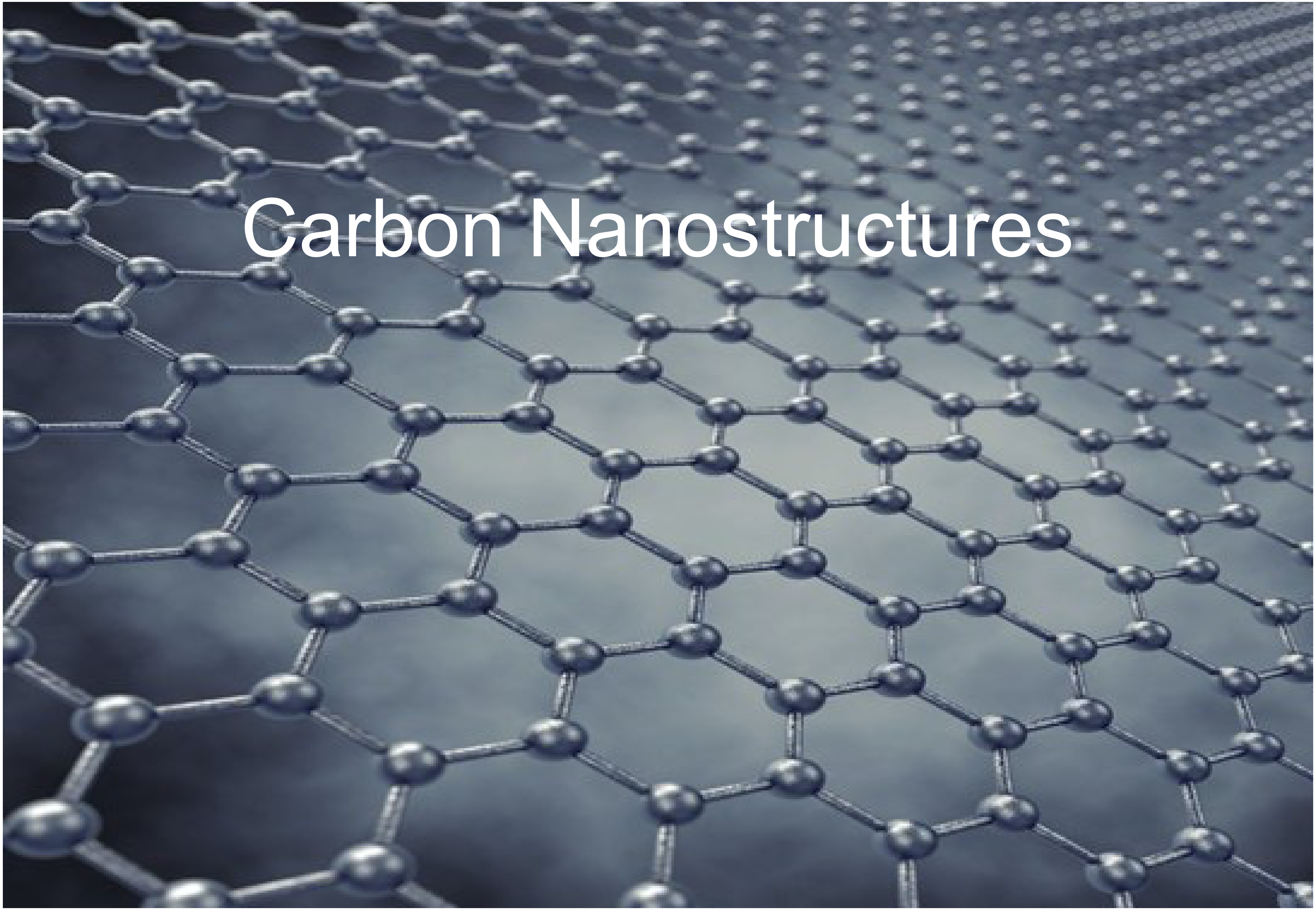
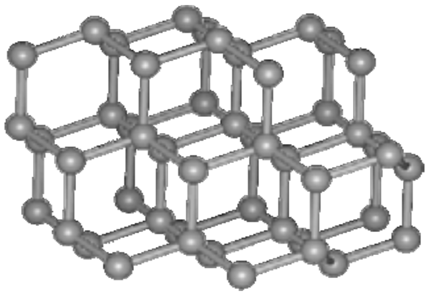
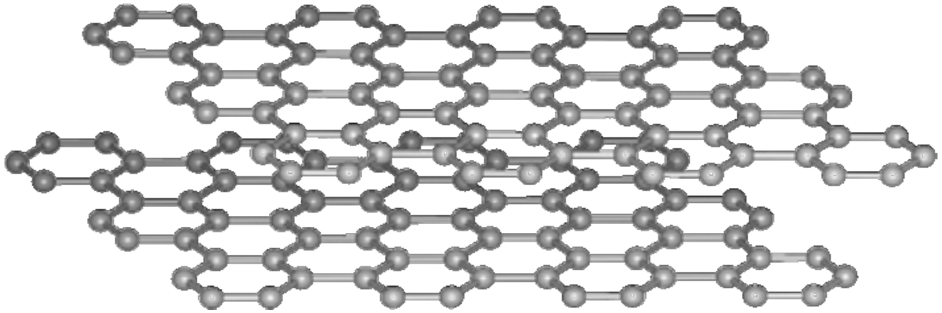
Carbon Nanostructures



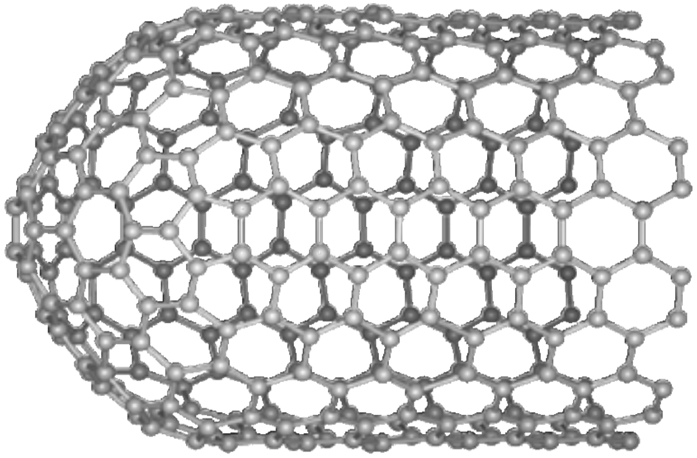
Carbon Structures



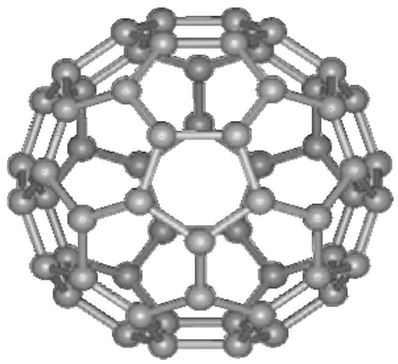
diamond (3D)



planar graphite (2D)

