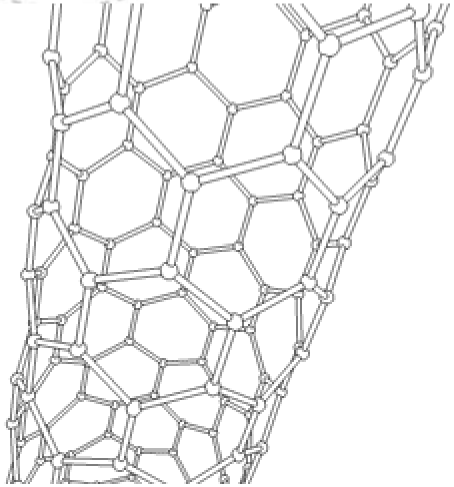
Norwegian University of
Science and Technology

TMT4320 Nanomaterials
October 18th, 2016

- Nanoscience – Chapter 8
  Fullerenes and carbon nanotubes



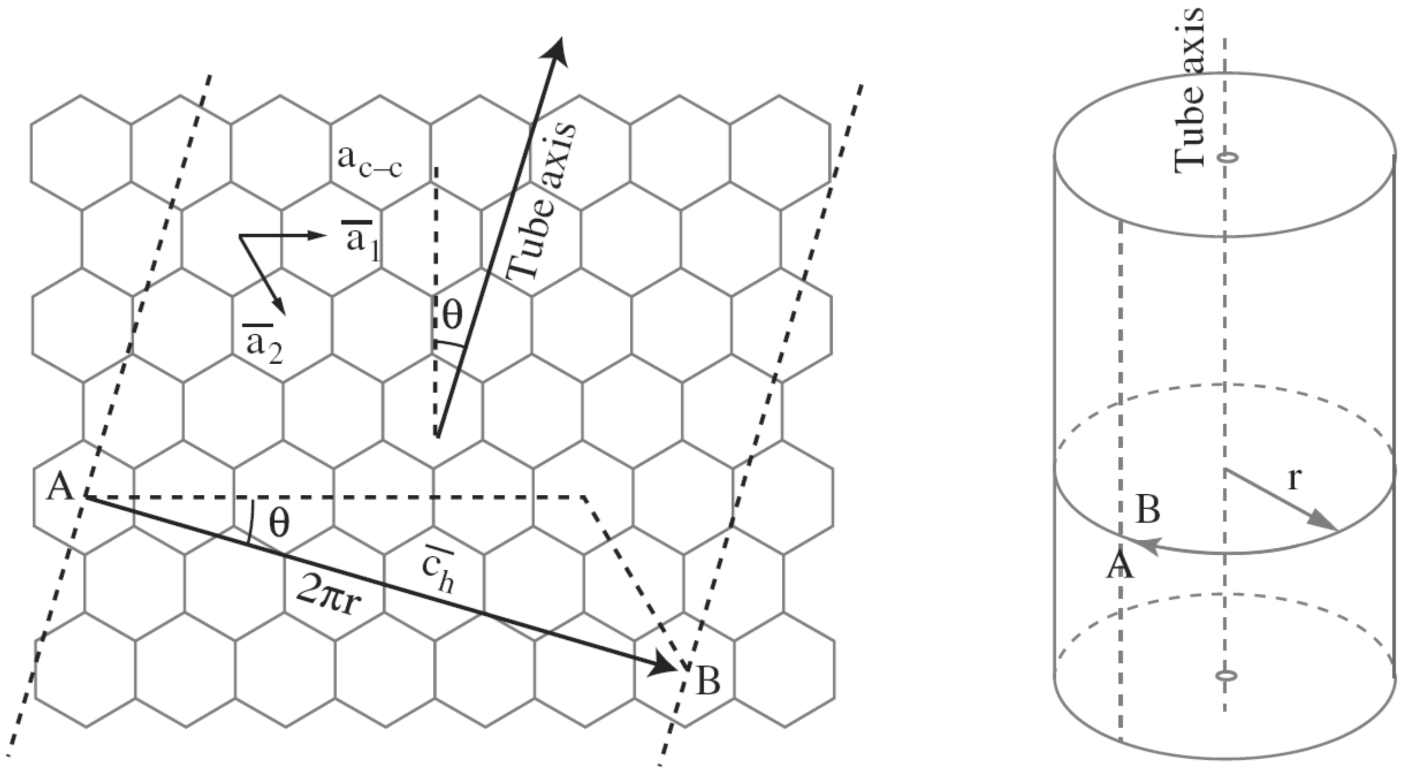
Wikipedia

Crystal structure of carbon nanotubes

- Length: usually several microns
- Diameter: typically in the range 1–10 nm
- The atomic structure
  - Rolled up graphene sheet (open ended)
- Closed ended tubes
  - Curvature is achieved by introducing pentagons
  - Each end of a nanotube corresponds to the closure of a half-sphere which is achieved by introducing 6 pentagons into the hexagonal lattice

Graphene sheet roll-up

- Superposing two hexagons A and B of the lattice



Construction of a nanotube by rolling up a graphene sheet.

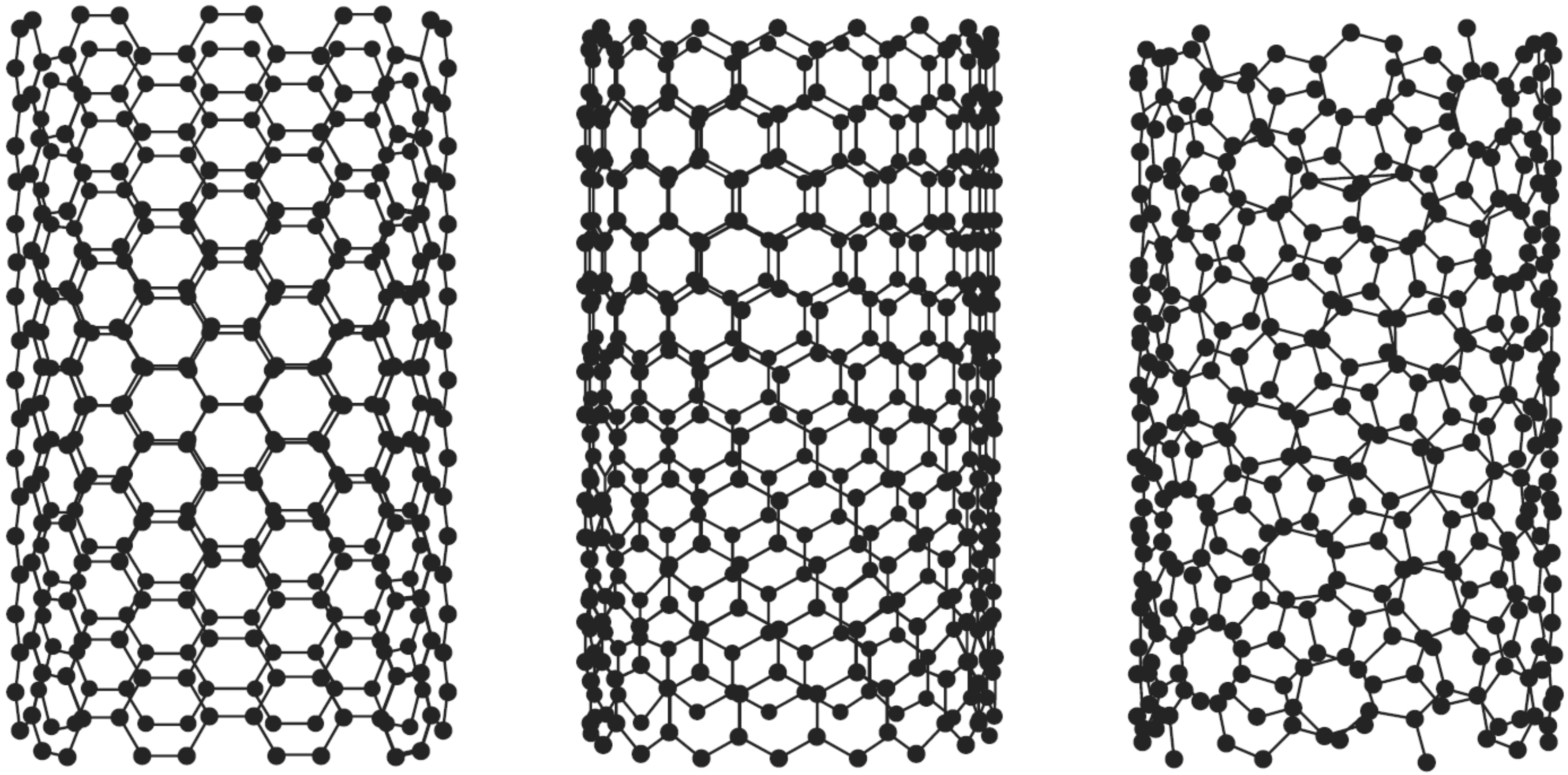
Armchair, zigzag and chiral

- Zigzag tube
  - Chiral angle equal to 0°
- Armchair tube
  - Chiral angle equal to 30°

•Hexagons in the upper part of the tube have the same orientation with respect to the axis as those in the lower part

•Tubes are said to be achiral

- Chiral
  - Chiral angle θ different from 0° or 30°
  - The rows of hexagons in the upper region make an angle 2θ with the rows of hexagons in the lower region



a

b

c

(**a**) $\theta = 30°$, armchair

(**b**) $\theta = 0°$, zigzag

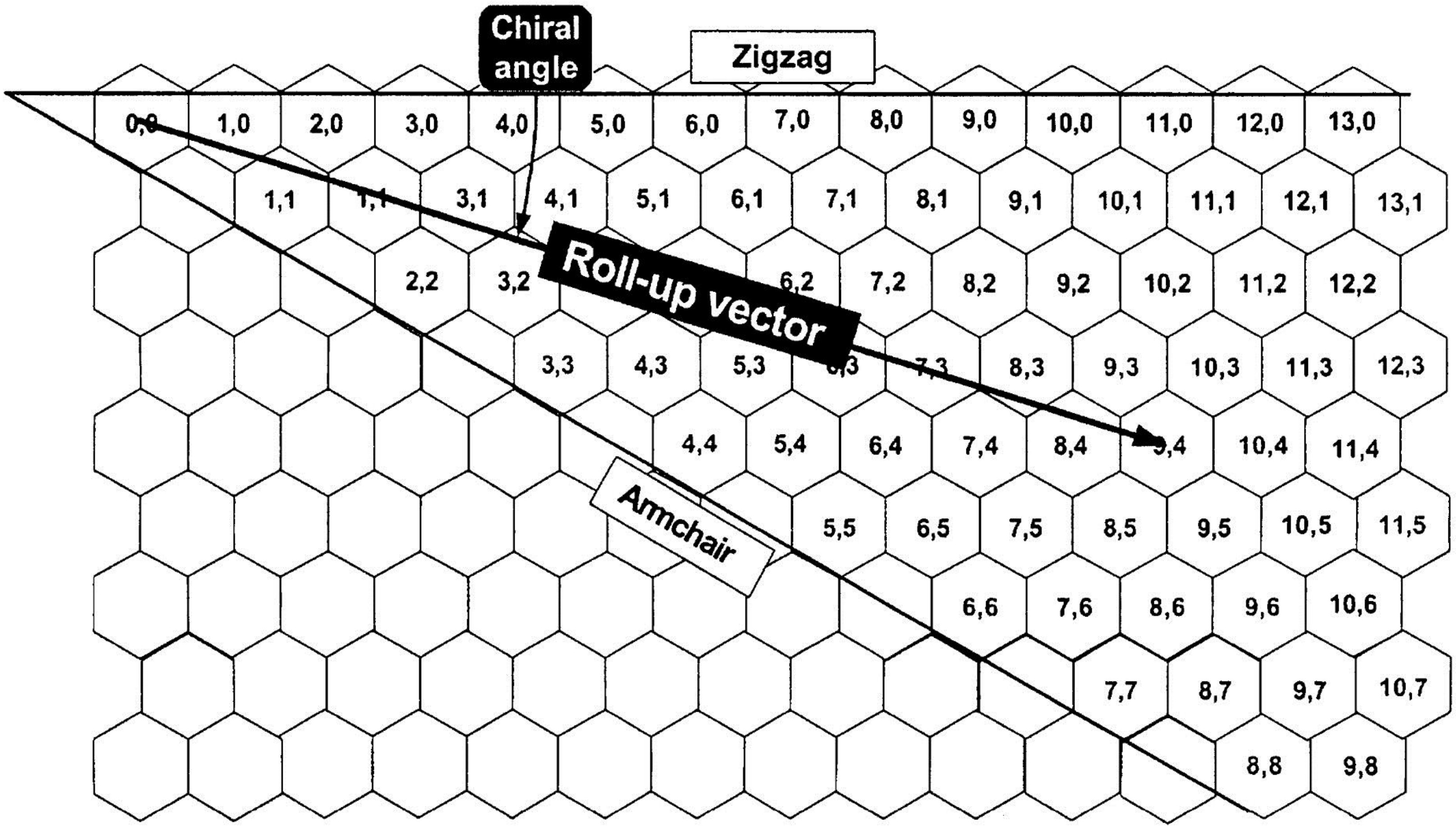
(**c**) $\theta \neq 0°$ or $30°$, chiral

Chiral vector

- Or roll-up vector
- $\boldsymbol{C} = n\boldsymbol{a}_1 + m\boldsymbol{a}_2$, with n,m whole numbers

- Armchair tube: (n,n)
- Zigzag tube: (n,0)
- Chiral tube: (n,m)

