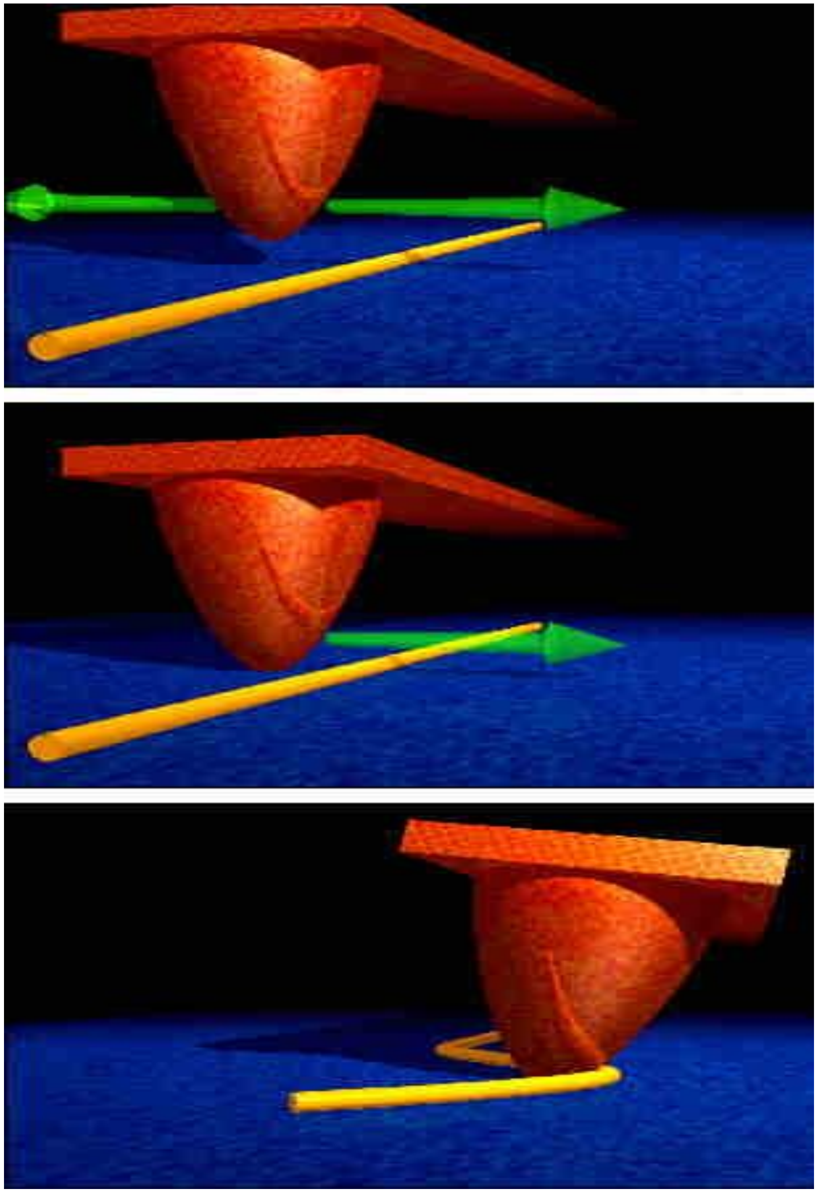
a) Ultra Fast Pulses from a Free Electron Laser(FEL) Method:

The pulse and the repetition rate of the pulse are increased.If this system is upgraded with full power a yield of 45gm/ hr can be achieved.

b) Continuous Wave Laser-Powder Method:

Instead of Nd laser, CO_2 laser is used in an argon stream. Thermal conductivity losses are significantly reduced. It is more economical in comparison with Nd(Neodymium) laser system and yield is 5gm/hr.