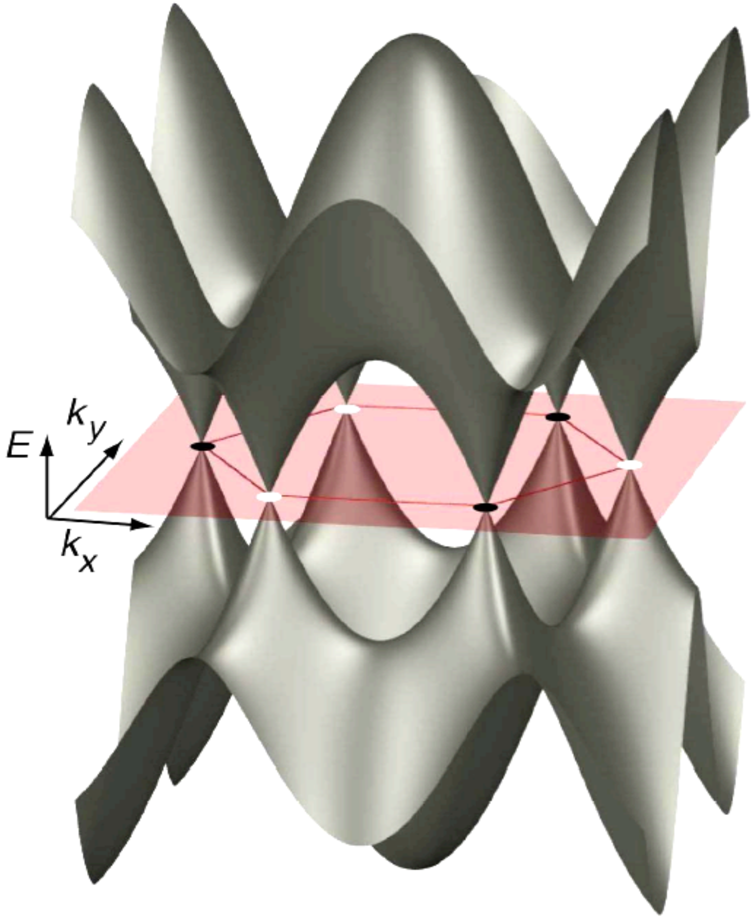


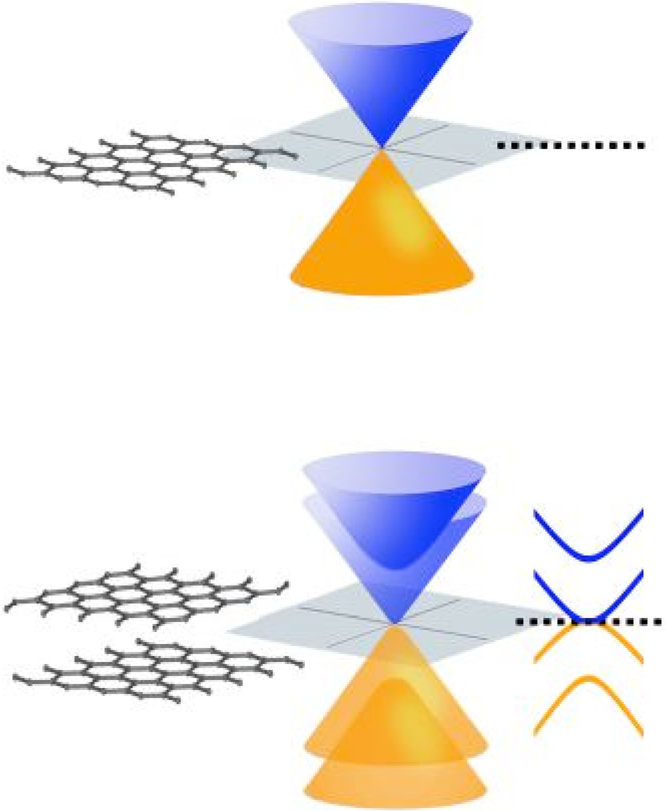
single-walled carbon nanotube (1D)

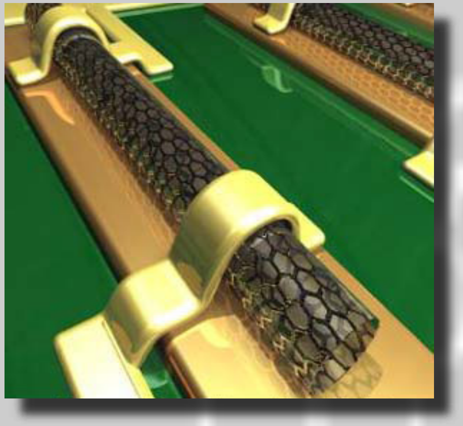


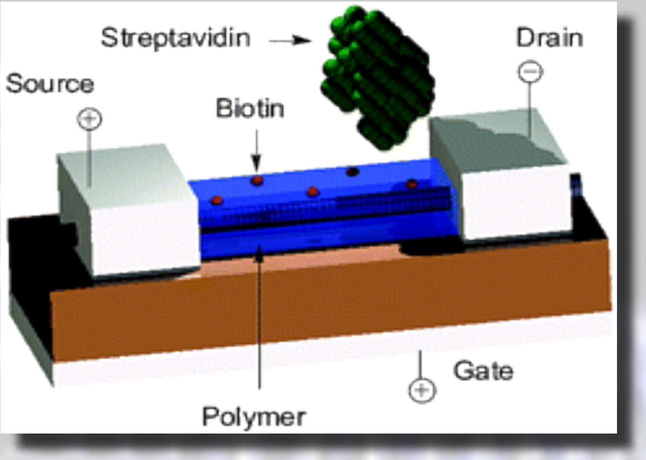
C_{60} (0D)

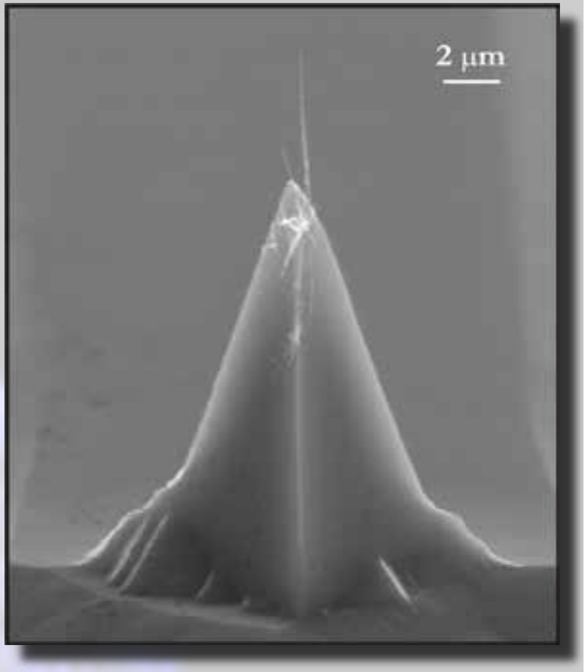
Graphene: monolayer has no band gap!