- The electronic properties of nanotubes are directly dependent on the chiral vector



http://www.freepatentsonline.com/7074310-0-large.jpg

Armchair tube

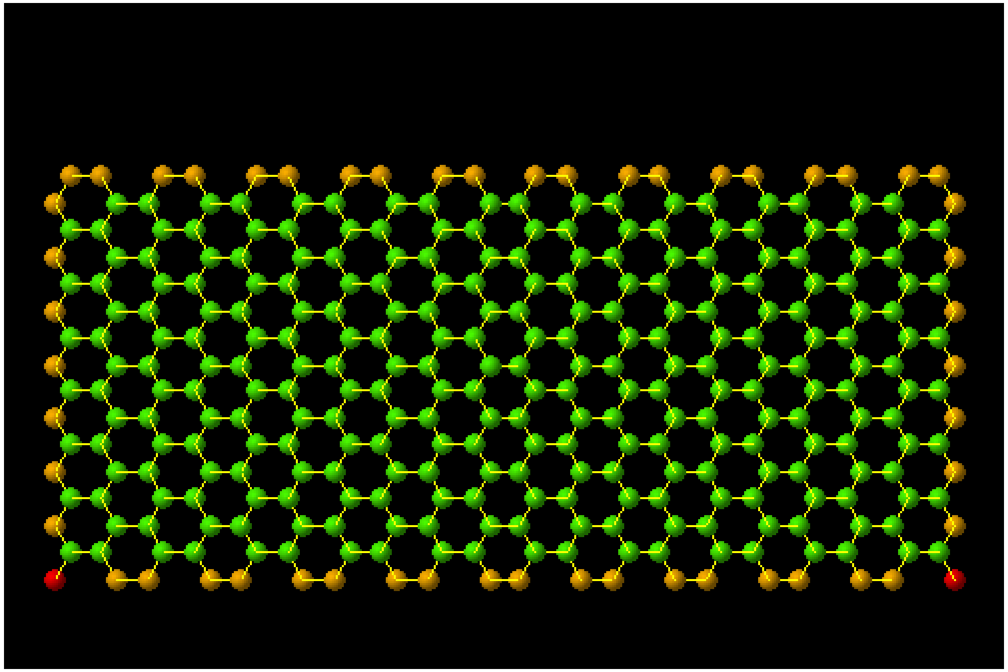


Illustration for acquiring the (10,10) nanotube by rolling up a sheet of graphene.

These animations are the work of Dr. Shigeo Maruyama
http://virag.elte.hu/kurti/rollup.html

Chiral tube

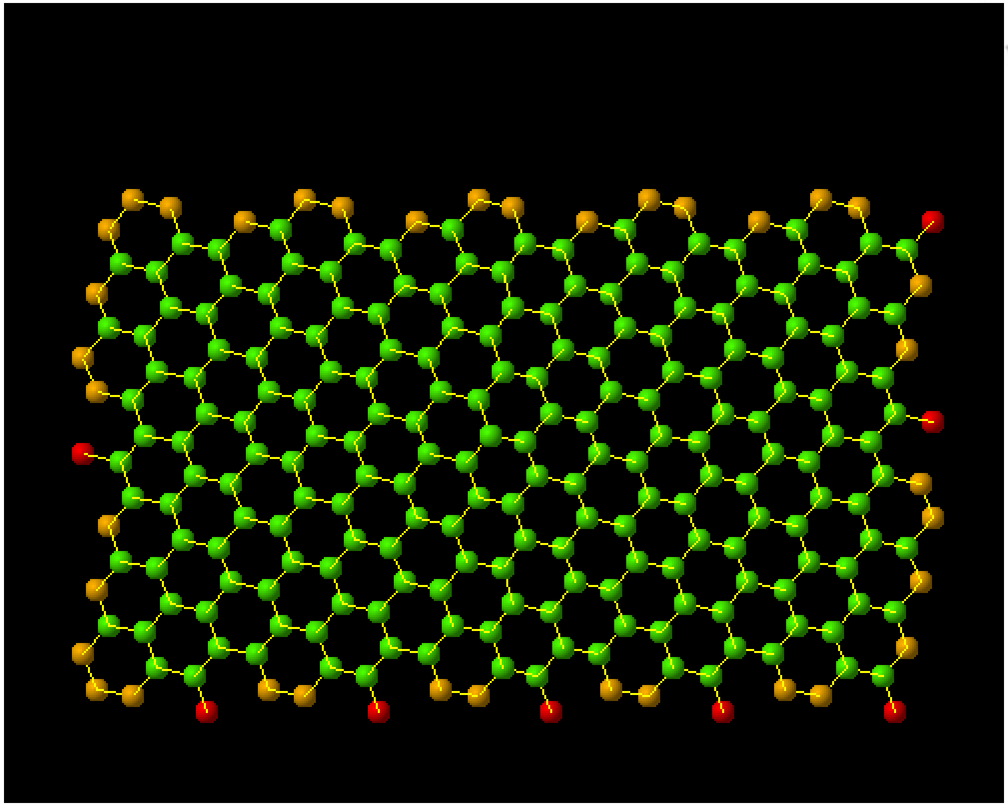
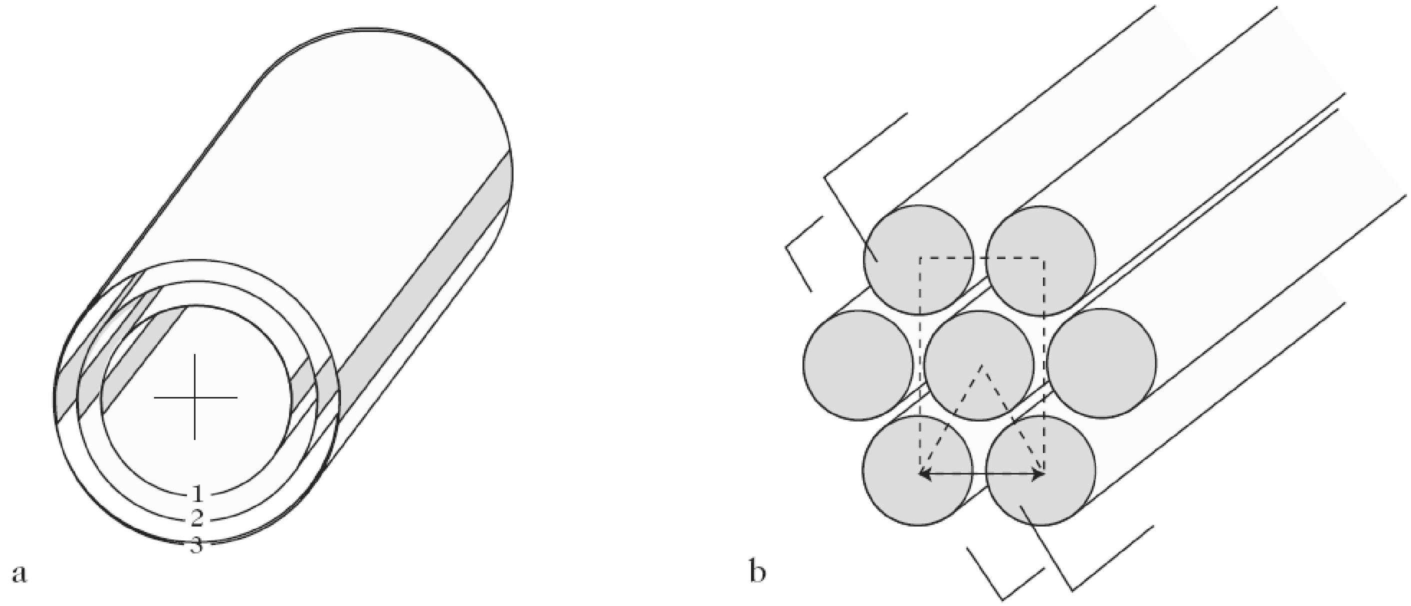


Illustration for acquiring the (10,5) nanotube by rolling up a sheet of graphene.

These animations are the work of Dr. Shigeo Maruyama
http://virag.elte.hu/kurti/rollup.html

Self-organisation of nanotubes during growth



The two modes of self-assembly for carbon nanotubes.
(**a**) Structure of a multiwalled nanotube (MWNT).
(**b**) Crystallised bundle of single-walled tubes (SWNT).

Synthesis of nanotubes

- Carbon nanotubes may exist in the natural state, but at the present time only synthetic nanotubes have been observed

- High temperature synthesis
- Moderate temperature synthesis

- In one experiment on the laboratory scale typically anything between a few hundred milligrams and one gram of unpurified nanotubes can be produced

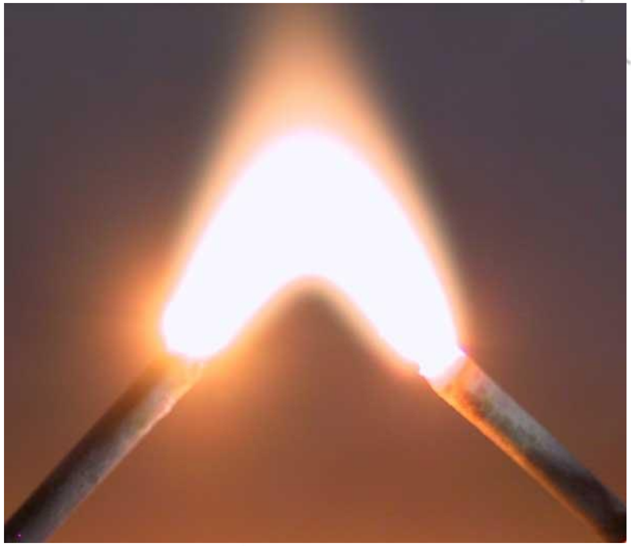
High-temperature synthesis

- Vaporizing graphitic carbon (graphite sublimes at 3200 °C) and then condensing it in a vessel where there is a strong temperature gradient and an inert gas such as helium or argon at partial pressures typically around 600 mbar

- The various methods using this basic idea can be distinguished from one another by the process used to vaporize the graphite

Arc process (high temperature)

- Krätschmer–Huffmann process
- Electric arc (30–40 V, 100 A) between two graphite electrodes
- The anode is consumed to form a plasma at a temperature of up to 6000 °C
- Condensed plasma is deposited on the cathode, containing the nanotubes
- Product may contain either multiwalled (MW) or single walled (SW) carbon nanotubes



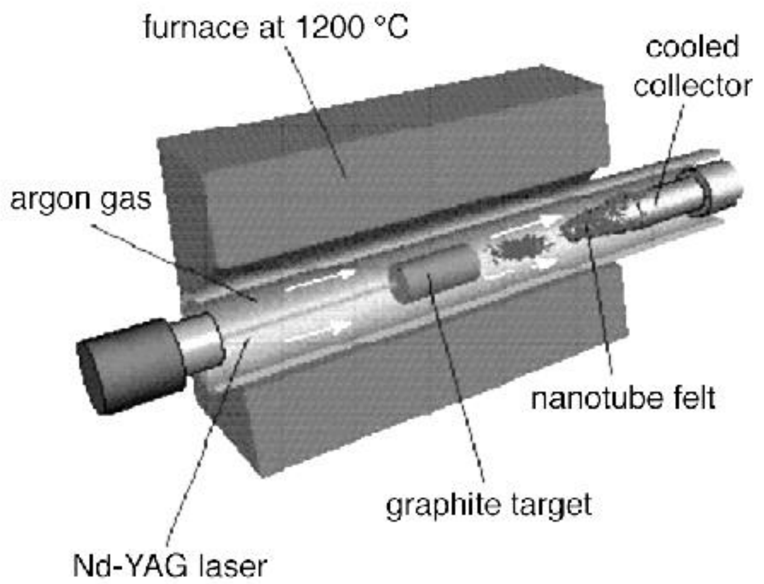
Arc process contd.

- How do we produce MW carbon nanotubes?
  - Cathode must be made from pure graphite
  - MW tubes then form directly in the vapor phase in the hottest region of the arc (minimum temperature of 3 000 °C)

- How do we produce SW carbon nanotubes?
  - Must use a metallic catalyst
  - A few percent of catalyst is introduced into the graphite powder
  - Catalyst materials include: Ni, Co, Pd or Pt, or a metal in the rare earth series, such as Y or La
  - SW carbon nanotubes form in a colder region of the arc

Laser process (high temperature)

- Bombarding a target by high energy laser radiation
- Nature of the nanotubes depends on synthesis conditions
  - Pulsed laser (Nd:Yag-type laser)
  - Continuous wave laser (1–5 kW CO_2 laser)



Laser process contd.