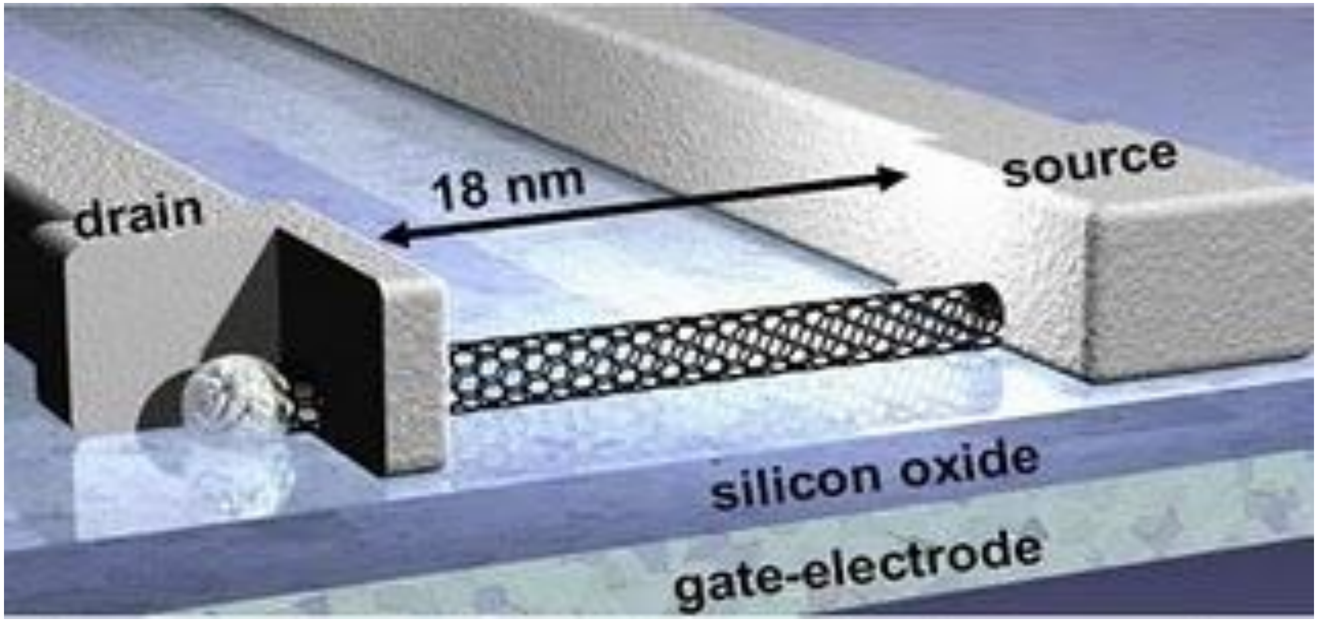
Nanotube manipulation



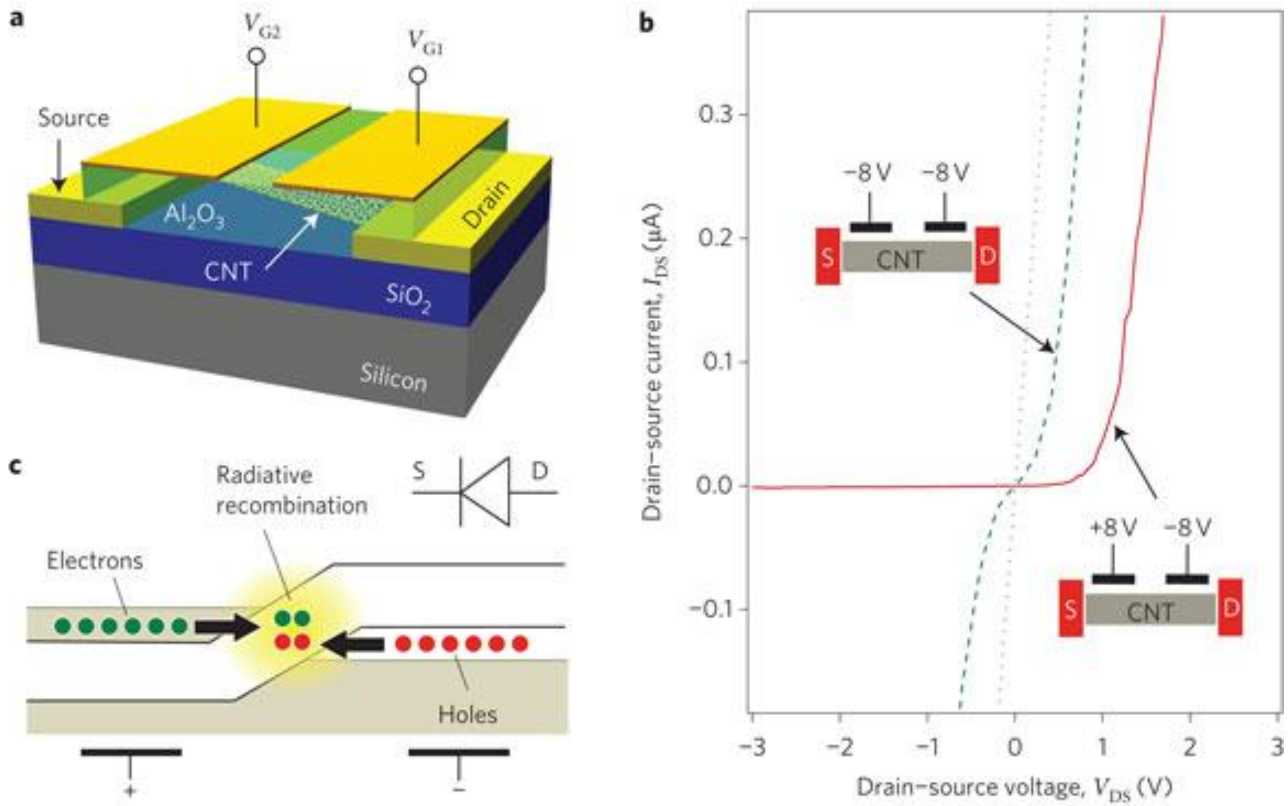
- Atomic force microscope (AFM) is used

Applications

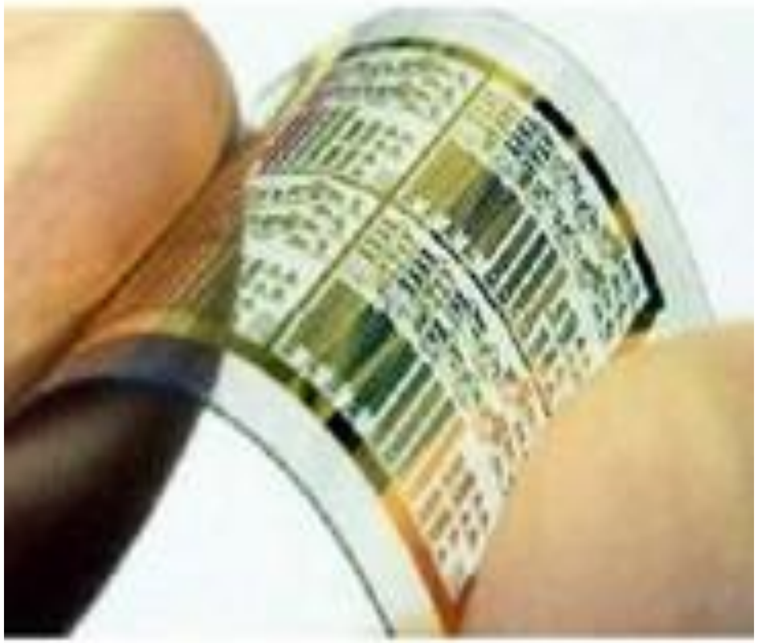
- **Field-effect transistors**

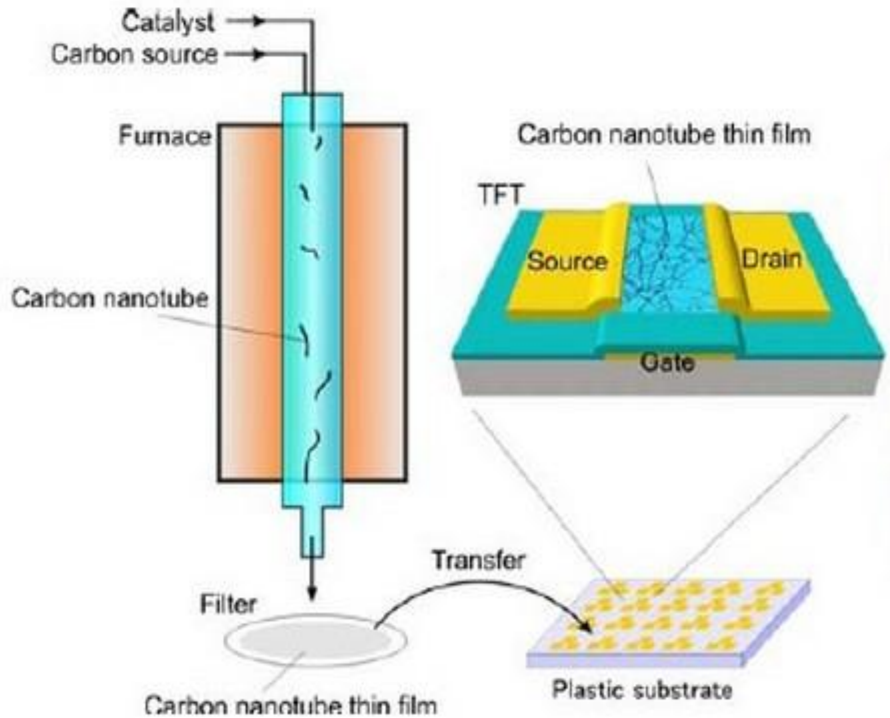


- **Diodes**


a
V_{G2}
V_{G1}
Source
Drain
Al_2O_3
CNT
SiO_2
Silicon
b
0.3
0.2
0.1
0.0
−0.1
Drain−source current, I_{DS} (μA)
−8 V −8 V
S CNT D
+8 V −8 V
S CNT D
−3 −2 −1 0 1 2 3
Drain−source voltage, V_{DS} (V)
c
Radiative recombination
S D
Electrons
Holes
+
−

- **Logic circuits**





Disadvantages

- Difficulties in manipulating individual NTs.