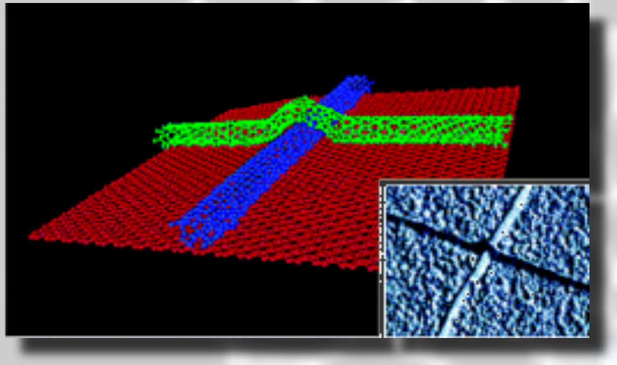




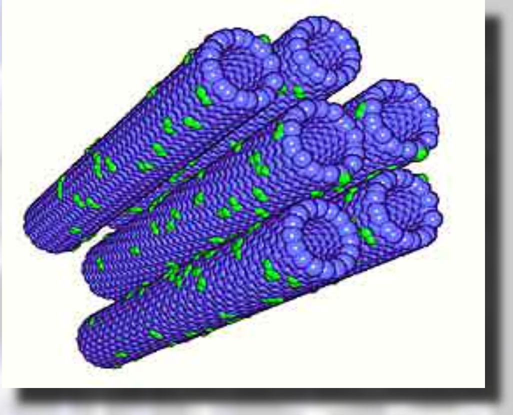


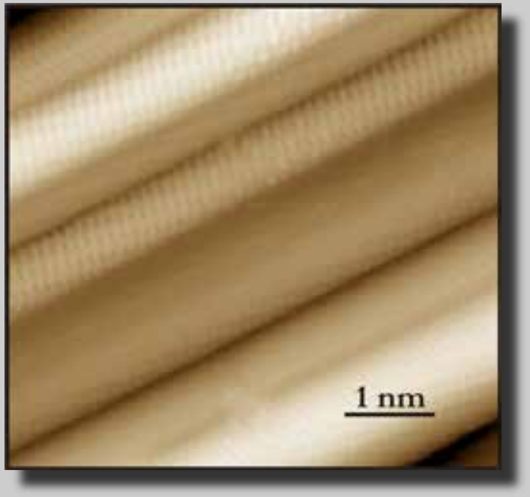


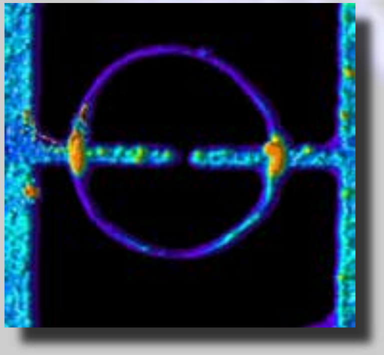


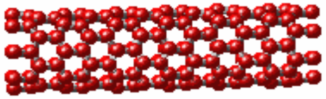


Carbon Nanotubes





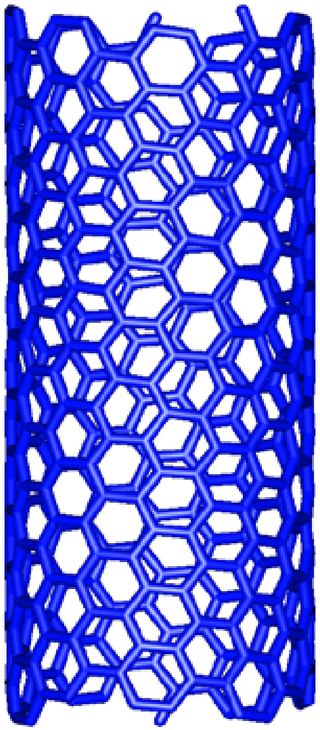




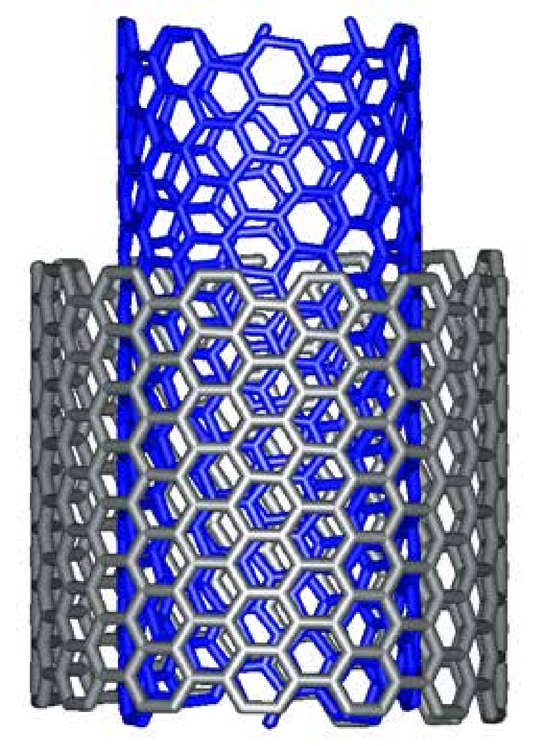
Carbon Nanotubes

- introduction
- synthesis
- electronic structure
- electrical transport
- applications

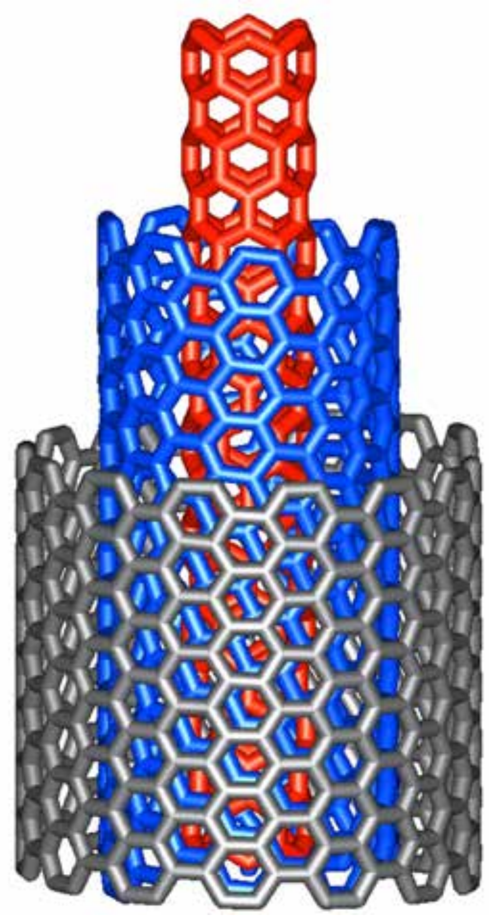
CNTs – Types



single wall nanotubes
(SWCNTs)