- Pulsed laser
  - Small clusters of carbon form and recombine into a crystal structure if the reactor is heated (by external oven) to at least 800 °C
  - Only produces bundles of single-walled tubes.
  - Graphite target contains a metal catalyst based on Ni, Co and Fe

- Continuous wave laser
  - Target is heated by a laser to at least 3 000 K and gradually vaporizes
  - The gas in the vicinity of the target surface is overheated and plays the role of a local oven (no external oven)
  - Pressure and flow of carrier gas can be adjusted in order to control temperature gradients
  - MWNTs are obtained by vaporizing pure graphite and SWNTs by vaporizing graphite doped with a metal catalyst

CVD (moderate and “low” temperature)

- Chemical vapor deposition (CVD)
  - A carbon-bearing gas (precursor) is decomposed at the surface of particles of a metal catalyst in an oven heated to between 500 and 1100 °C
  - The released carbon precipitates onto the surface of the particle → results in the growth of graphitic tubular structures
  - Precursor: carbon monoxide (CO) or a hydrocarbon such as acetylene, methane, etc.
  - Catalyst is a transition metal (Fe, Ni, Co)
  - Catalyst particles must be a few nanometers to synthesize nanotubes

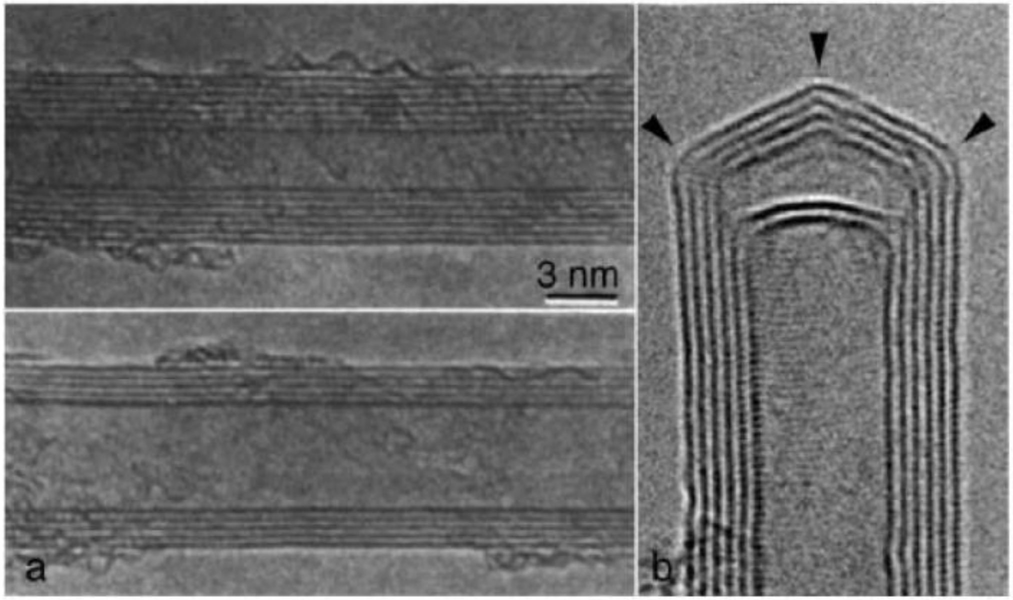
CVD contd.

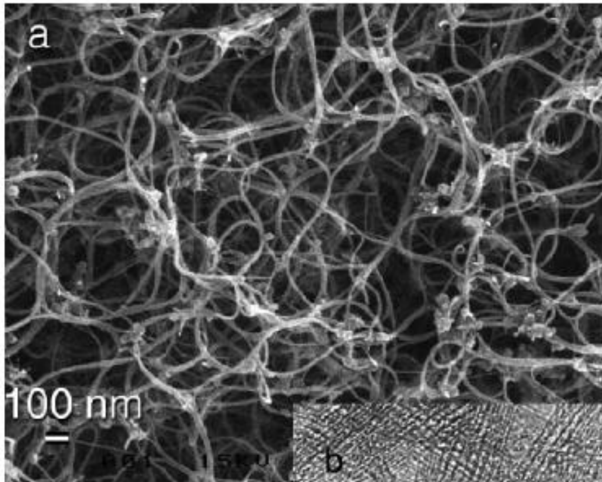
- How do we controll the product (SW or MW) using CVD?
  - Operating conditions such as oven temperature, pressure and flow rate of the gases, and size of catalyst particles, MWNTs or SWNTs are produced.
  - Generally, SWNTs are synthesised at higher temperatures than MWNTs and using smaller catalyst particles (NB! Different from arc process)

- Medium-temperature processes can be scaled up to the production levels of carbon fibres, something that is much more difficult to achieve using high temperature channels

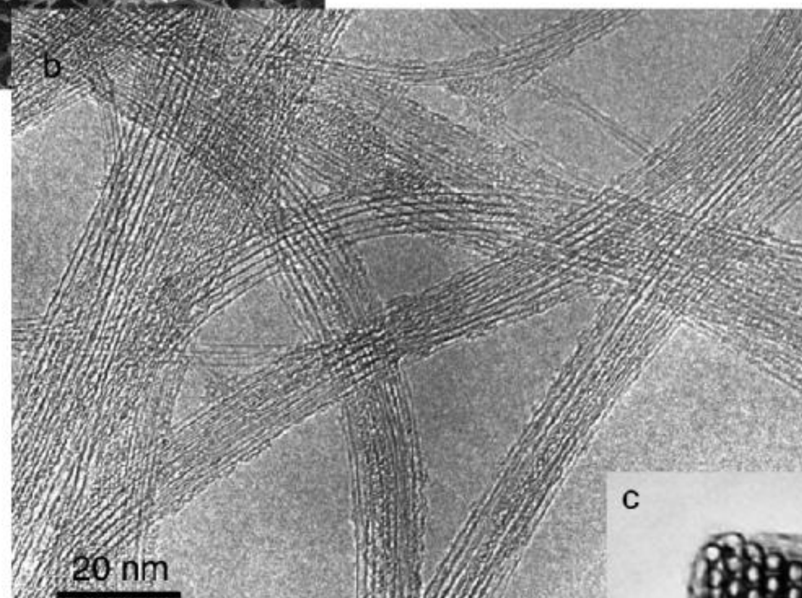
Observation of nanotubes

- Transmission electron microscopy (TEM)

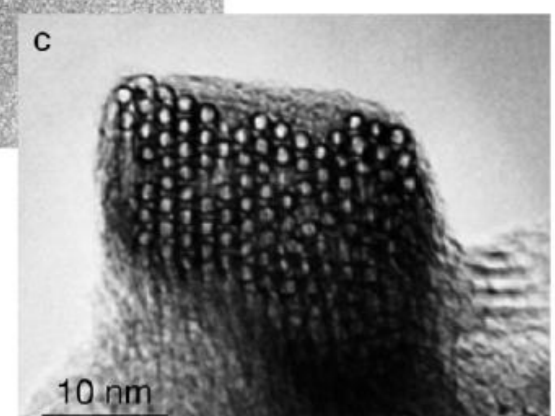




Scanning electron microscope image of SWNT ropes.

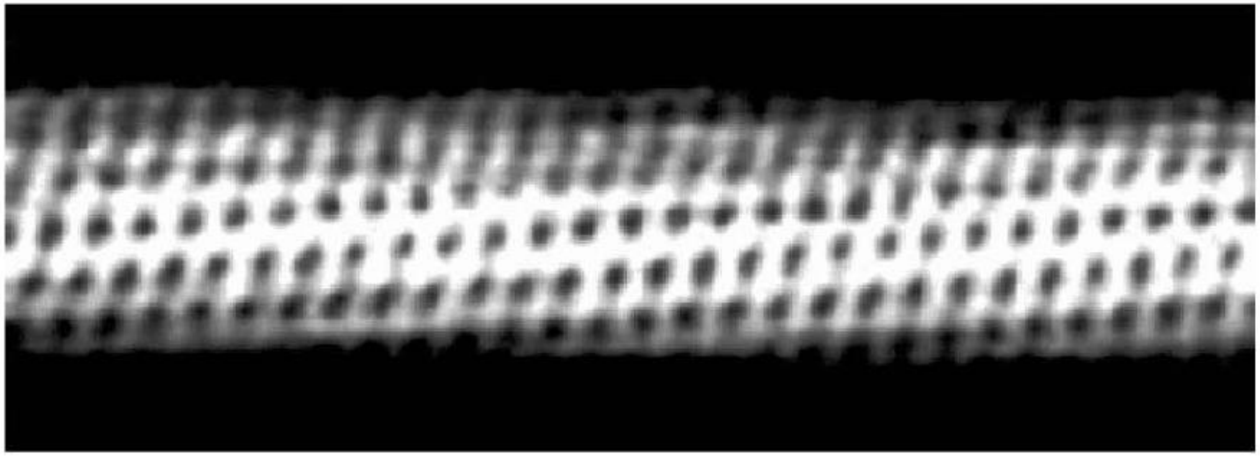


TEM micrograph of ropes observed perpendicularly to their axis. *Black lines* correspond to projected rows of tubes.



TEM micrograph of a rope looking along its axis. Each *black circle* corresponds to one nanotube.

- Scanning tunneling microscopy (STM)



STM image of a chiral nanotube showing the hexagonal arrangement of the carbon atoms.

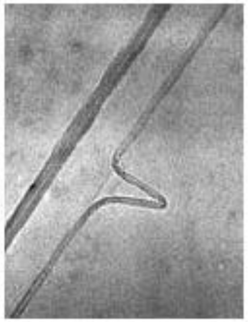
Properties of nanotubes

- Can control properties of the nanotubes by adapting the properties of graphite to the conditions imposed by rolling up the graphene sheets

- Electrical properties
  - Metallic or semiconducting
  - Resistance measurements on a nanotube connected between two metal electrodes is highly dependend on the contacts.
  - Ohmic contacts can be made by evaporation of a metal on the nanotube to give values close to the theoretical value ($h/4e^{2}$) of the conductance (6.5 kΩ)
  - Extremely high current densities, ~10^{10} A/cm^2, at least two orders of magnitude greater than metals

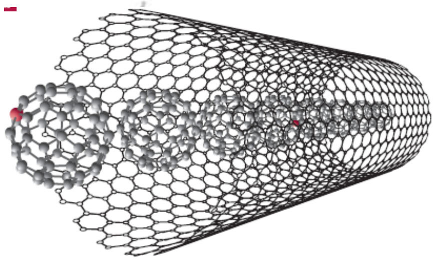
Mechanical properties

- Due to its structural anisotropy, graphite has a very high elastic modulus in the hexagonal plane (up to 10^{12} Pa or 1 TPa), but much lower values out of the plane (4×10^9 Pa)
- Nanotube have similar or higher elastic modulus than graphene. 1 TPa have been calculated and measured
- High level of flexibility, due to the partial sp^2–sp^3 hybridization of the C–C bond
- Incredible ability to bend, and also to deform and twist about its axis
- Elastic properties are considerably downgraded in MWNTs compared to SWNTs.

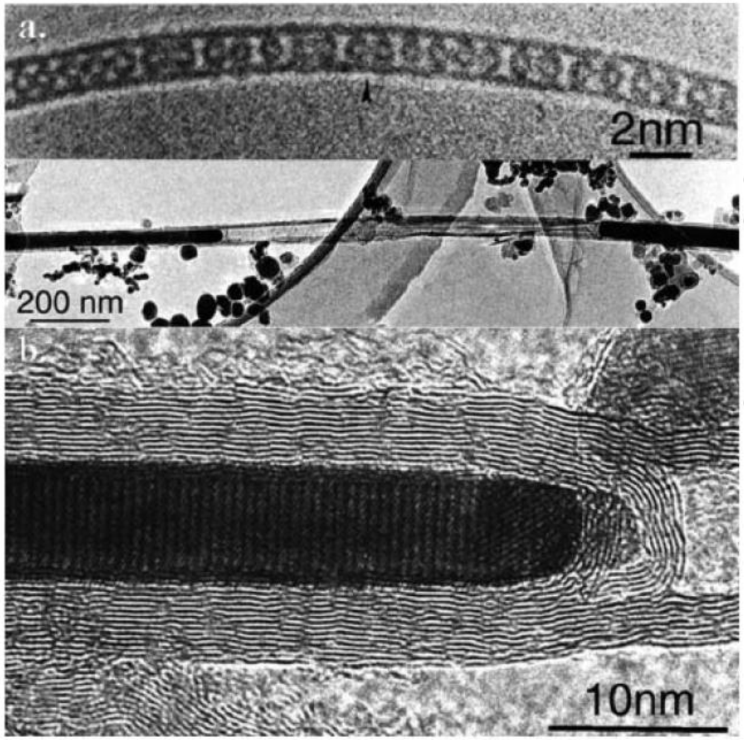


- Young's modulus (stiffness):
  - Carbon nanotubes 1250 GPa
  - Carbon fibers 425 GPa (max.)
  - High strength steel 200 GPa
- Tensile strength (breaking strength)
  - Carbon nanotubes 11- 63 GPa
  - Carbon fibers 3.5 - 6 GPa
  - High strength steel ~ 2 GPa
- Elongation to failure : ~ 20-30 %
- Density:
  - Carbon nanotube (SW) 1.33 – 1.40 gram / cm^3
  - Aluminium 2.7 gram / cm^3