- Difficulties to control whether building blocks are semiconducting or metallic.

- Up to date,device fabrication by NT largely is a random event , posing a significant barrier to achieving highly integrated nanocircuits.

- Stretching a nanotube can either increase or decrease its conductivity--depending on the type of nanotube.

Section III:

Synthesis of Nanowires

Most commonly used methods

- CVD (Chemical Vapor Deposition)
- Solution phase synthesis
- Electrodeposition

UNIVERSITÄT PADERBORN

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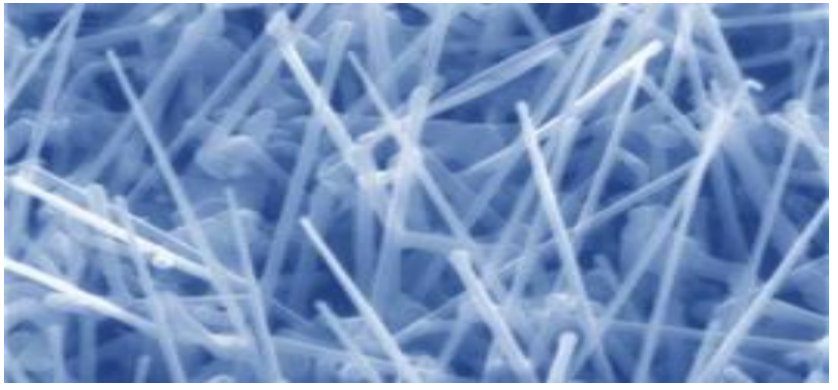
Fakultät für Naturwissenschaften
Department Physik

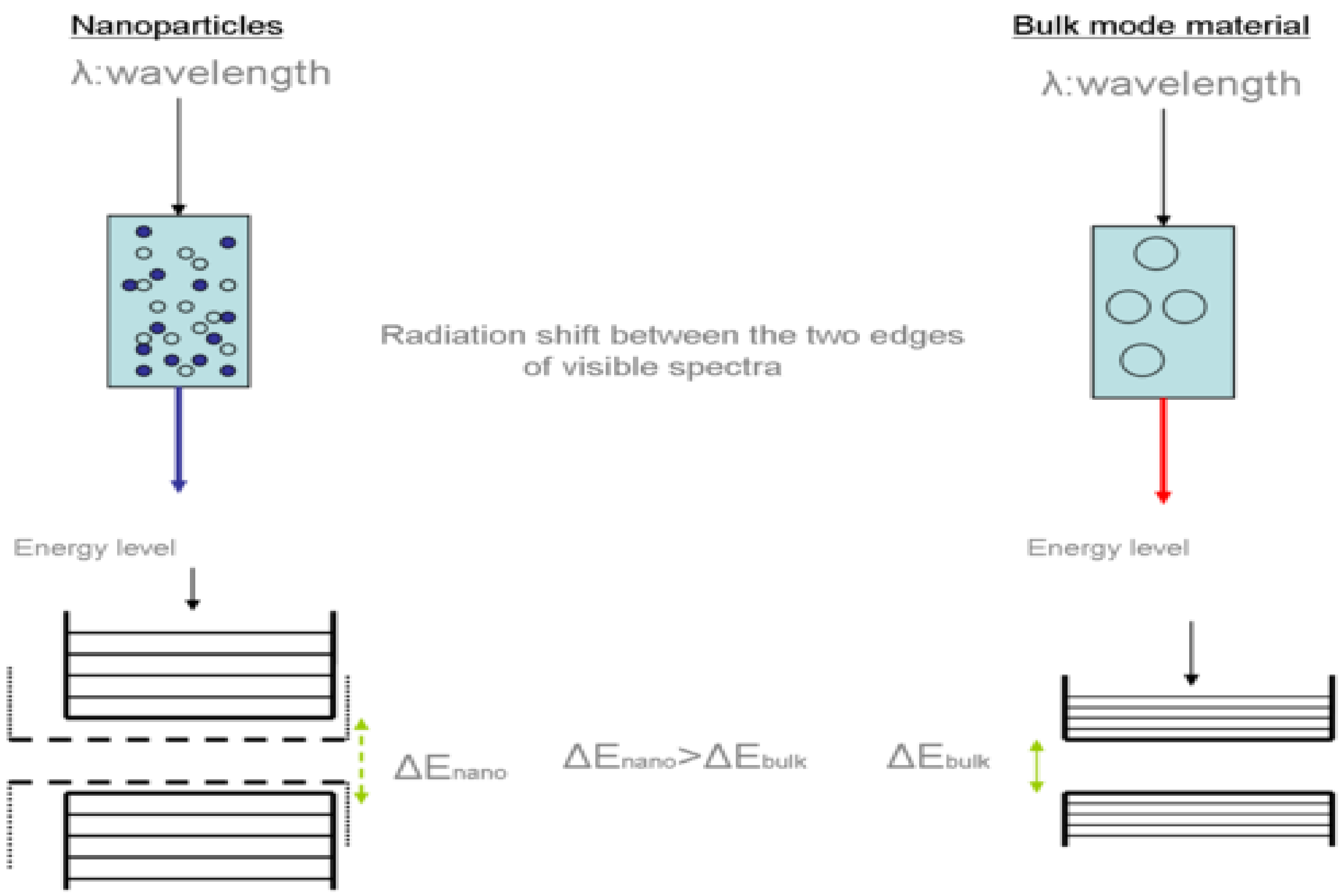
ATOMIC SCALE NANOWIRES



What is a Nanowire?

- It is a nanostructure with the diameter of the order of a nanometer (10^{-9} meters) which is extremely small.
- There is no restriction on how wide they can grow, but cannot grow more than a few nanometers in height.
- Have nanometer size in one of the dimension which produces quantum confinement in material and changes its properties.