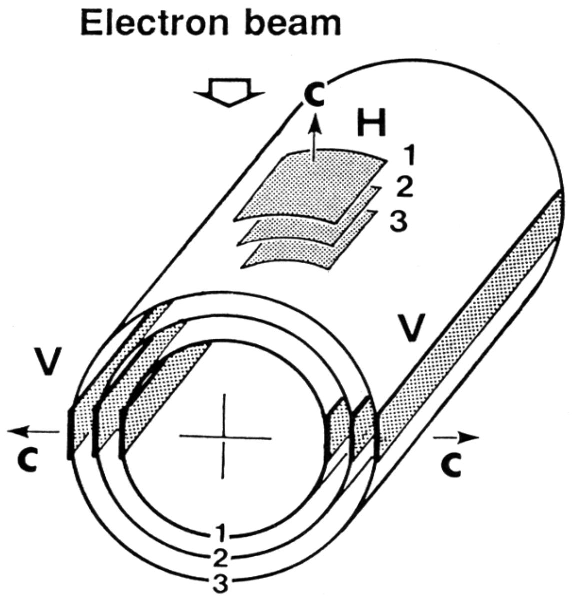
double wall nanotubes
(DWCNTs)

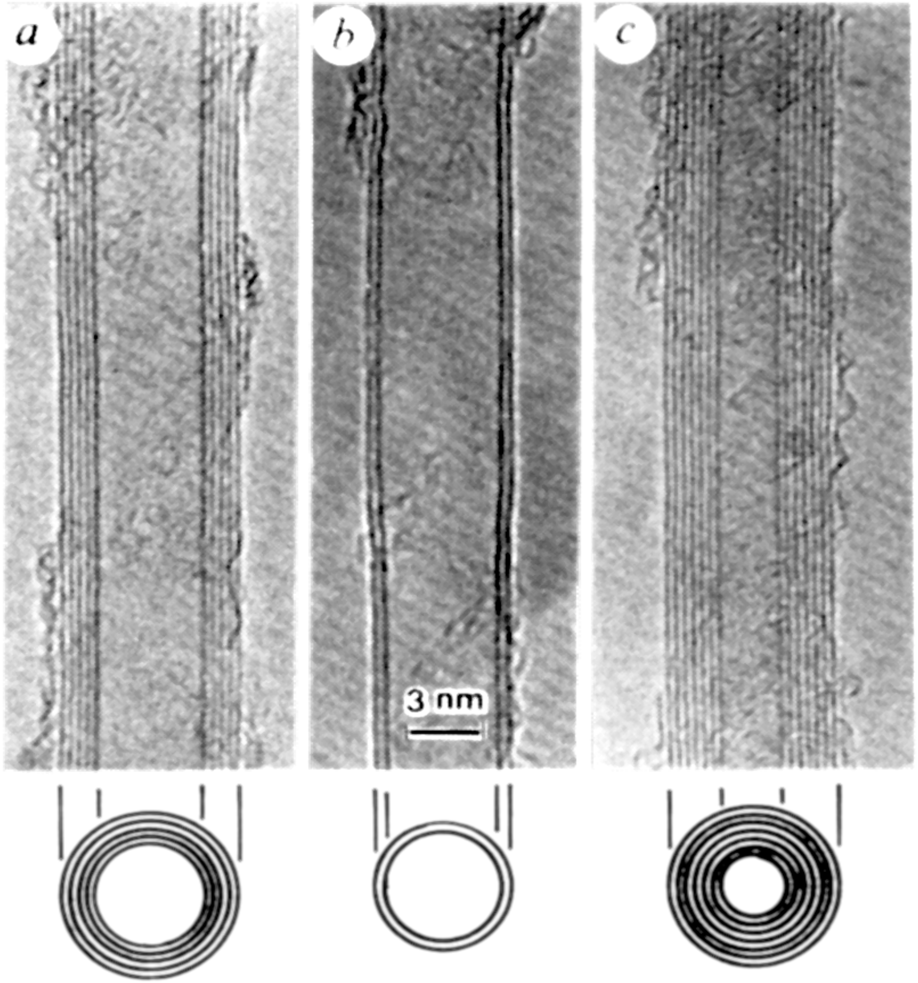


multi wall nanotubes
(MWCNTs)

CNTs – Discovery

- ❑ In 1991 by Iijima (NEC, Japan)





- ❑ Multiwall nanotubes (MWNTs)

Transmission Electron
Mmicroscope (TEM) images

Iijima, Nature 354, 56, (1991)