Chemical properties



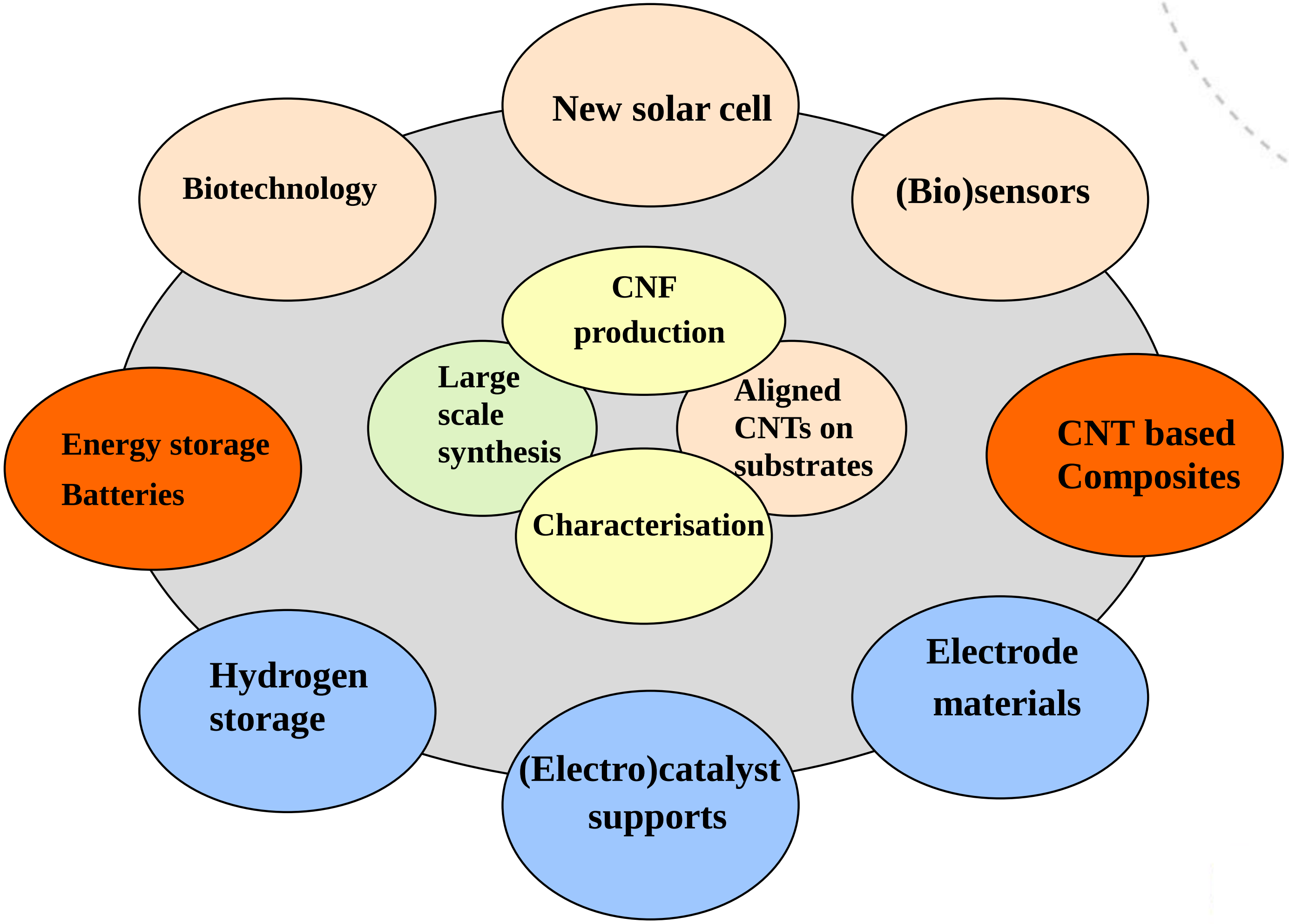
- NTs can be filled by capillary effect with fullerene molecules, or crystal compounds (metals, sulfides, metal chlorides)
- Molecules can be attached to the NT surface
- Can be used to separate types of nanotubes



NTNU research

- Catalysis [Chemical engineering]
  - Carbon nanotubes and nanofibres as supports for metal nanoparticles
  - Production of carbon nanofibres
  - Electrochemistry
- Carbon nanotubes in solar cells [Chemical engineering]
- Carbon nanostructures formed during electrolysis [Materials Sci. Eng.]
- Carbon nanocones [Materials Sci. Eng.]
- Spin-orbit coupling in various carbon nanostructures (theoretical) [Physics]
- Allergic responses in mice of carbon nanotubes [Fac. of medicine]

NTNU Network on Carbon Nanomaterials



Super strong concrete

Polymer composites

Al, Mg composites

C-CNT composite

CNT-ceramic

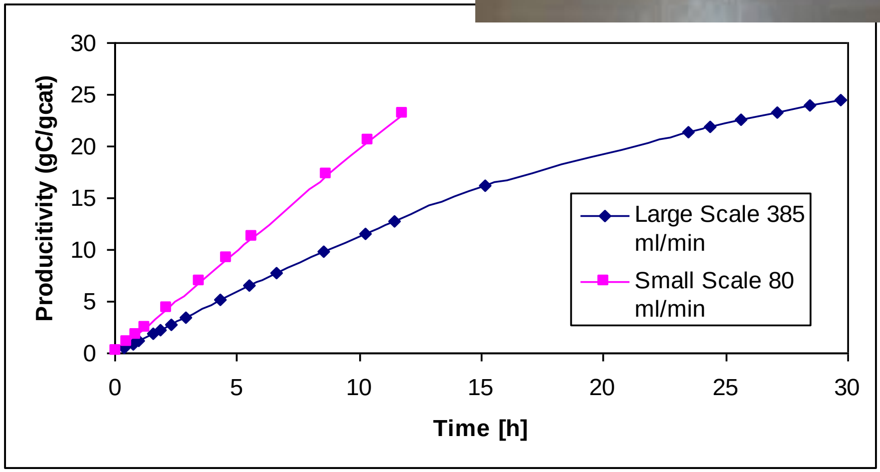
Li_2FeSiO_4-CNT composite

MnO_2-CNT composite

De Chen, "Activities in NTNU Network of Carbon Nanomaterials", Dep. Chem. Eng.

Scale-up of CNF synthesis process

A quartz-reactor is used for small-scale and a ceramic reactor for large-scale synthesis



KOSK,GASMAKS

De Chen, "Activities in NTNU Network of Carbon Nanomaterials", Dep. Chem. Eng.

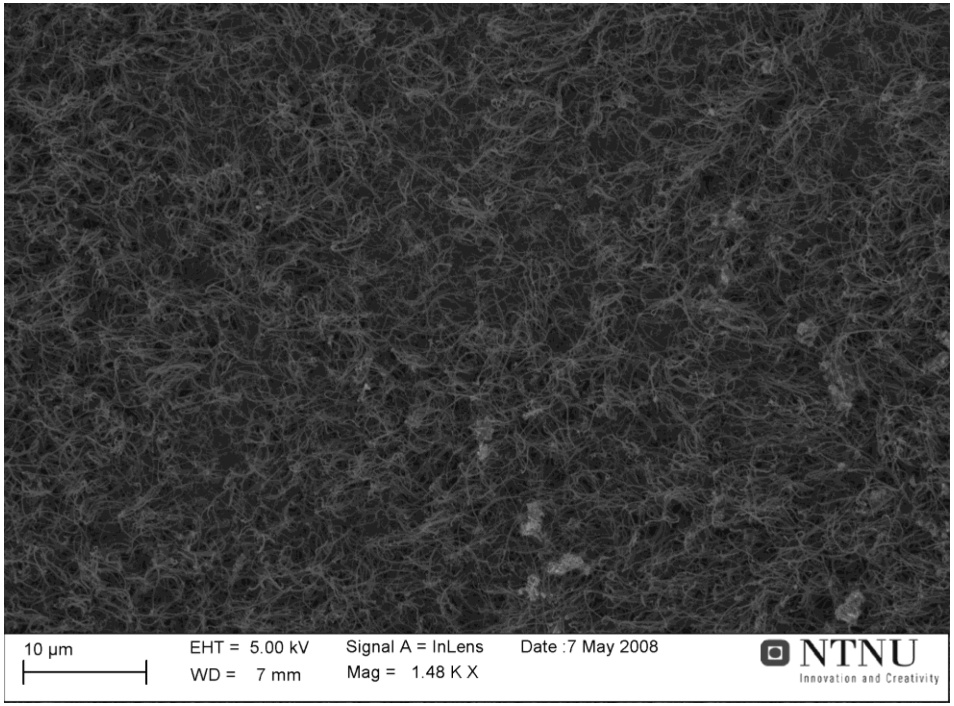
Ti Foils + acidic pretreat. – Fe nitrate

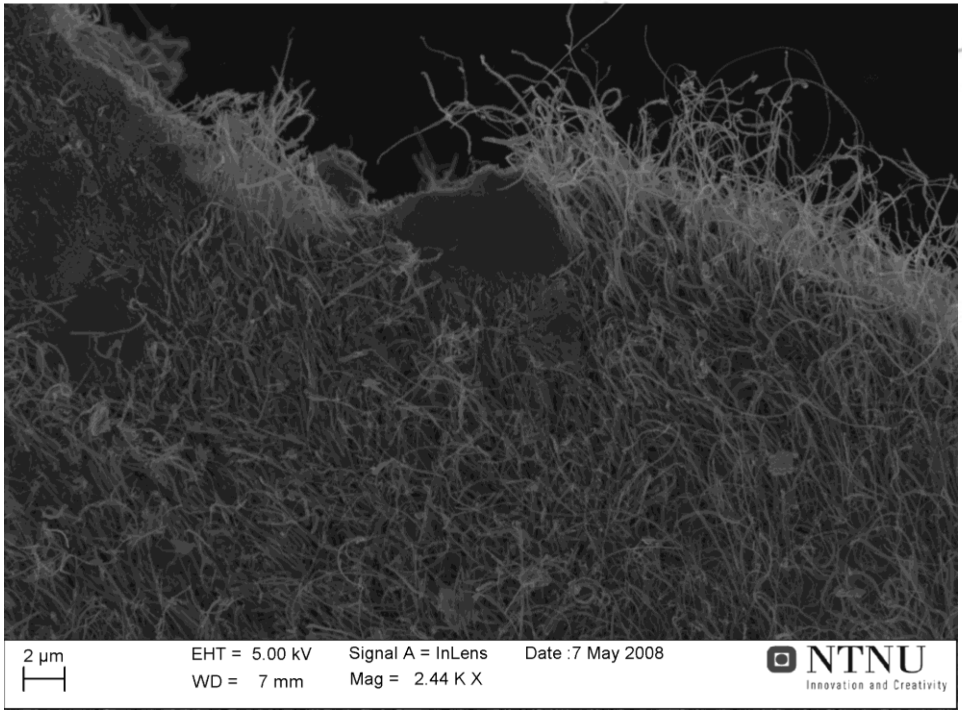
Synthesis conditions

Reduction step : Ar / H_2, up to 750 °C

Synthesis step : H_2 / C_2H_6, 120 min at 750 °C

→ homogeneous film all over the foil ; but fragile foil



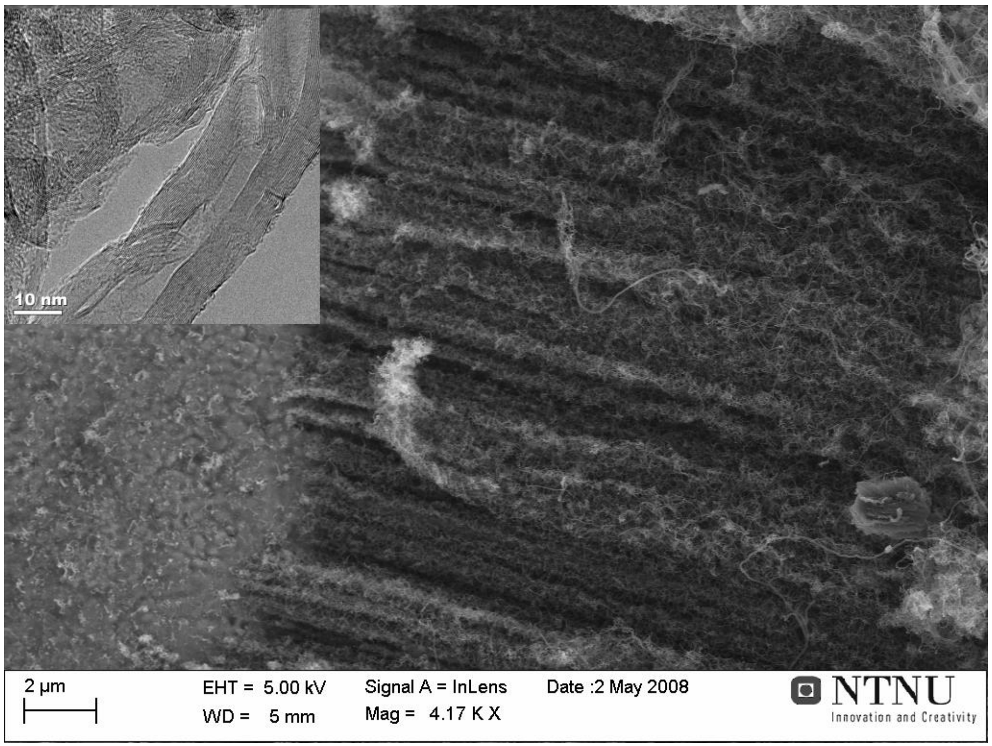


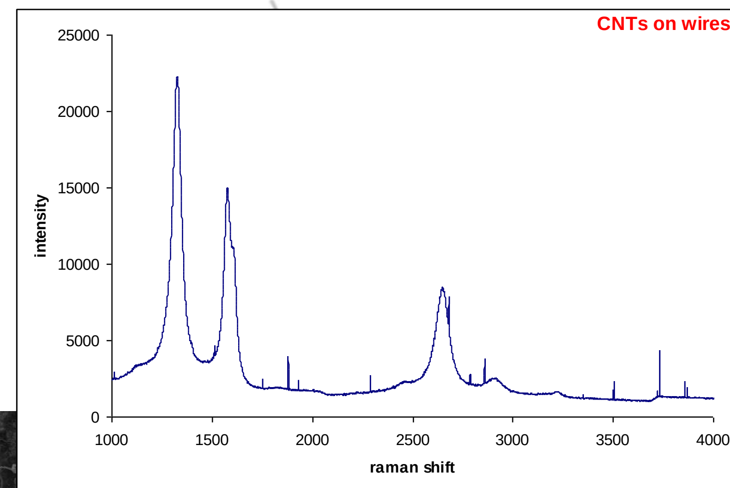
→ Really ”hard” pretreatment on Ti foil

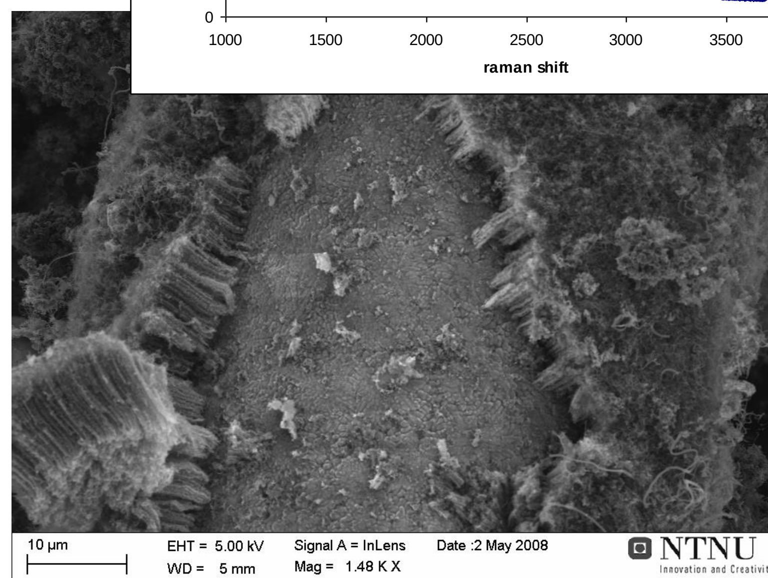
De Chen, “Activities in NTNU Network of Carbon Nanomaterials”, Dep. Chem. Eng.