Quantum confinement is responsible for the increase of energy difference between energy states and band gap.



1D nanostructures(Quantum Wires)

- 1D nanostructures represent the smallest dimension structure that can efficiently transport electrical carriers.

- 1D nanostructures can also exhibit such device functions that can be exploited as both **wiring** and **device elements** in future architectures for functional nanosystems.

- In this regard, two material classes:
  I. **(NTs) carbon nanotubes**
  II. **(NWs) nanowires**

  have shown particular promise

Types of Nanowires

- **Metallic - **Made from Nickel,Platinum or Gold
- **Semi-conducting - **Comprises of Silicon,Indium phosphide or Gallium Nitride
- **Insulating - **Silicon Dioxide or Titanium dioxide
- **Molecular –** Involves repeating organic or inorganic molecular units

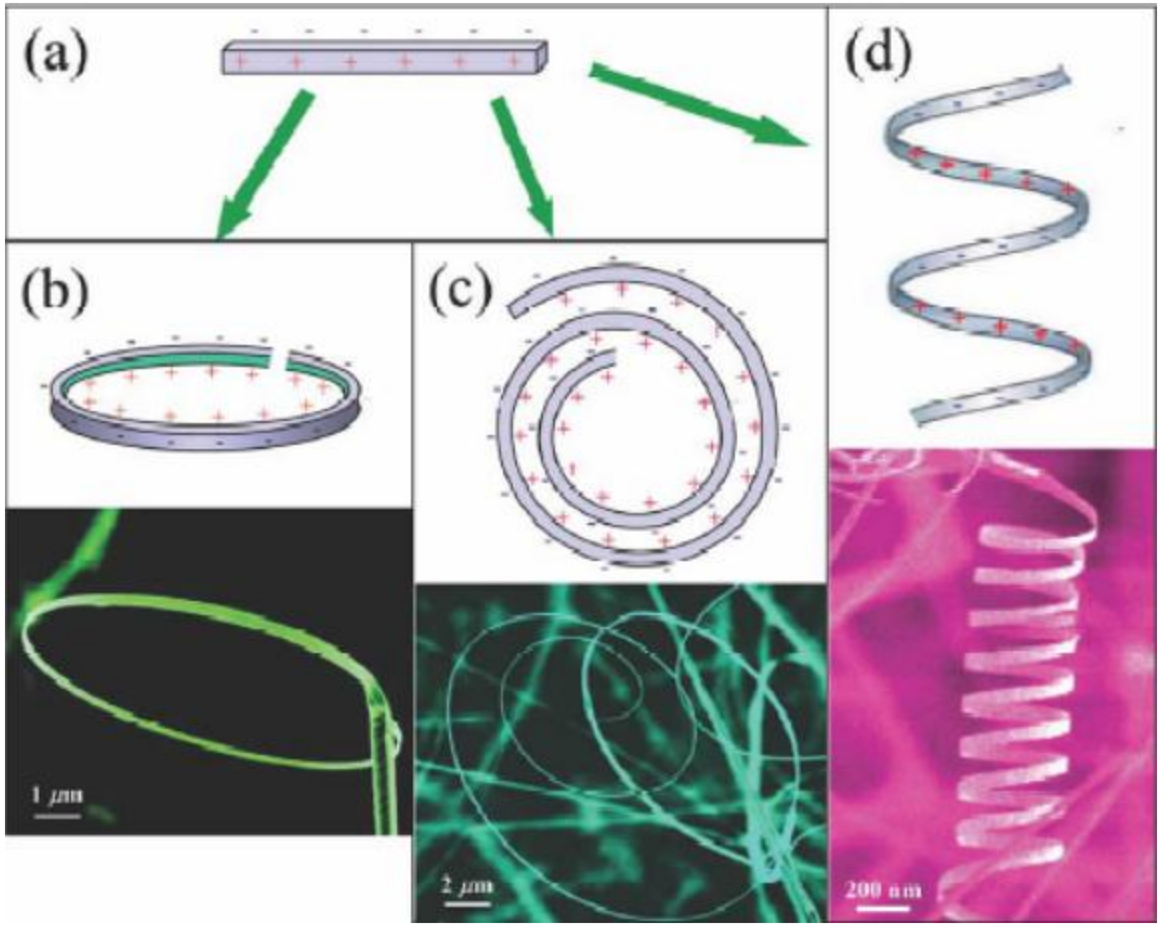
Synthesis

- **Spontaneous growth**
  - Evaporation(Dissolution) condensation
  - Vapor(or solid)-Liquid-Solid growth(VLS or SLS)
  - Stress induced re-crystallization
- **Template-based synthesis**
  - Electrochemical deposition
  - Electrophoretic deposition
  - Colloid dispersion,melt or solution filling
  - Conversion with chemical reaction
- **Electro-spinning**
- **Lithography (**top-down)