CNTs – Physical Structure

rollup vector

$\mathbf{C_h} = n\mathbf{a_1} + m\mathbf{a_2}$

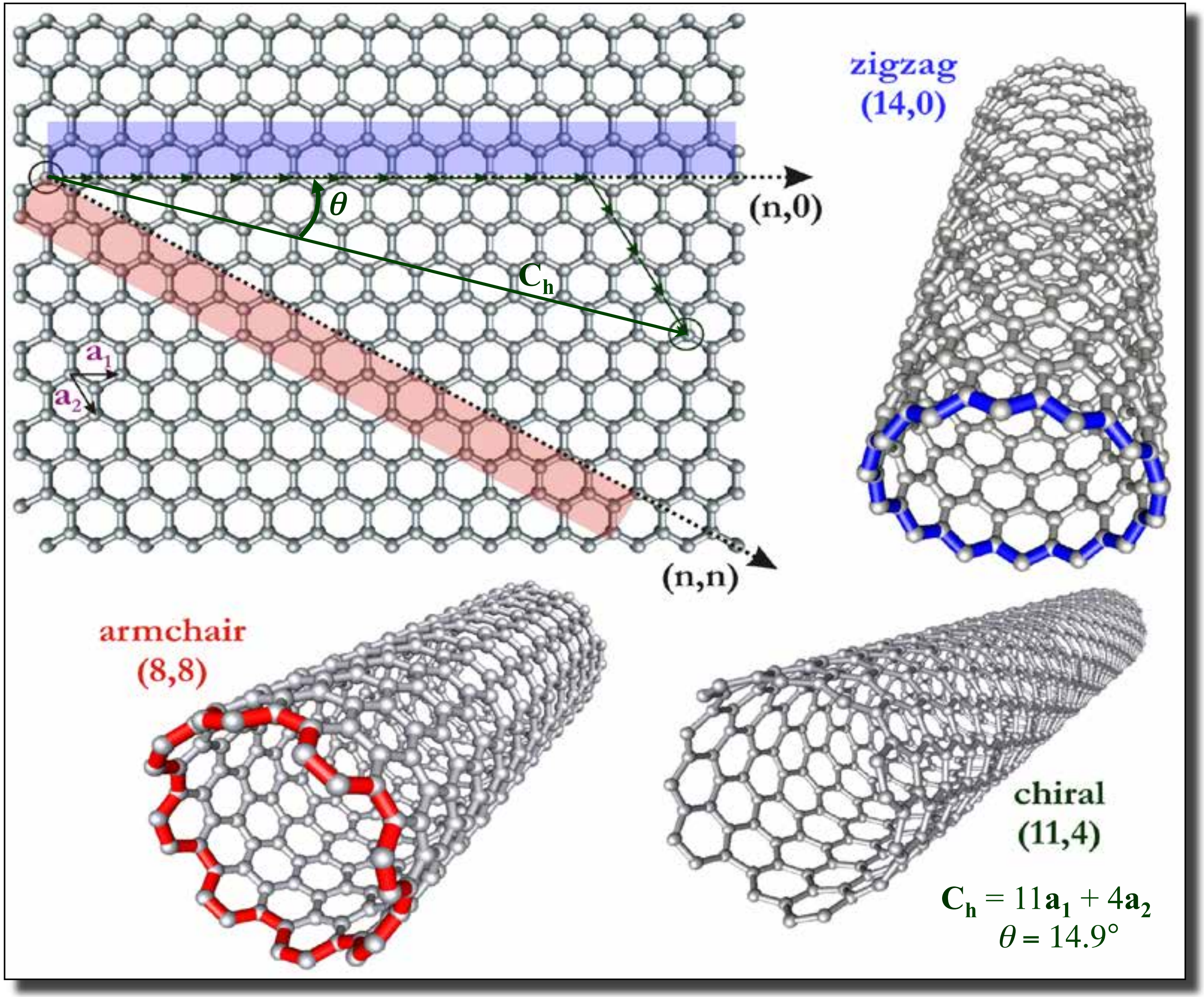
↓

SWNTs specified as

(n, m)

chiral angle

$\theta = \tan^{-1}[\sqrt{3}m/(2m+n)]$



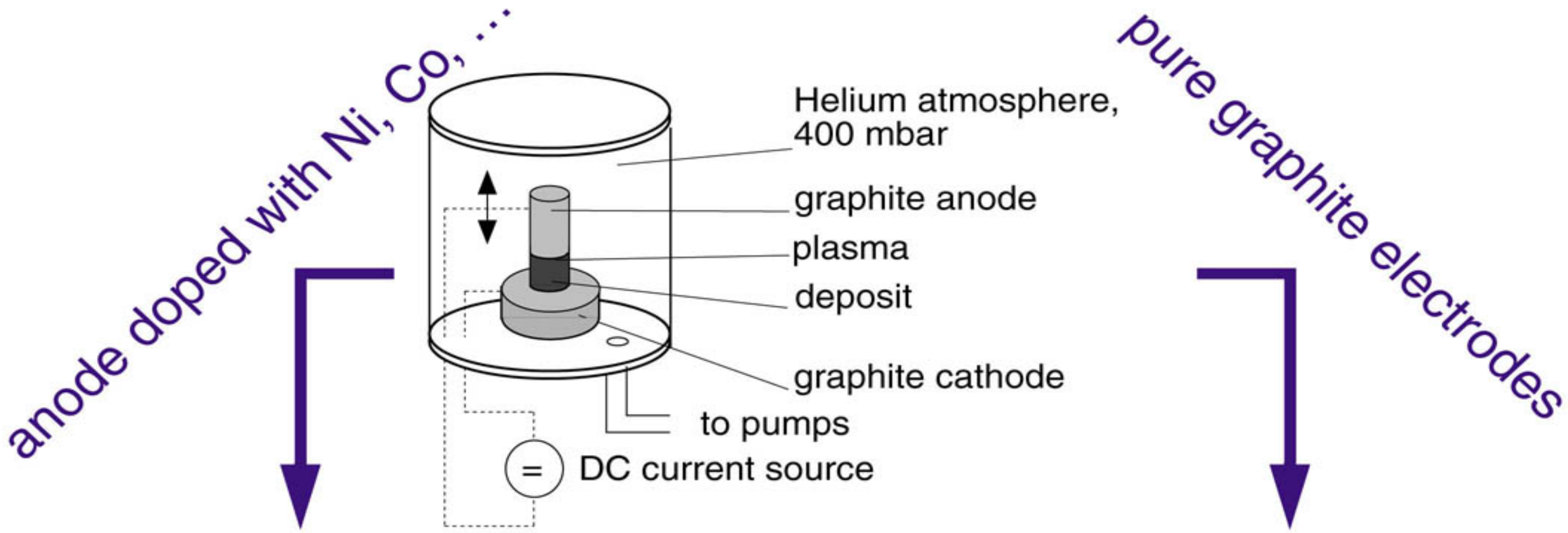
Outstanding properties of CNTs

Attribute	Comment
Thermal conductivity: 10^4 $Wm^{-1}K^{-1}$	**> that of diamond**
Young´s modulus: 1TPa	**stiffer than any other known material**
Tensile strength: 150GPa	**~600 times the strength/ weight of steel**
Supports current density of $10^9 A/cm^2$	**~100 times greater than for copper wires**
Carrier mobility: 10^4-$10^5 cm^2/Vs$ (at RT)	**> that of GaAs**
Thermally stable up to 2800°C (vacuum)	

Carbon Nanotubes

- introduction
- synthesis
- electronic structure
- electrical transport
- applications