Wires

2 batches reproducibility
Pretreatment : HNO_3 70% 30 min
Impregnation : drop by drop 1%-wt Fe solution EtOH/Water
Conditions : $Ar/H_2/C_2H_6$ 40/10/80 ml/min





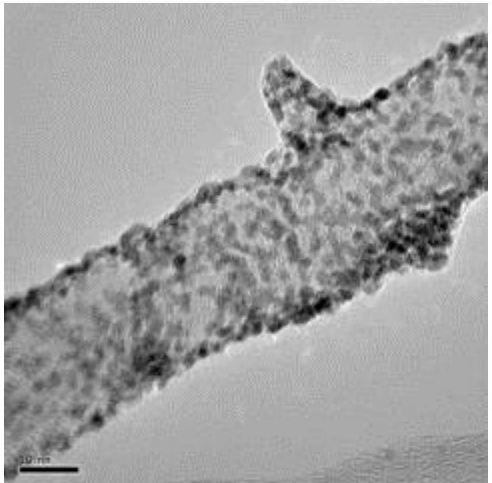


CNTs obtained

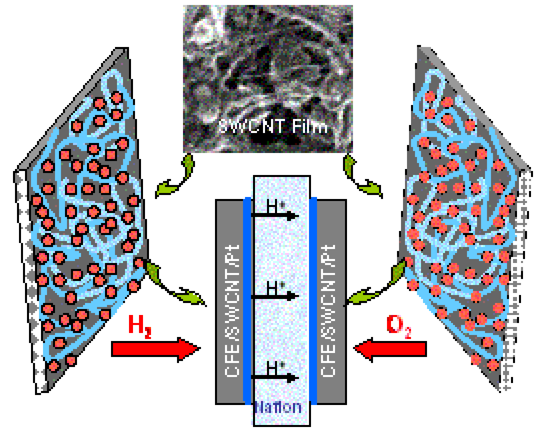
Reproducible; wires easier support for the flow

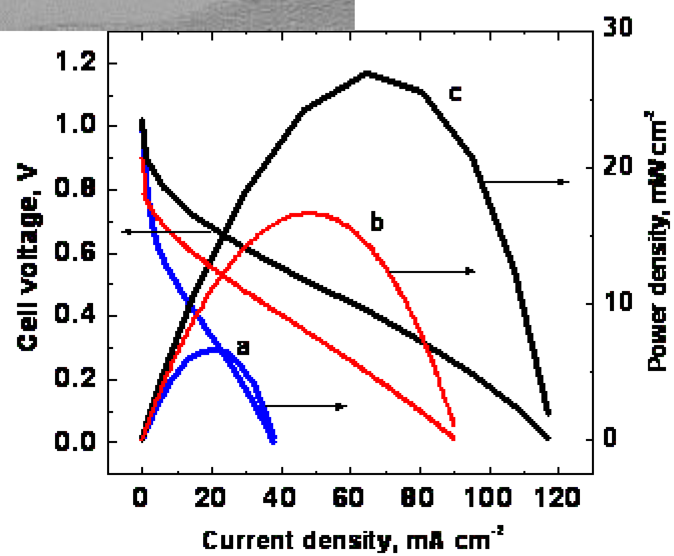
De Chen, “Activities in NTNU Network of Carbon Nanomaterials”, Dep. Chem. Eng.

CNT based electrodes in fuel cells

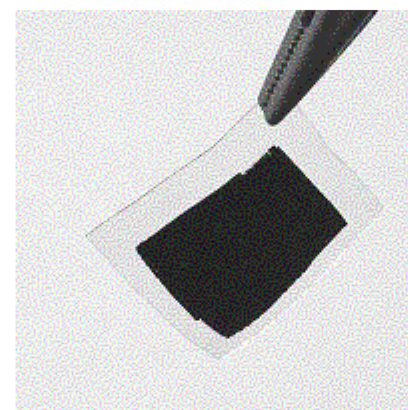


Pt/CNF





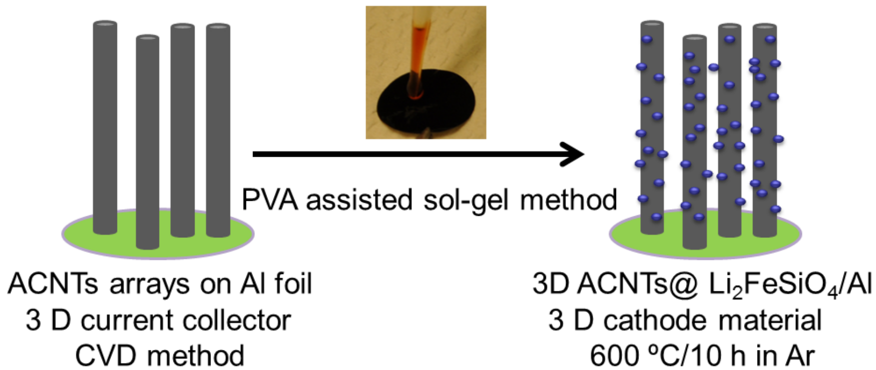
SWCNT Supported MEA



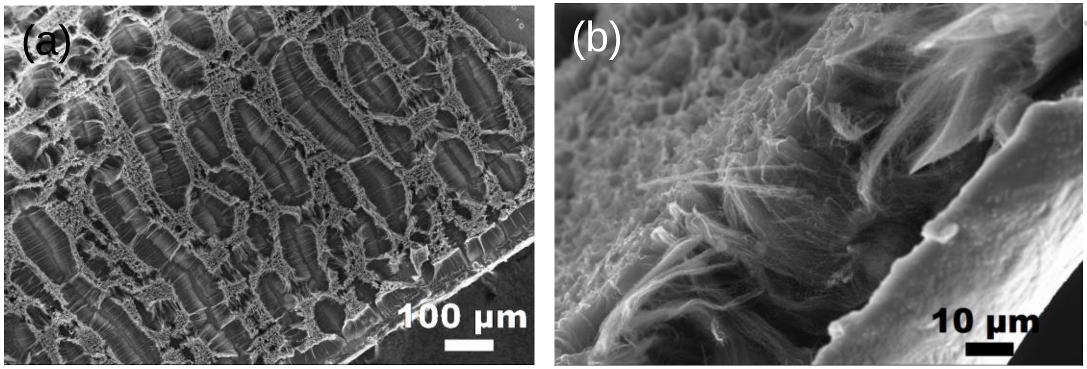
NANOMAT

De Chen, “Activities in NTNU Network of Carbon Nanomaterials”, Dep. Chem. Eng.

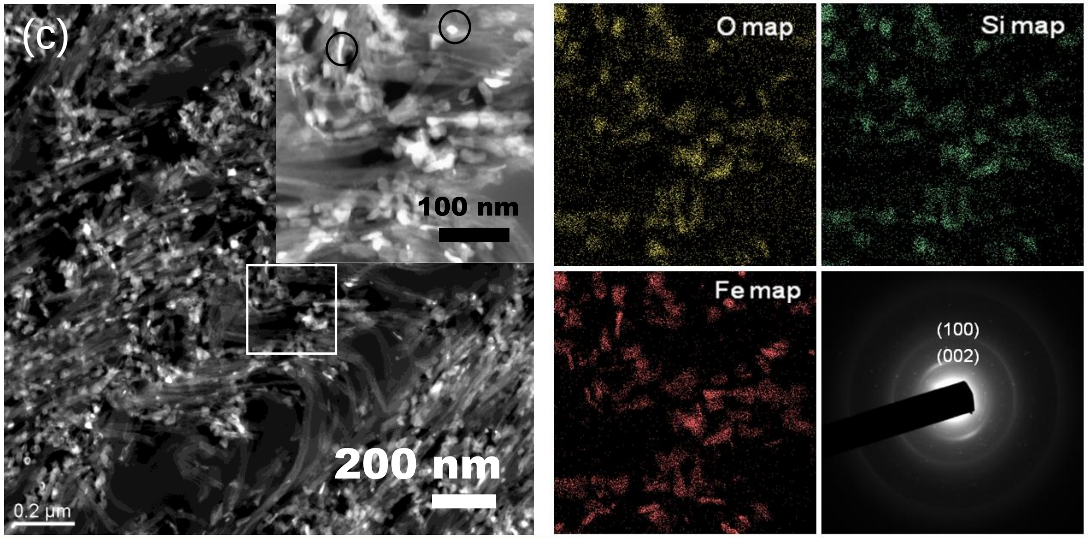
Li_2FeSiO_4 on aligned carbon nanotubes



Field emission SEM



Low angle annular dark field (LAADF) scanning TEM



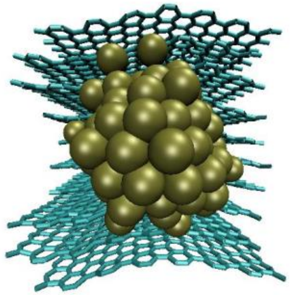
Energy dispersive x-ray spectroscopy (EDS)

Electron Diffraction (in TEM)

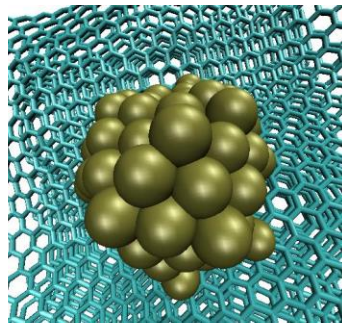
Atomistic simulations of binding of Pt clusters to carbon nanostructures