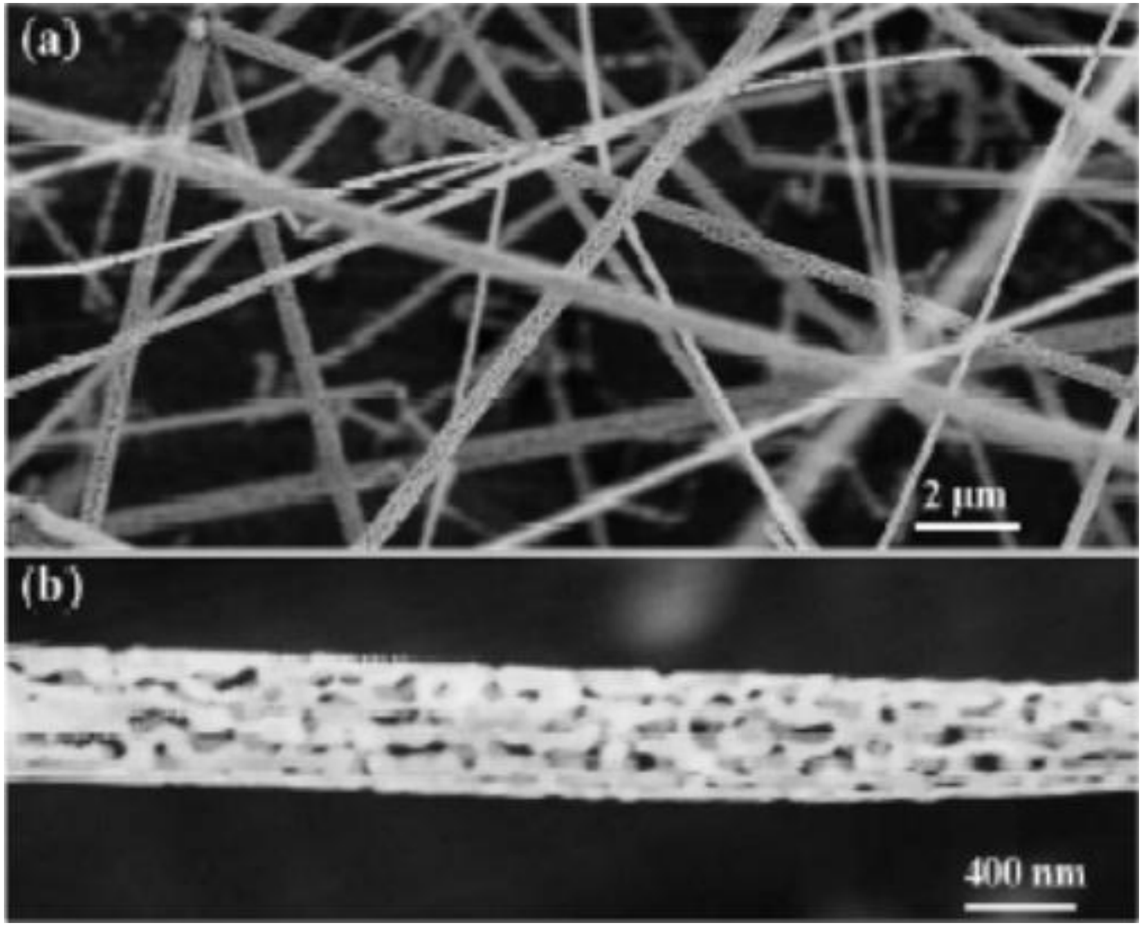
Spontaneous Growth

General Idea:

- Anisotropic growth is required.
- Crystal growth proceeds along one direction, where as there is no growth along other direction.
- Uniformly sized nanowires (i.e. the same diameter along the longitudinal direction of a given nanowire)

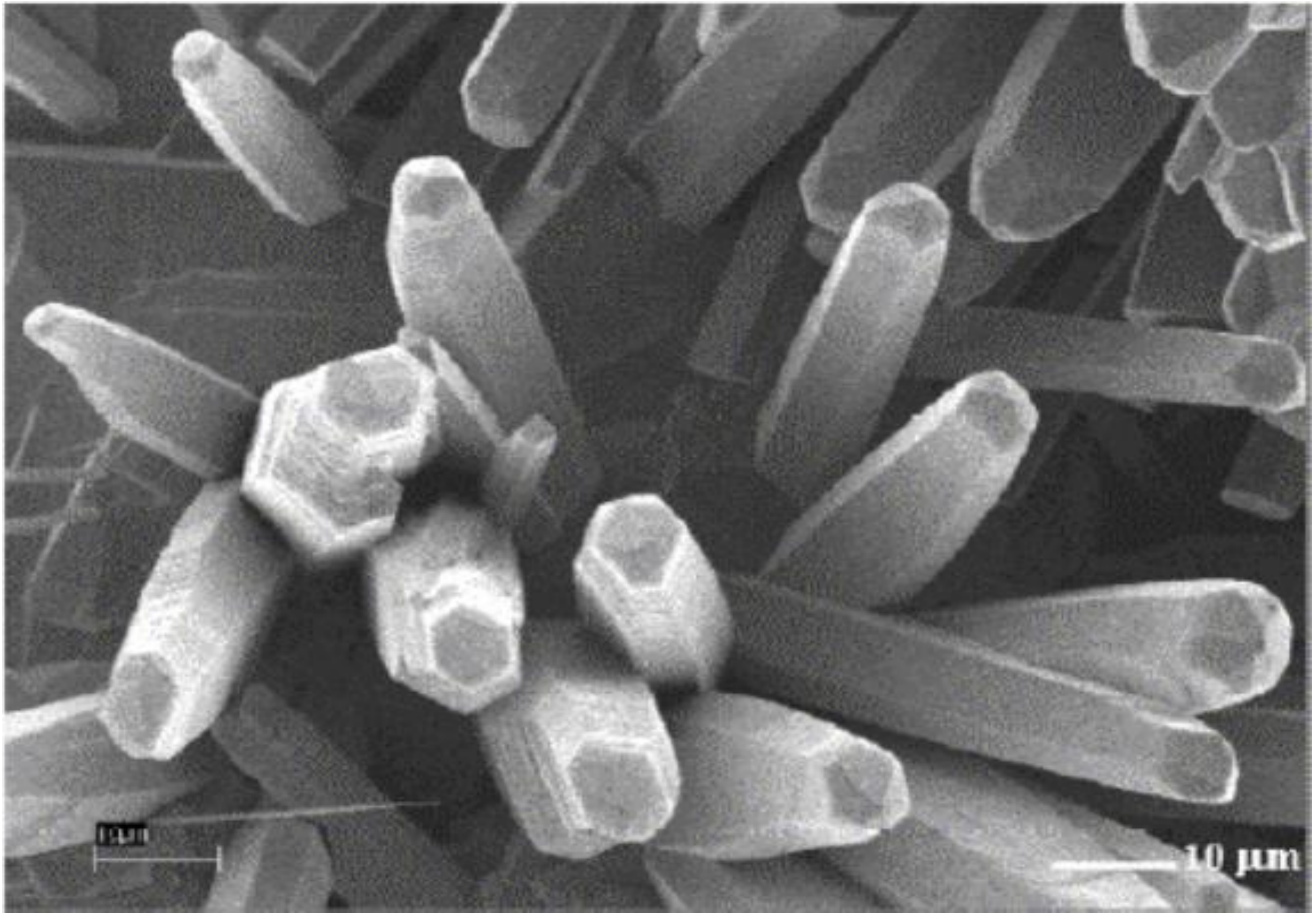


Nanostructures of zinc oxide
http://www.materialstoday.com/pdfs_7_6/zhang.pdf)



Mesoporous, single-crystal ZnO nanowires .

http://www.materialstoday.com/pdfs_7_6/zhang.pdf)



A Non-Traditional Vapor-Liquid-Solid Method for Bulk Synthesis of Semiconductor Nanowires

www.cvd.louisville.edu/Publications/recentpublications/proceedings_mrs_fall2001.pdf

Template Base synthesis

General Idea:

- Use in fabrication of nanorods, nanowires, and nanotubes of polymers, metals, semiconductors, and oxides.

- Some porous membrane with nano-size channels(pores) are used as templates to conduct the growing of nanowires.