Arc discharge process



anode doped with Ni, Co, …

Helium atmosphere, 400 mbar

graphite anode

plasma

deposit

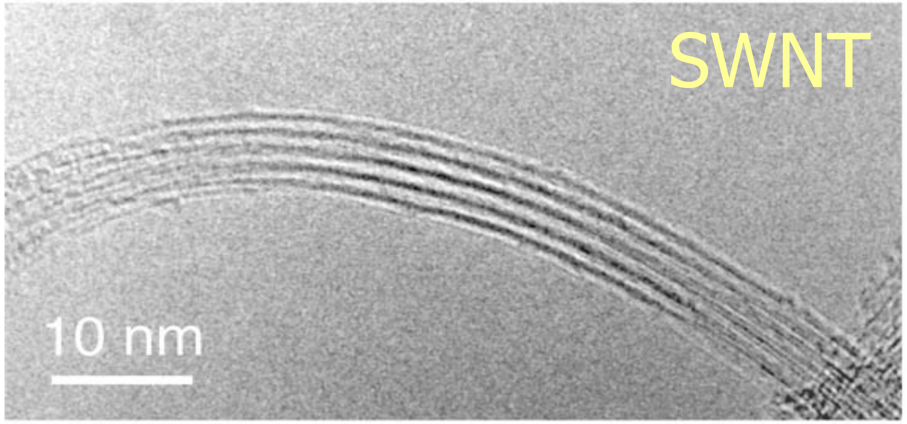
graphite cathode

to pumps

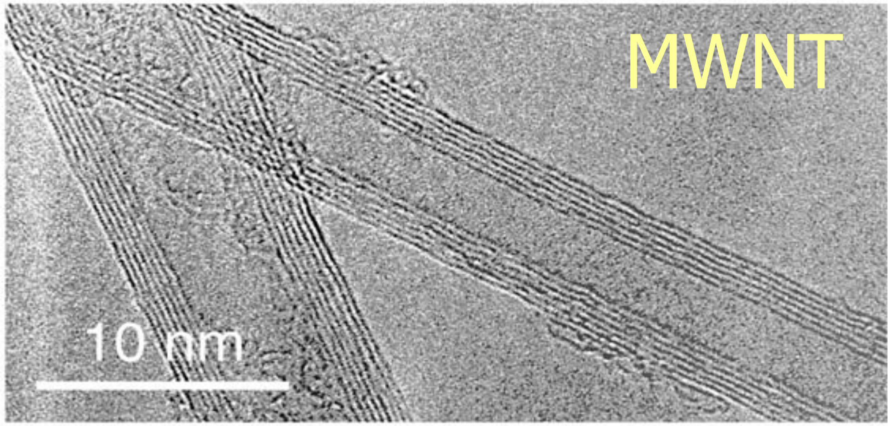
= DC current source

pure graphite electrodes

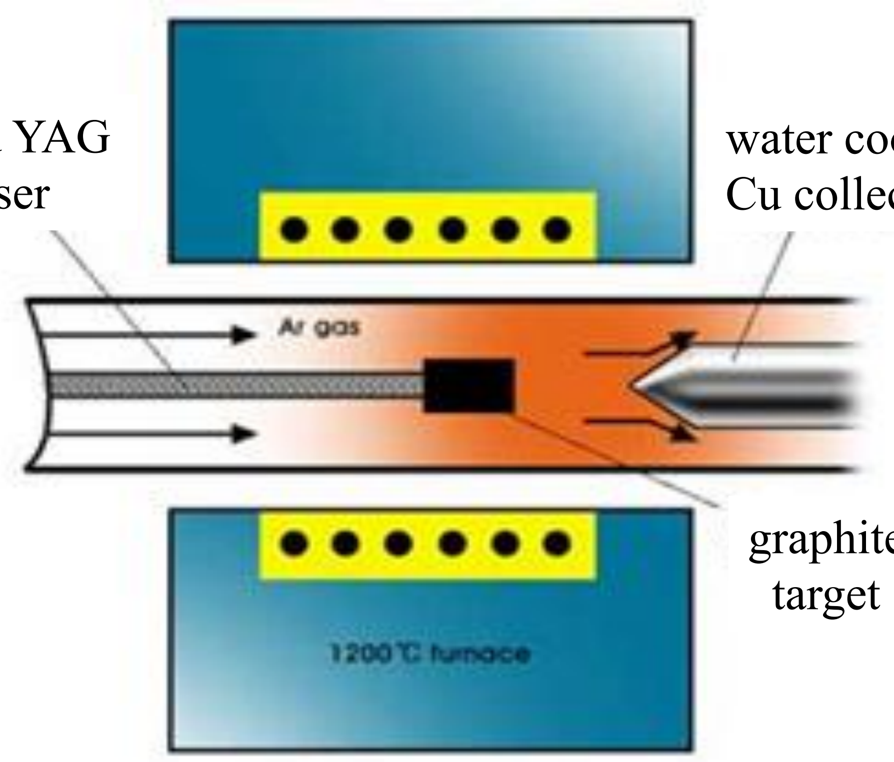
Single wall nanotubes



Multiwall nanotubes



Laser ablation method



Nd YAG
Laser

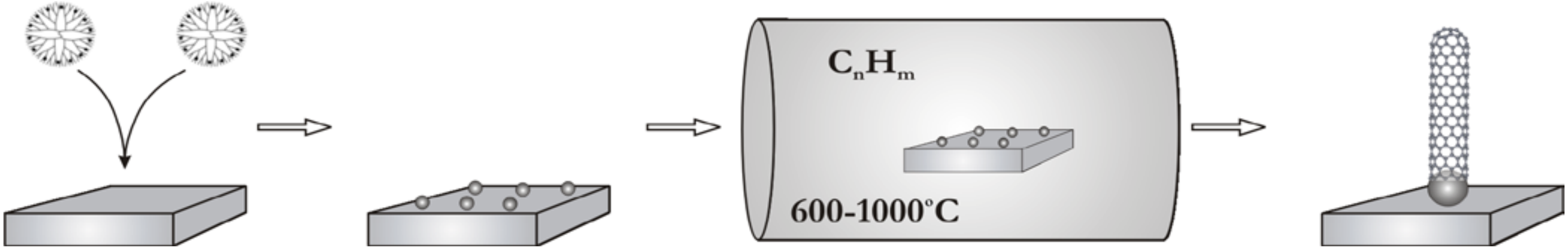
water cooled
Cu collector

graphite
target

- ~1.4nm average tube diameter
- NTs are formed as bundles

Ajayan et al., Carbon Nanotubes 80, 391, (2001)

Chemical Vapor Deposition (CVD)



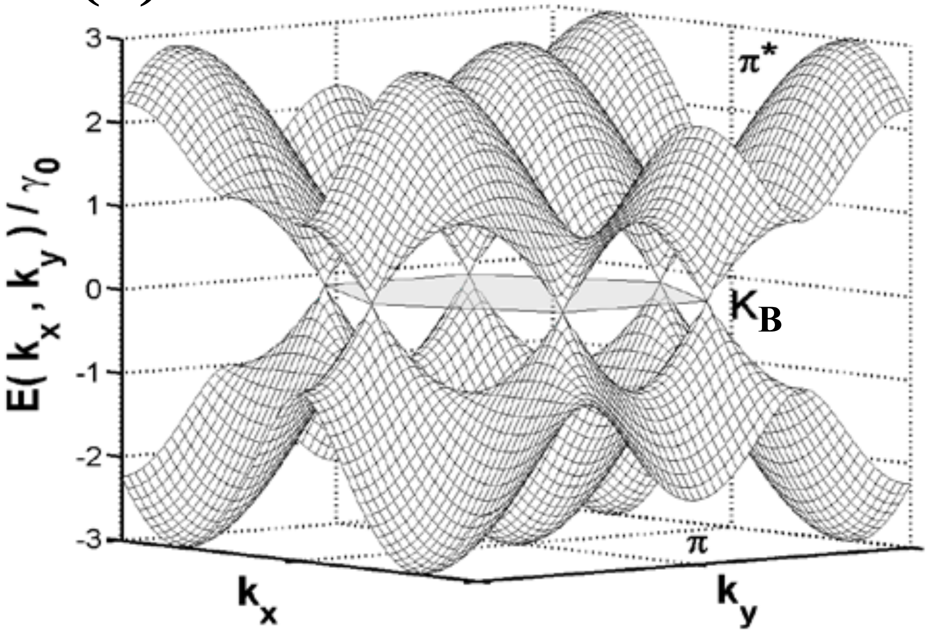
- relatively low temperature (600°-1000°C)
- Fe, Ni, or Co nanoparticles as catalyst
- mostly isolated SWCNTs are obtained
- SWCNT diameter control through particle size

Carbon Nanotubes

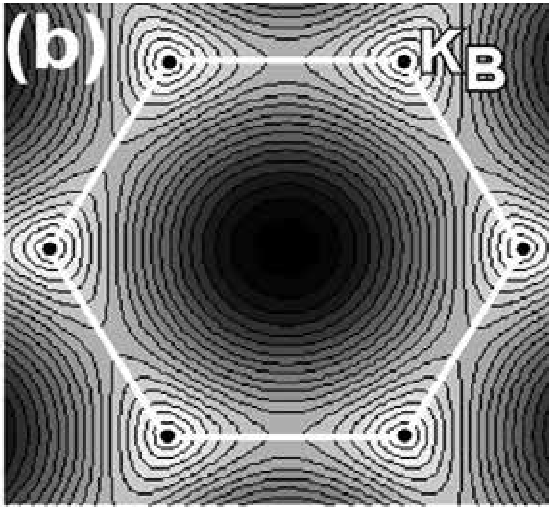
- introduction
- synthesis
- electronic structure
- electrical transport
- applications