isolated

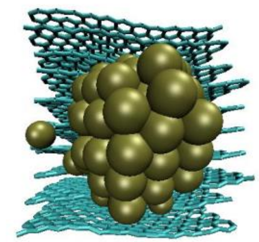
armchair



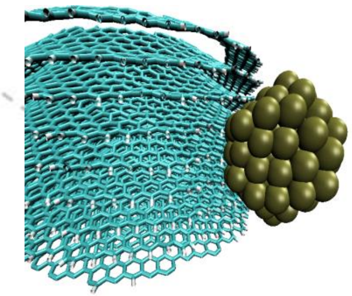
graphite surface

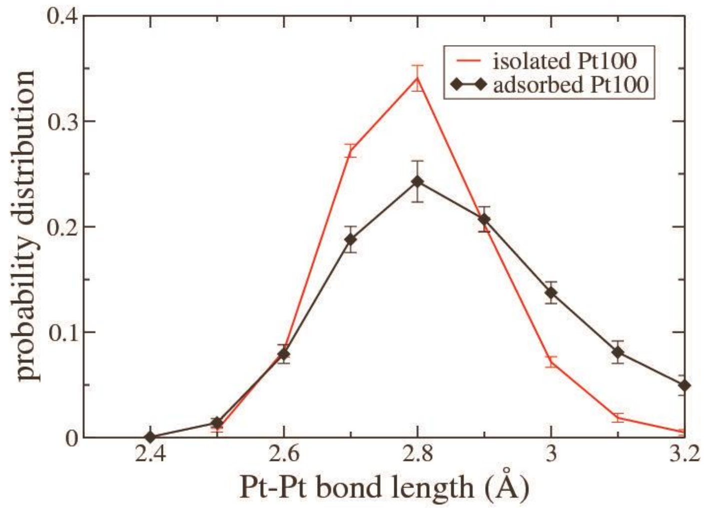


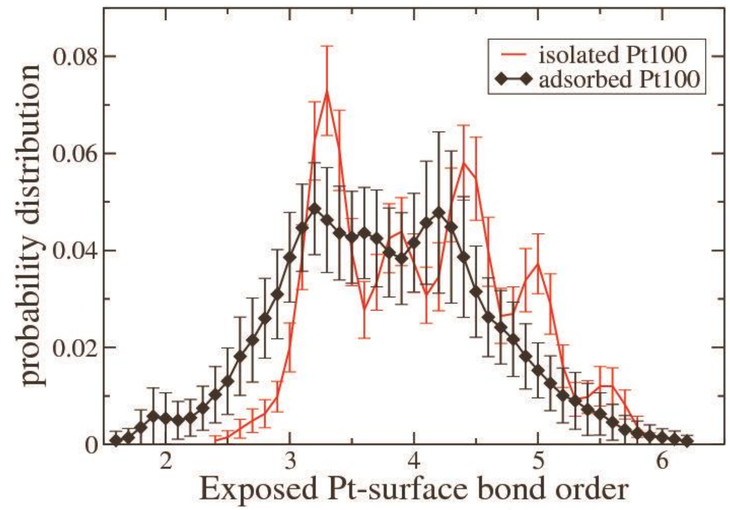
zigzag



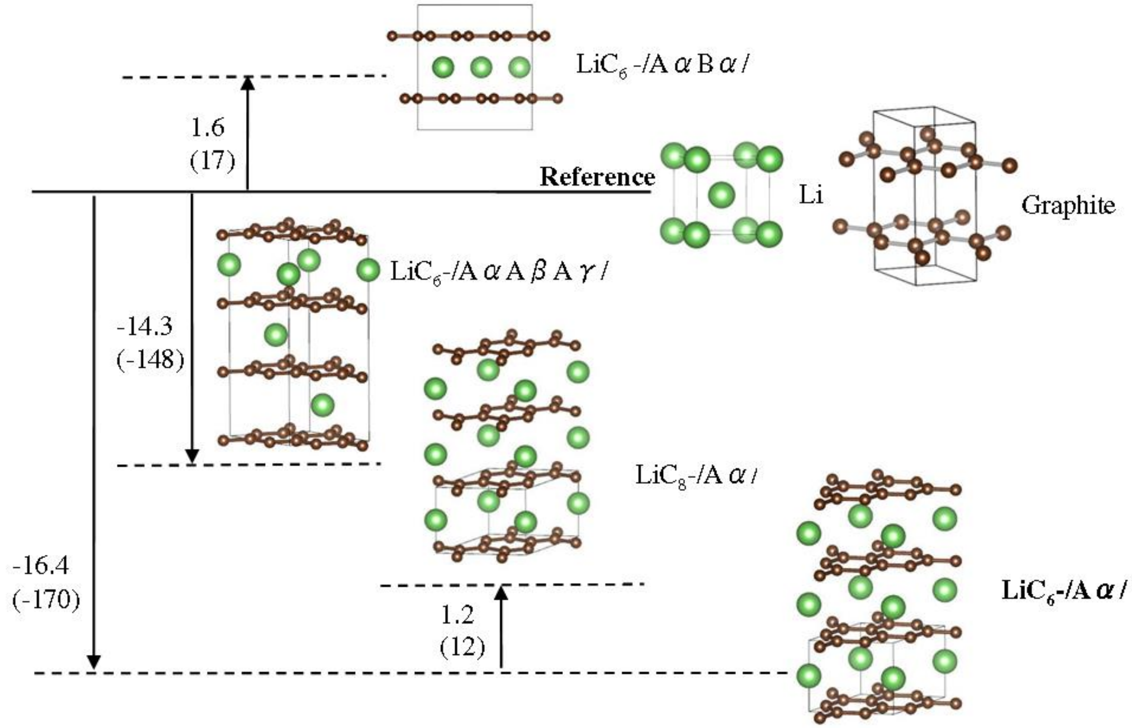
nanocone





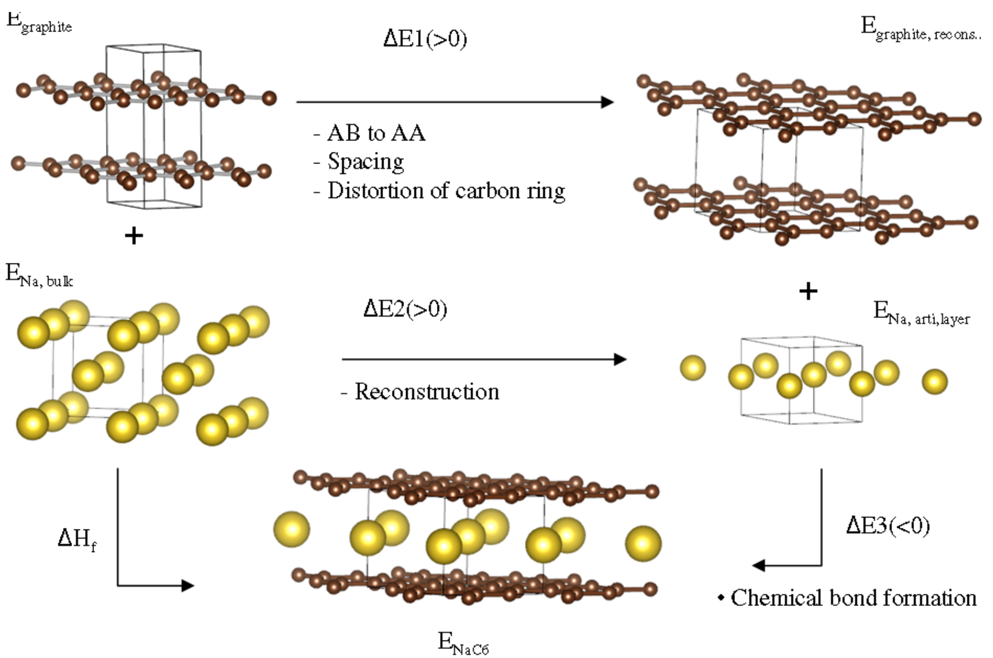


C.F. Sanz-Navarro, P.-O. Åstrand, D. Chen, M. Rønning, A.C.T. van Duin, T. Jacob, W.A. Goddard III:
Molecular Dynamics Simulation of the Interaction between Platinum Clusters and Carbon Platelets, J. Phys. Chem. A, 2008, *112* (7), pp 1392–1402



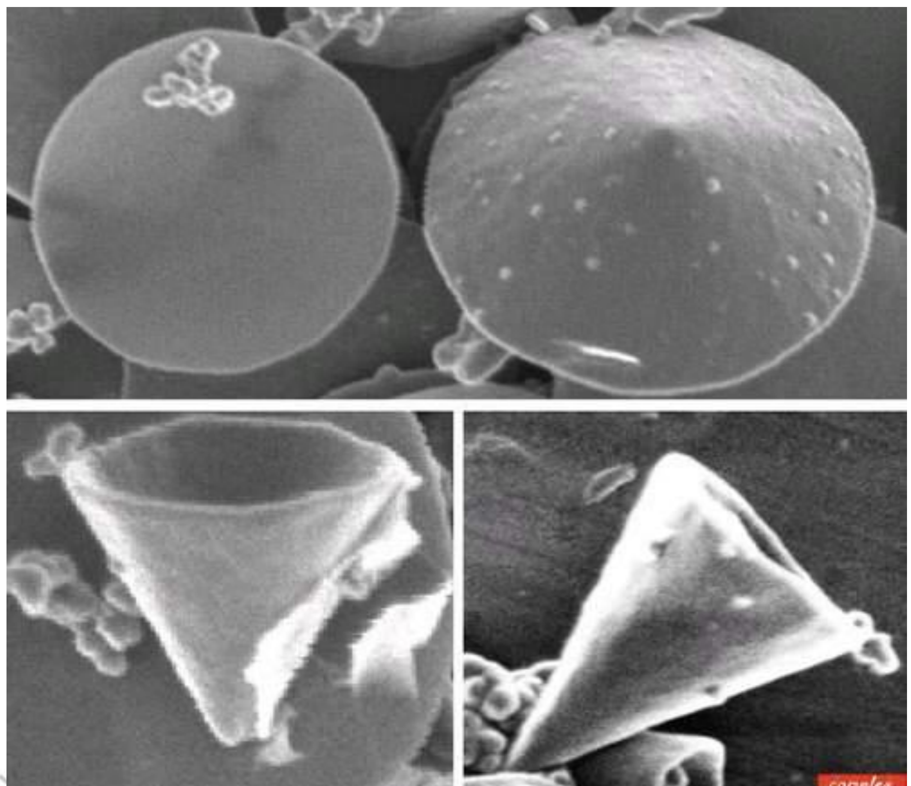
Understanding Li intercalation and diffusion in graphite from DFT.

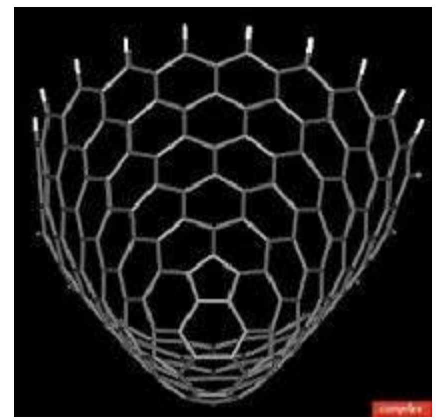
Why is Na intercalation in graphite unstable?



NTNU and Institutt for energiteknikk (IFE)

- Carbon nanocones
- Anode materials in Li-ion batteries (NTNU)
- Hydrogen absorption (IFE)

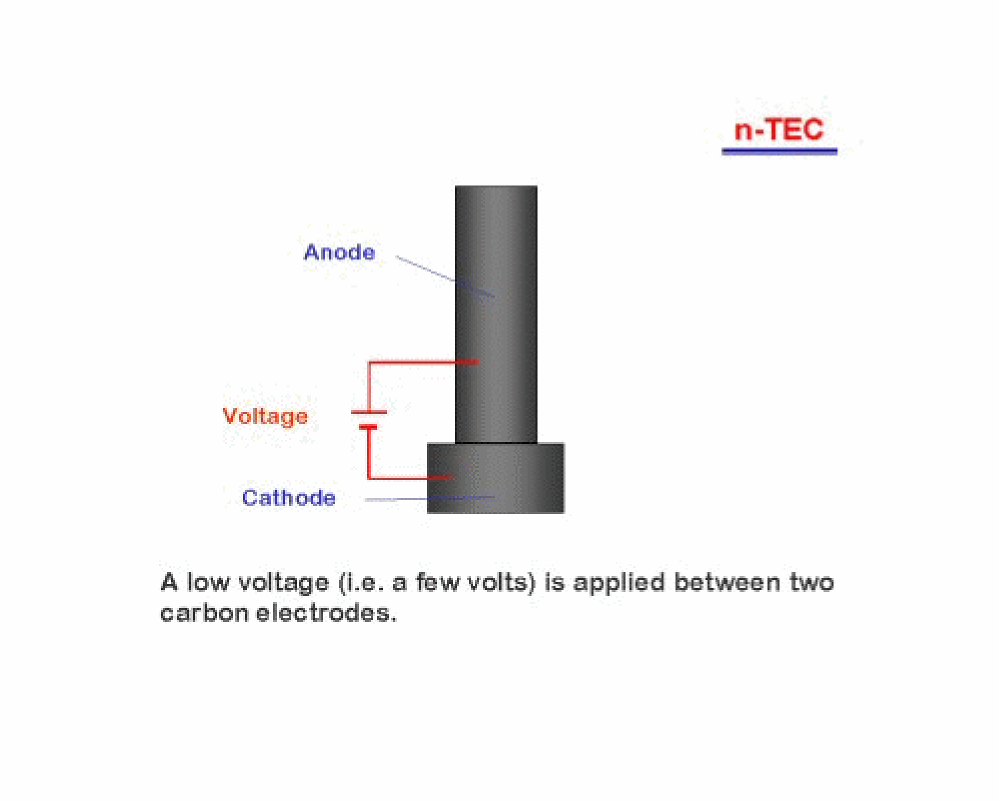




http://www.complexphysics.org/Projects/Nanocarbon.html

n-Tec

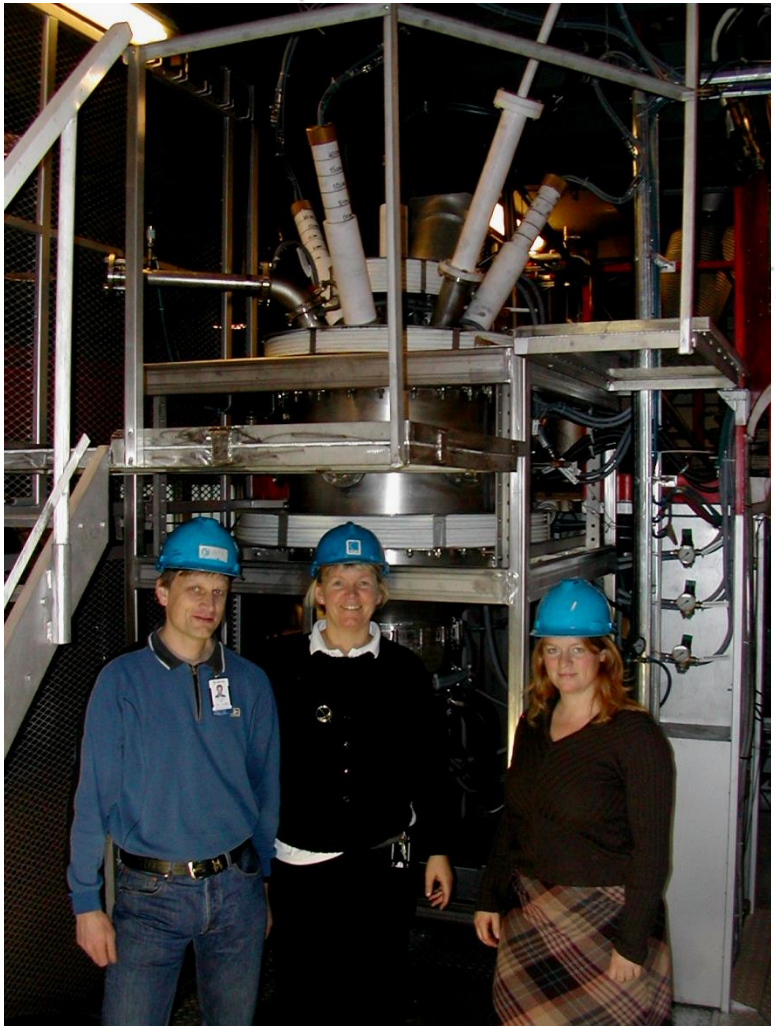
- Part of ScaTec
- Produces carbon nanotubes and nanocones



http://www.n-tec.no/Leftmenu/Facts/~/media/migration%20folder/upload/ntec/nanotubes/animation.gif.ashx

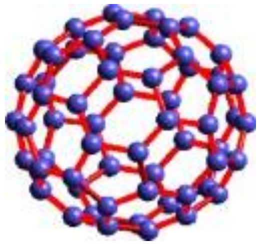
SINTEF

- Developed and patented a plasma process for production of carbon nanotubes from methane.
- Due to the high production temperature the process produces straight carbon nanotubes with few structural defects.
- Development of high temperature plasma reactor at SINTEF (patented)



http://www.sintef.no/Materialer-og-kjemi/Metallurgi/Materialer/Karbon-nanoror-CNT/

Applications of carbon nanostructures



- Fullerenes are used in for example Zelens day cream – works as antioxidant (reduces wrinkles).