- Pore size ranging from 10 nm to 100 mm can be achieved.

Electrochemical deposition

- This is a self-propagating process
- Only applicable to electrically conductive materials

(metals, alloys, semiconductors, and electrical conductive Polymers)

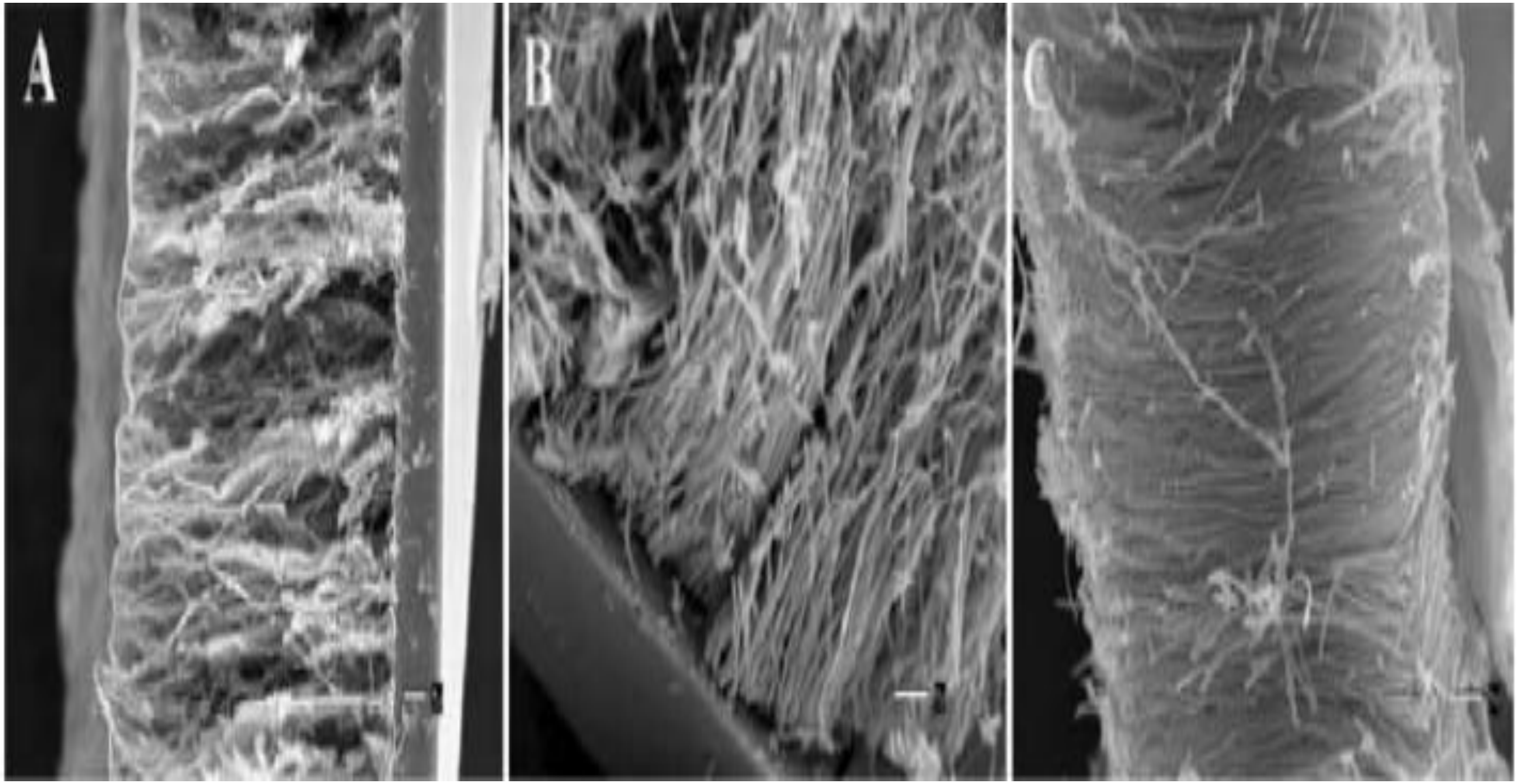
- Use prefabricated cylindrical nanopores in a solid material as templates.
- If dissolve away the host solid material, freestanding nanowires are obtained.

Advantages

- The ability to create highly conductive nanowires because electro-deposition relies on electron transfer, which is the fastest along the highest conductive path.
- Electro-deposited nanowires tend to be dense continuous and highly crystalline in contrast to other deposition methods.
- The ability to control the aspect ratio of the metal nanowires by monitoring the total amount of passed charge.

Electrophoretic Deposition

- Differs from electrochemical deposition in several aspects.
- The deposit doesn’t need to be electrically conductive.
- Particular method for obtaining oxide nanowires like SiO_2, TiO_2, Bi_2O_3, etc.