Electronic structure of CNTs derived from graphene

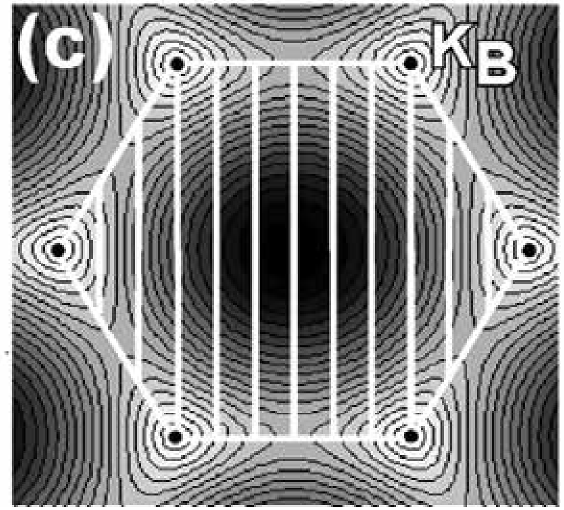
(a) energy bands of graphene sheet



energy contour (2D) plot



allowed 1D wavevectors
for **(9,0)** tube

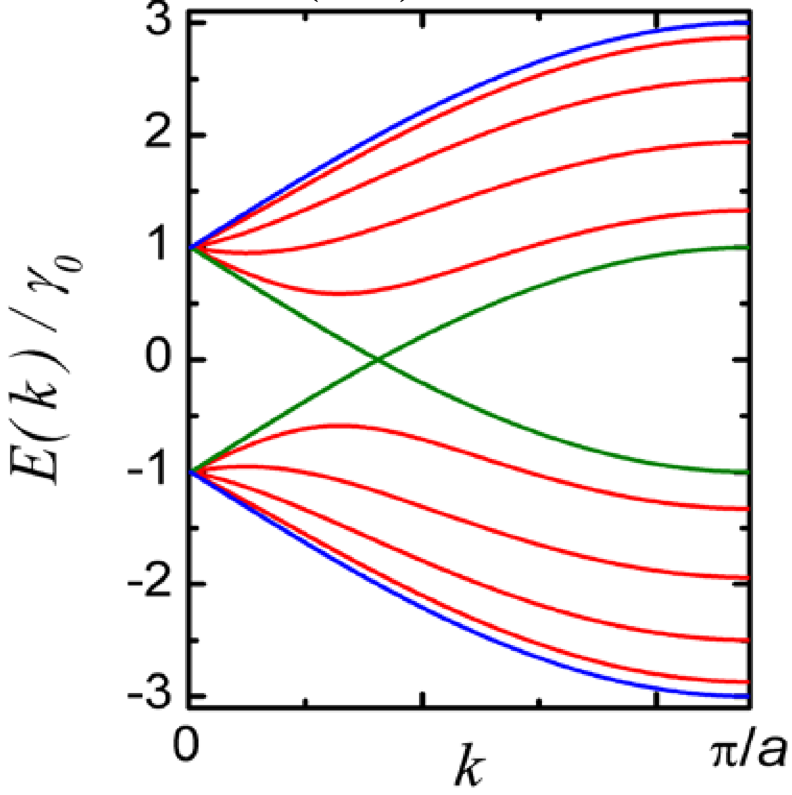


periodic boundary conditions:

$$\underline{\mathbf{C}}_h \cdot \underline{\mathbf{k}} = 2\pi q$$

CNTs – Electronic Structure

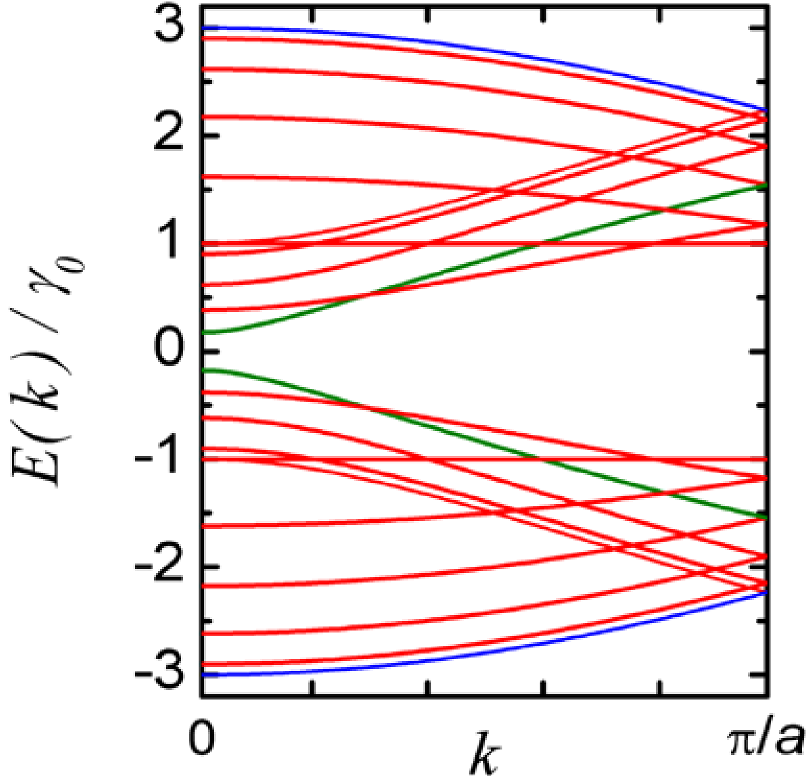
Bad structure of a
(5,5) SWCNT



armchair (n=m)