- Carbon nanotubes in tennis rackets
  - Used to strengthen the most brittle parts between the handle and the net.
  - Increased stiffness reduces the energy absorbed by the racket.
- Carbon nanofibers are also used in other types of sports equipment such as hockey sticks – makes them stronger and lighter.
- Used to strengthen epoxy

Applications of carbon nanotubes

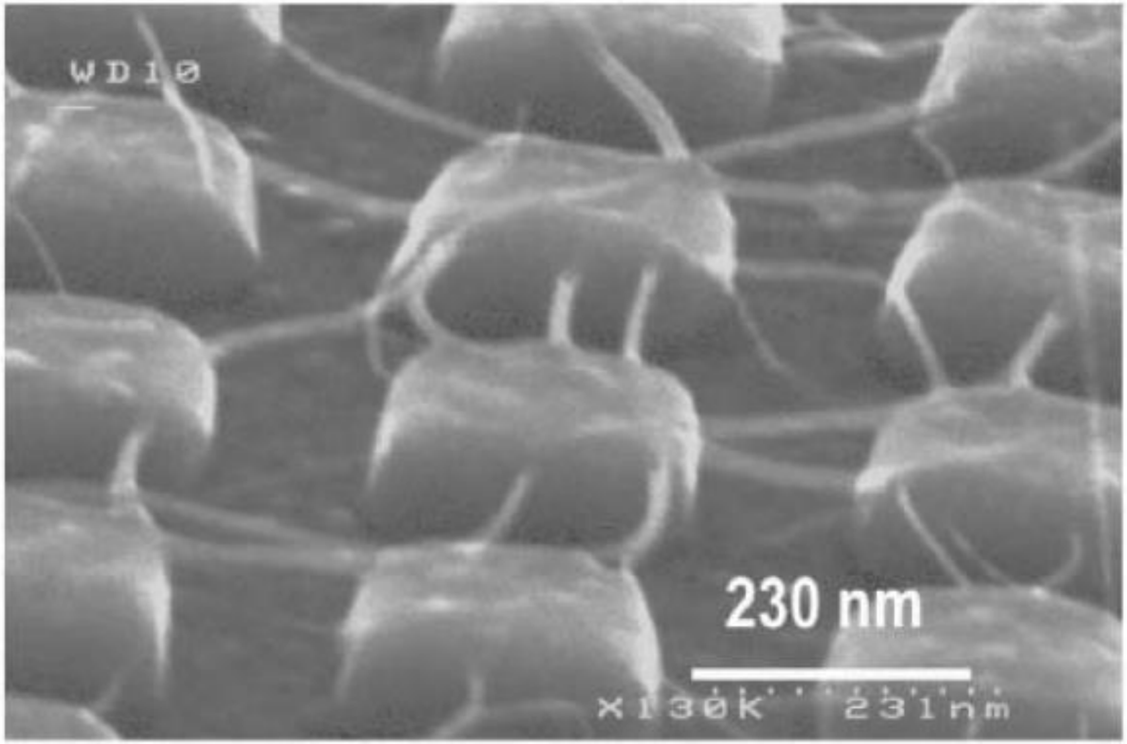
- NTs as a component of a composite material whose functionalities are thereby reinforced or modified
  - Structural materials in which the nanotube serves as a mechanical strengthener
  - Electrically conducting materials
  - Thermal materials
  - Absorbent materials, or
  - Optically limiting materials for use in the bulk or as a surface coating
- NTs as a nano object
  - Electronics
  - Probes
  - Sensors

Electronics

- Nanotubes may be considered as a model for conducting wires or functional components

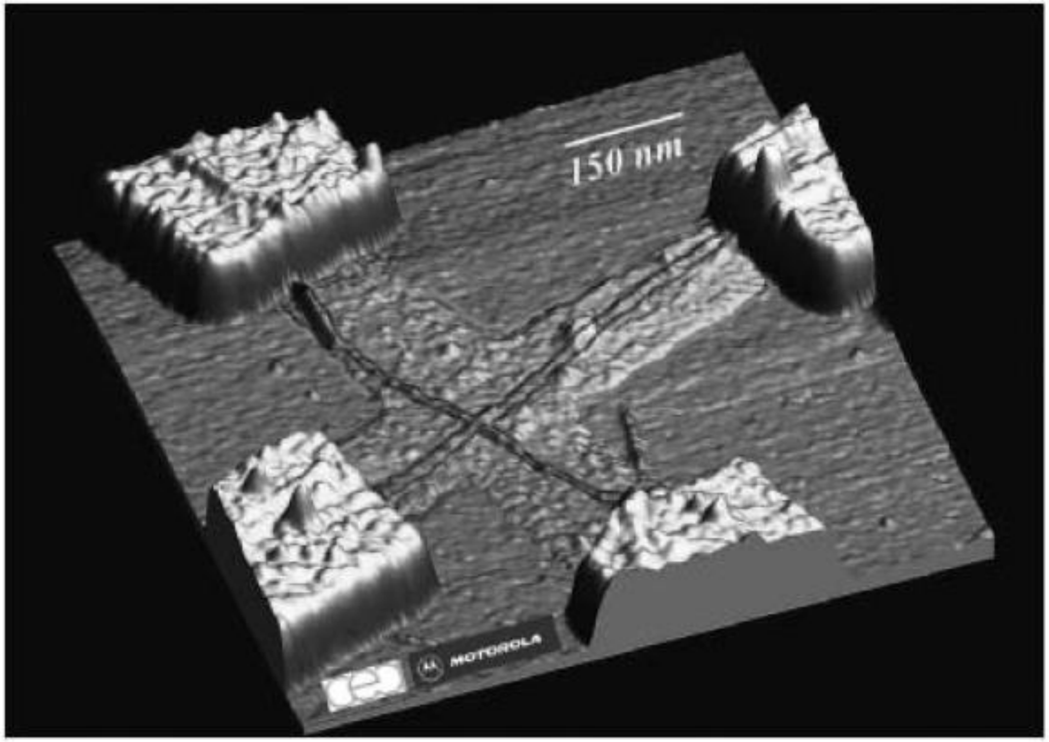
- Replacing copper interconnects in today's integrated circuits with carbon nanotubes?
  - We still don't understand the physical behaviour of these devices
  - Must establish the role played by the contacts between nanotubes and circuit elements
  - Must be able to control the helicity of the tubes during synthesis
  - Must be able to integrate nanotubes into devices and circuits (develop two- and three-dimensional architectures involving these entities)

- Integration of nanotubes
  - Synthesize nanotubes locally by CVD, and grow them on Si dots in a circuit.



Scanning electron microscope image of suspended nanotubes synthesised by hot filament CVD on Si dots coated with Co particles.

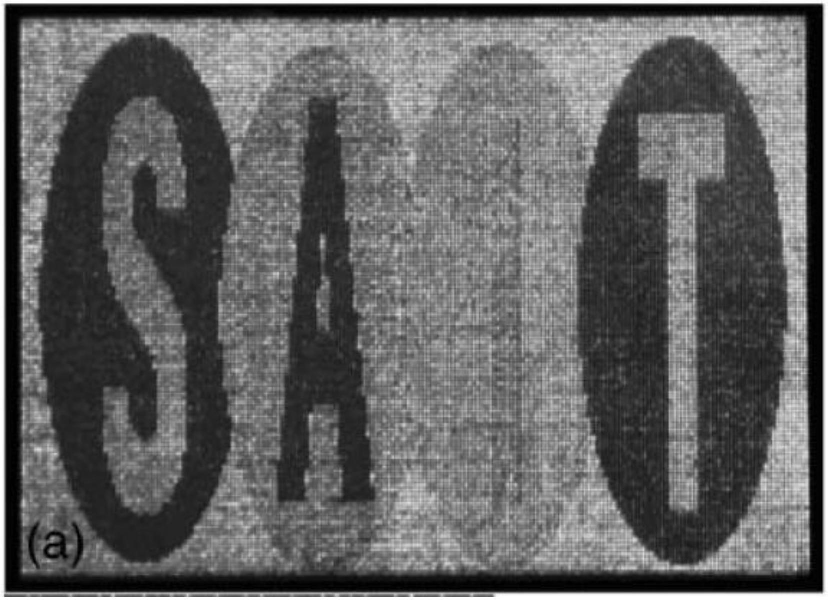
- Implementing nanotube self-assembly techniques driven by chemical recognition



AFM image of crossed nanotubes. The nanotubes are self-assembled on tracks which serve to localize the deposit. The tracks (150 nm × 0.7 nm), *grey* in the figure, consist of monomolecular layers of silane molecules terminated by amine functions, formed through a mask made by electron beam lithography.

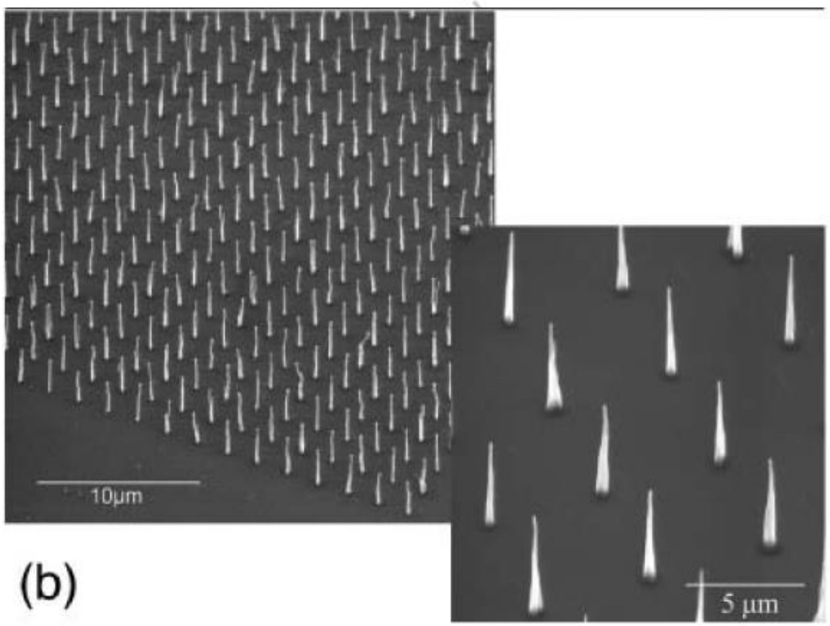
Electron emission

- Tunnel effect in an electric field
- Extremely effective emitters:
  - Large aspect ratios
  - Low emission threshold bias
  - Can supply large and stable currents
- Several industrialized applications for cold cathode devices and flat television screens



Photograph of a prototype flat screen using multiwalled nanotubes, with 576 × 242 pixels, made by Samsung.

- Using CVD synthesis techniques it is possible to synthesize custom-built oriented arrays of tubes starting from an array of catalyst dots obtained by lithographic methods.