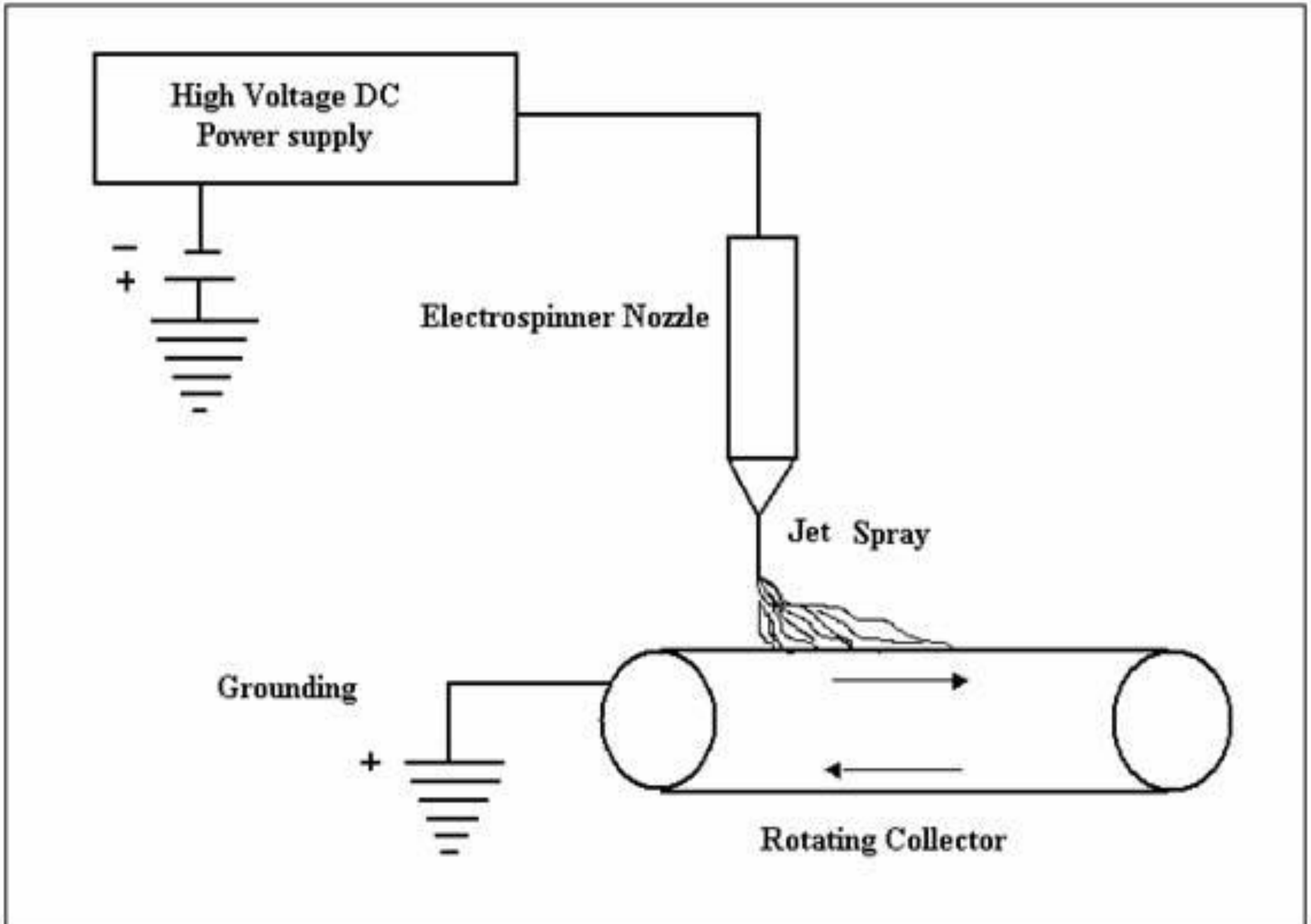


Different sizes of TiO nanorods grown in a membrane of electrophoretic deposition

Diameters: (A) 180 nm, (B) 90 nm, (C) 45 nm

Electro-spinning

- Uses an electrical charge to draw very fine (typically on the micro or nanoscale) fibres from a liquid.
- Sufficiently high voltage is applied to a liquid droplet and the body of the liquid becomes charged.
- When the electrostatic repelling force overcomes the surface tension force of the polymer solution, the liquid spills out of the spinneret and forms an extremely fine continuous filament.
- These filaments are collected onto a rotating or stationary collector with an electrode where they accumulate and bond together to form nanofiber fabric.


High Voltage DC
Power supply
−
+
Electrospinner Nozzle
Jet Spray
Grounding
+
Rotating Collector

Applications of Nanowires

Nanowires are promising materials for many novel applications for their unique geometry and unique physical properties such as:

– electrical

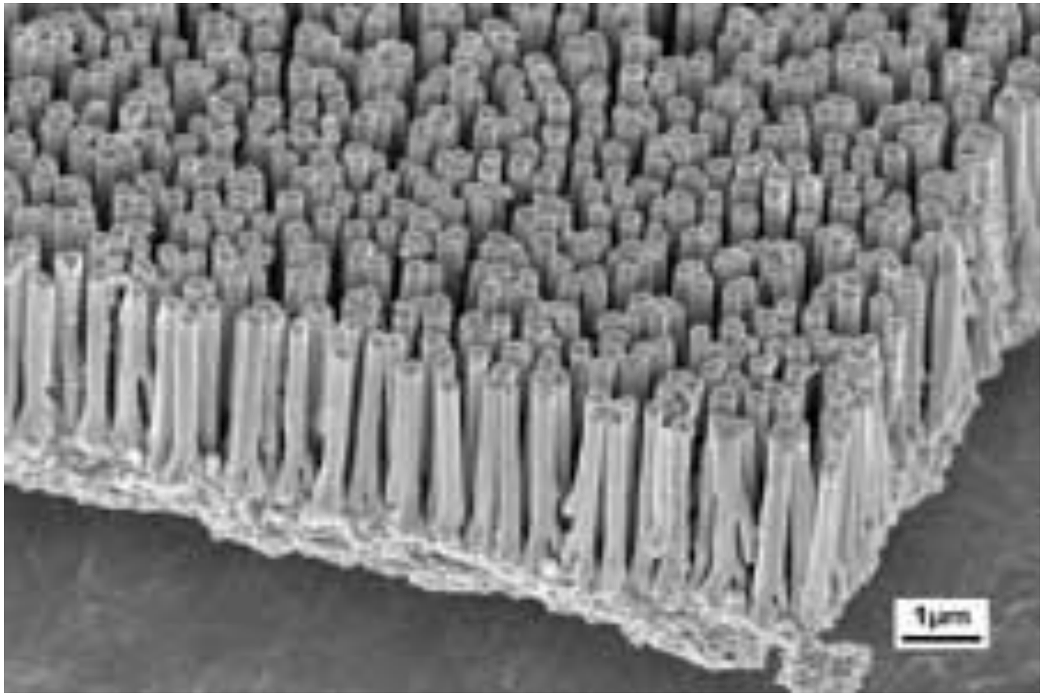
– magnetic

– optical

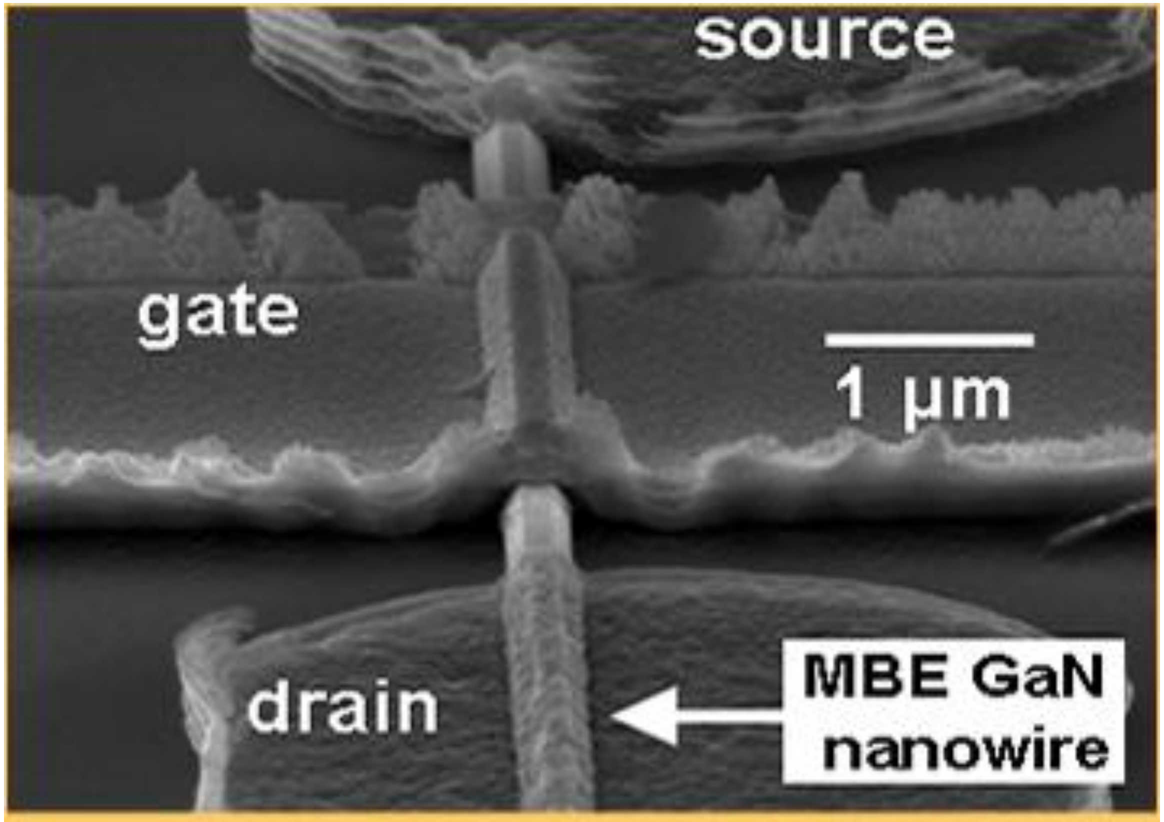
– mechanical

Types of Nanowires

- Metal nanowires
- Semiconductor nanowires (Silicon nanowires)
- Oxide nanowires
- Multi-segment nanowires
- Semiconductor quantum wires

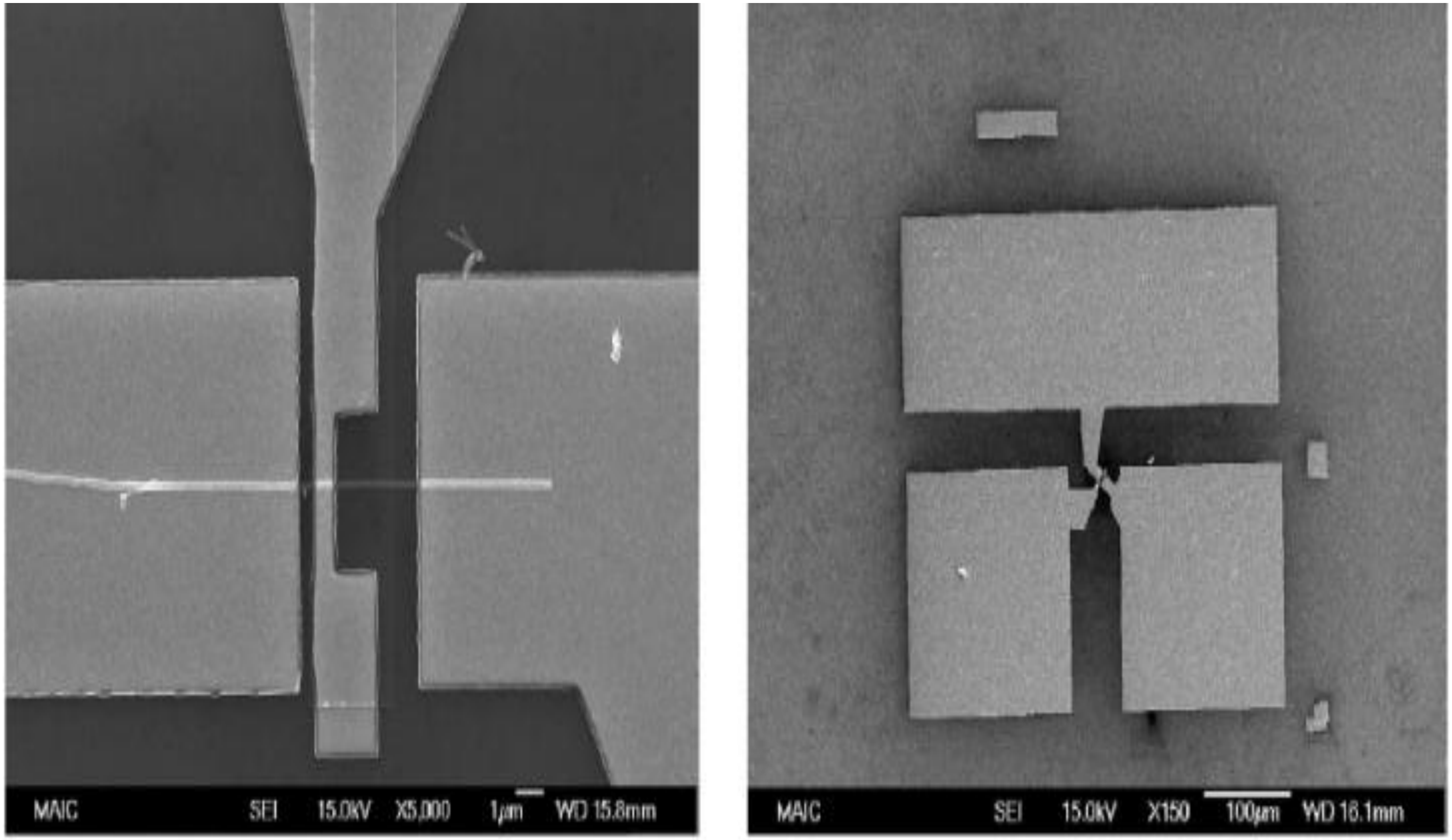


A forest of copper rods about 100 nanometers in diameter create much more surface area for high-capacity battery electrodes



Scanning electron micrograph of nanowire field-effect transistor

http://www.boulder.nist.gov/div815/OMM_Project/Accomplishments.htm



SEM micrographs of ZnO MOSFET structure(crossed nanowire device)

Conclusion

- Nanowires can be precisely controlled during:

- Synthesis
- Chemical composition
- Length
- Diameter
- Doping/electronic properties

- Enables the assembling of building blocks into increasingly complex structures.

- Low device-to-device reproducibility