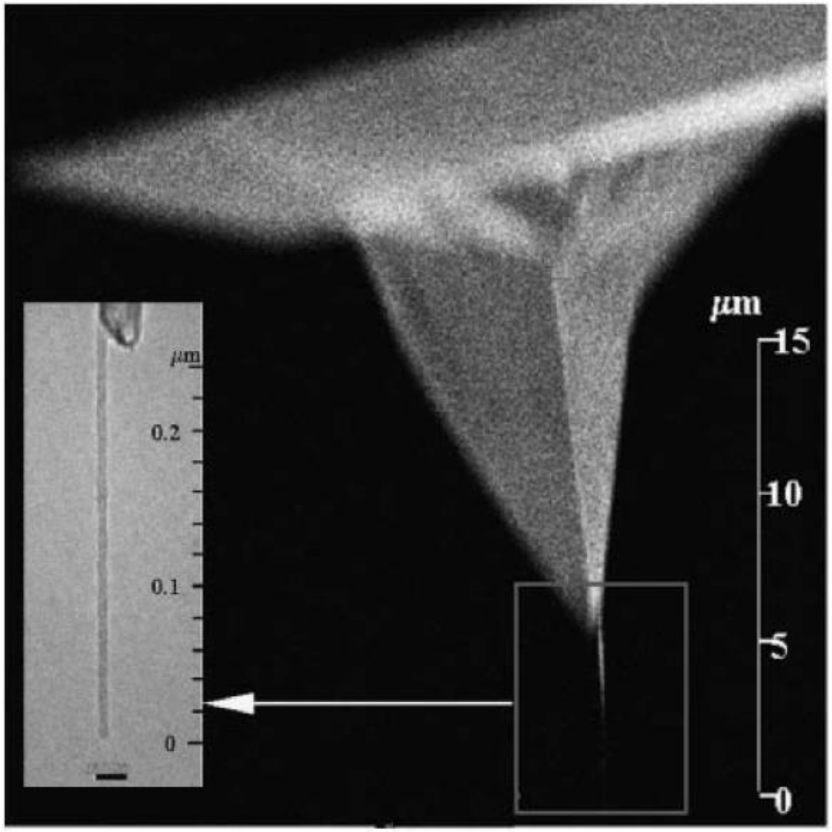


Scanning electron microscope images of an array of oriented multiwalled nanotubes, synthesised by a plasma CVD technique using as a starting point an array of Ni catalyst dots.

Probes for nanoscale systems

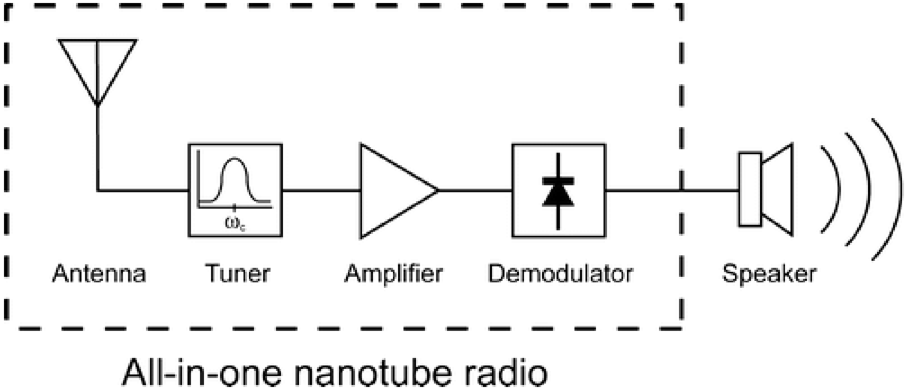
- CNTs has very small radius of curvature → can overcome the problem of convolution of the tip with the imaged object (Ch. 1)

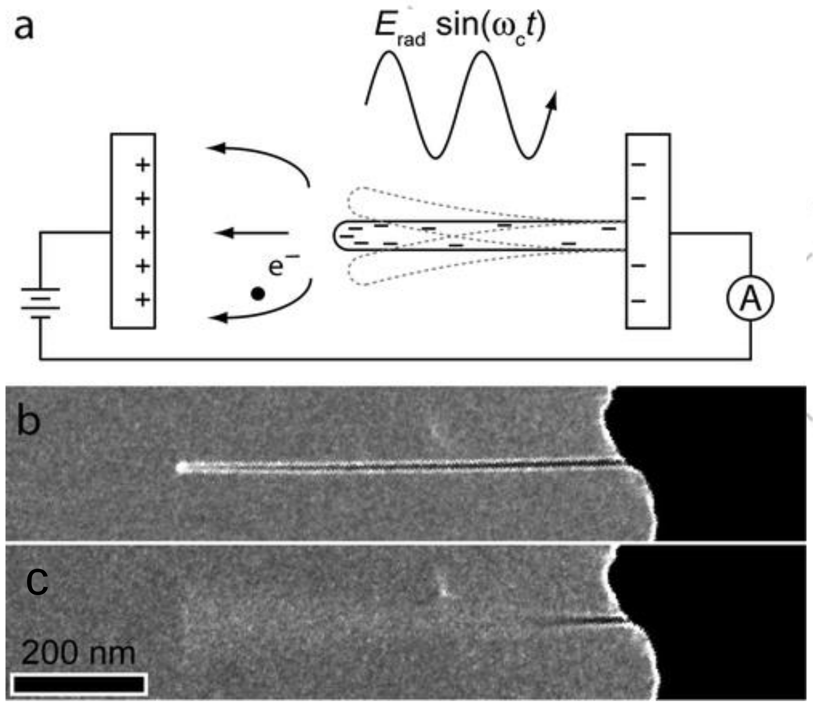
- Such tips are obtained by fixing a multiwalled nanotube at the end of a standard tip



Tip of an atomic force microscope with a multiwalled nanotube stuck onto it. *Insert*: TEM image of the nanotube.

Nanotube radio

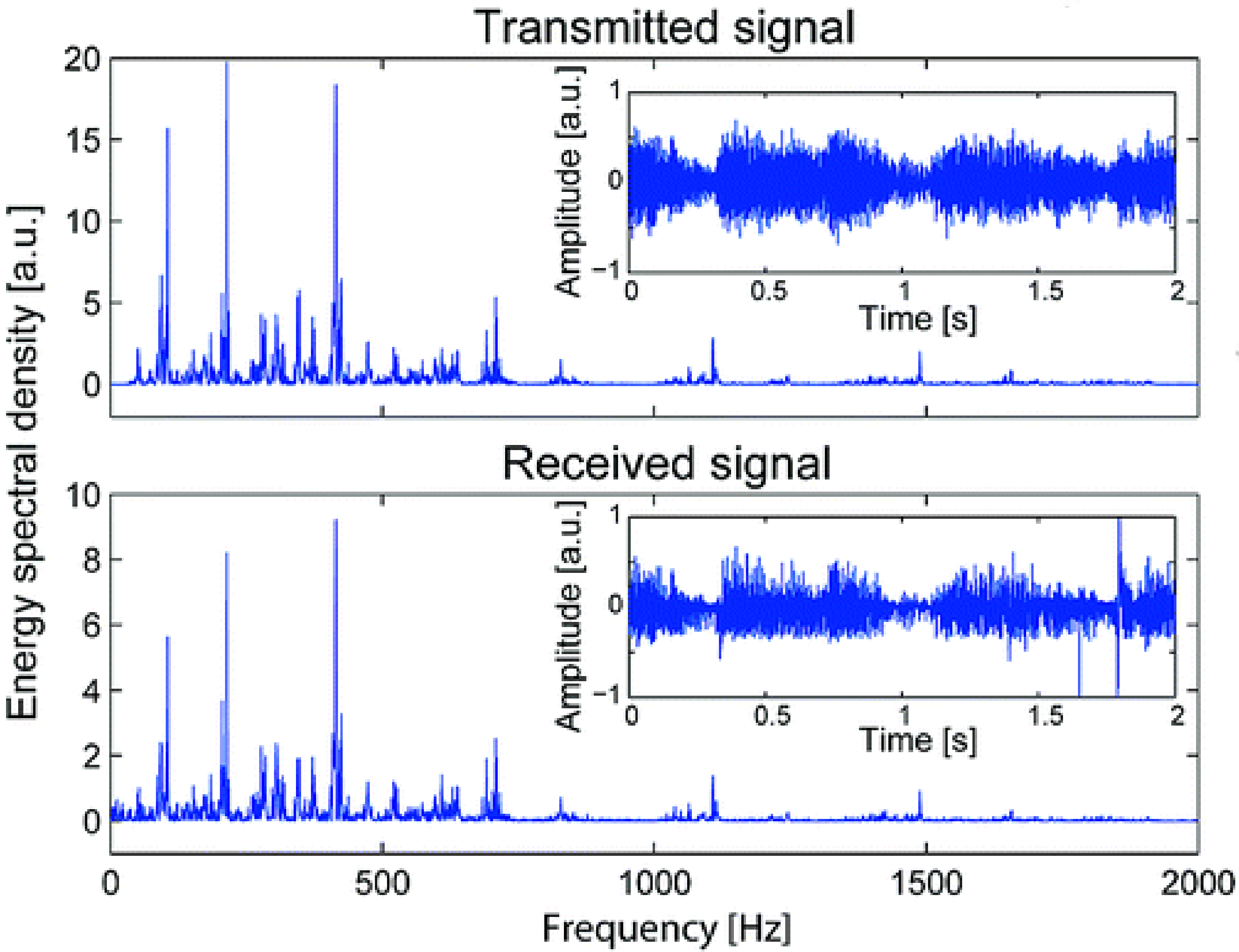




Block diagram for a traditional radio. All four essential components of a radio, antenna, tuner, amplifier, and demodulator may be implemented with a single carbon nanotube.

Transmission electron micrographs of a nanotube radio off (b) and on (c) resonance during a radio transmission.

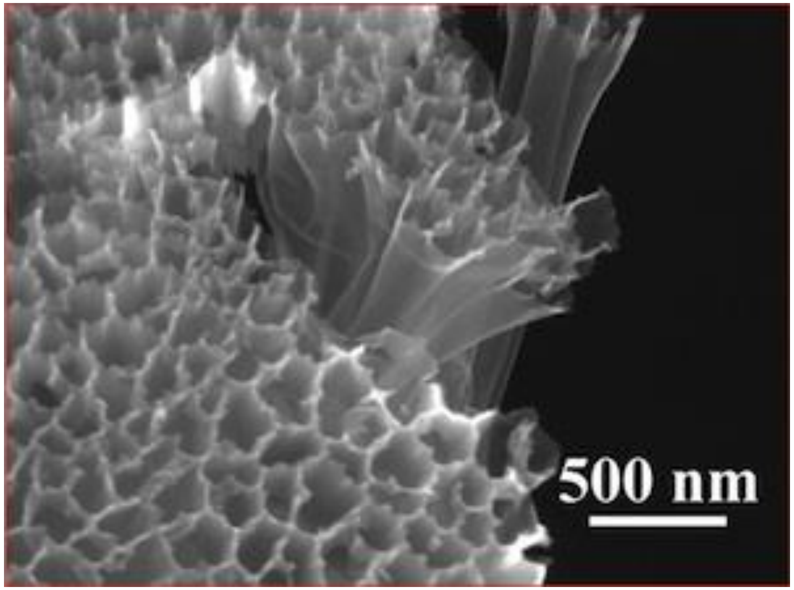
Jensen *et al.*, *Nano Lett.*, 2007, 7 (11), pp 3508–3511

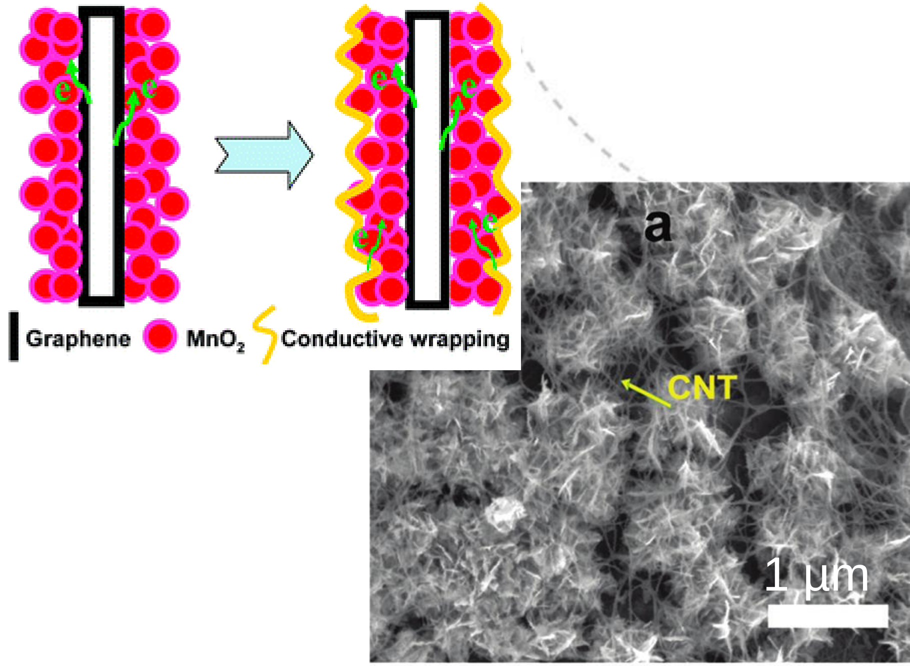


Transmitted and received audio waveforms (inset) and frequency spectra of 2 seconds of the song “Good Vibrations” by the Beach Boys. The nanotube radio faithfully reproduces the audio signal, and indeed the song is easily recognizable by ear.

Jensen *et al.*, *Nano Lett.*, 2007, 7 (11), pp 3508–3511

CNT and carbon nanofibers





- Carbon nanofiber coated with sulfur
- Application area: Li-ion batteries

Guangyuan Zheng et al, Nano Letters, Sept. 2011

- MnO_2 coated with SWCNT
- Application area: Supercapacitors

Guihua Yu et al, Nano Letters, Sept. 2011

Learning objectives NS-8

- Understand how carbon fullerenes and nanotubes are related to graphite
  - Graphene sheets
  - Isolated pentagon rule
- Structure and properties of various types of nanotubes
  - High mechanical strength, good electrical and thermal conductivities
  - Armchair, zigzag, chiral
  - Single-walled, multi-walled
- Synthesis of carbon nanostructures
- Be able to mention some applications
  - Electronics
  - Probes
  - Composite materials