metallic

Band structure of a
(10,0) SWCNT



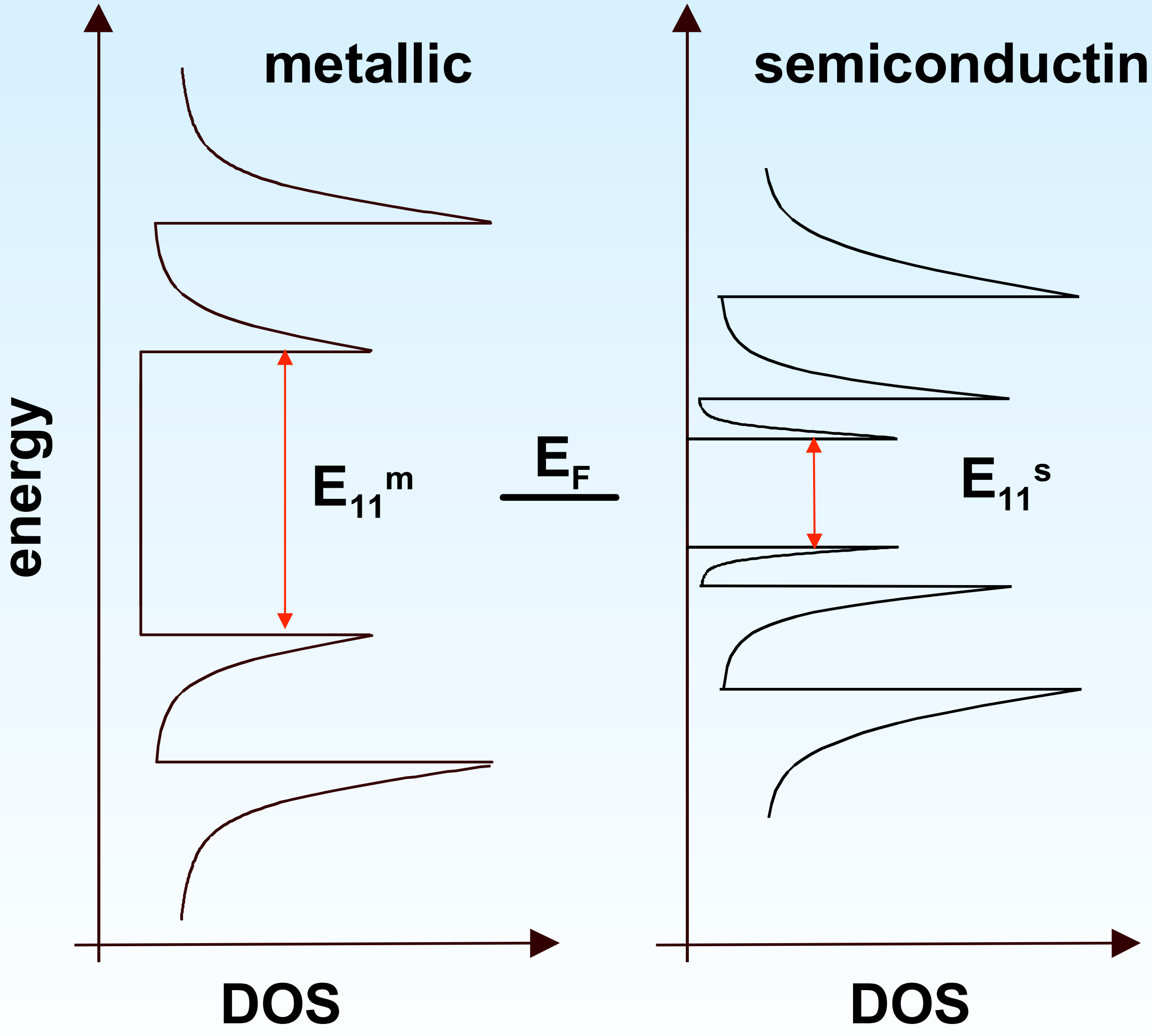
zigzag (n,0) & chiral (n,m)

metallic if (n-m)=3i

semiconducting if (n-m)≠3i

γ_0 = 2.5eV
a = 1.44 A°

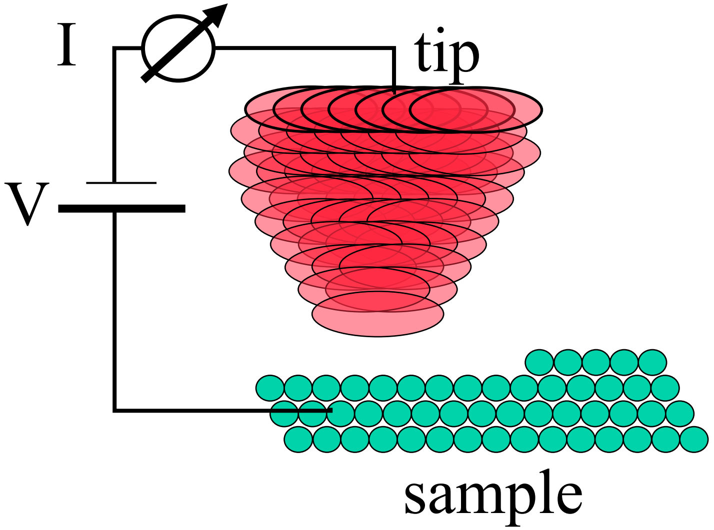
CNTs – Electronic Structure



$E_{gap} \propto 1/d$

0.4 – 1.3 eV

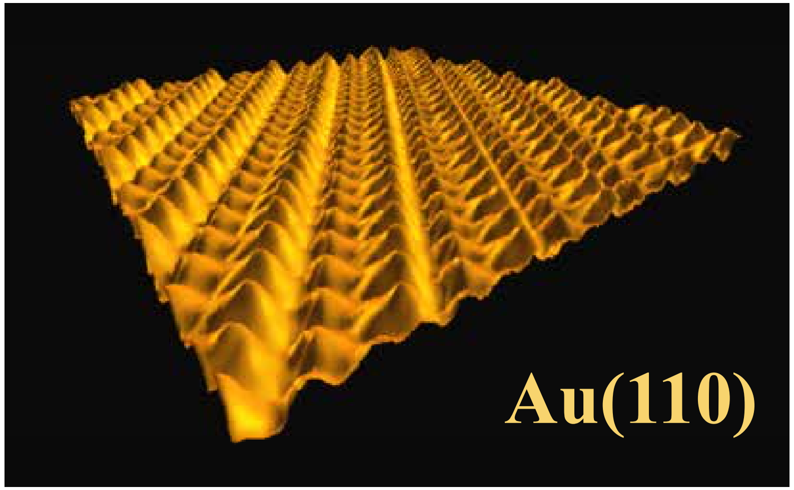
Scanning Tunneling Microscopy (STM)



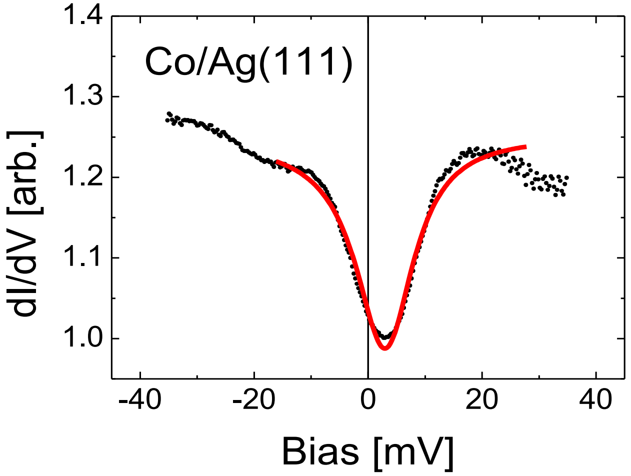
$$I(V,x,z) \propto e^{-A\cdot z}\int_{0}^{eV}\rho_s(E,x)\,dE$$

$$\frac{dI}{dV}(V,x,y) = \rho_S(eV,x,y)$$

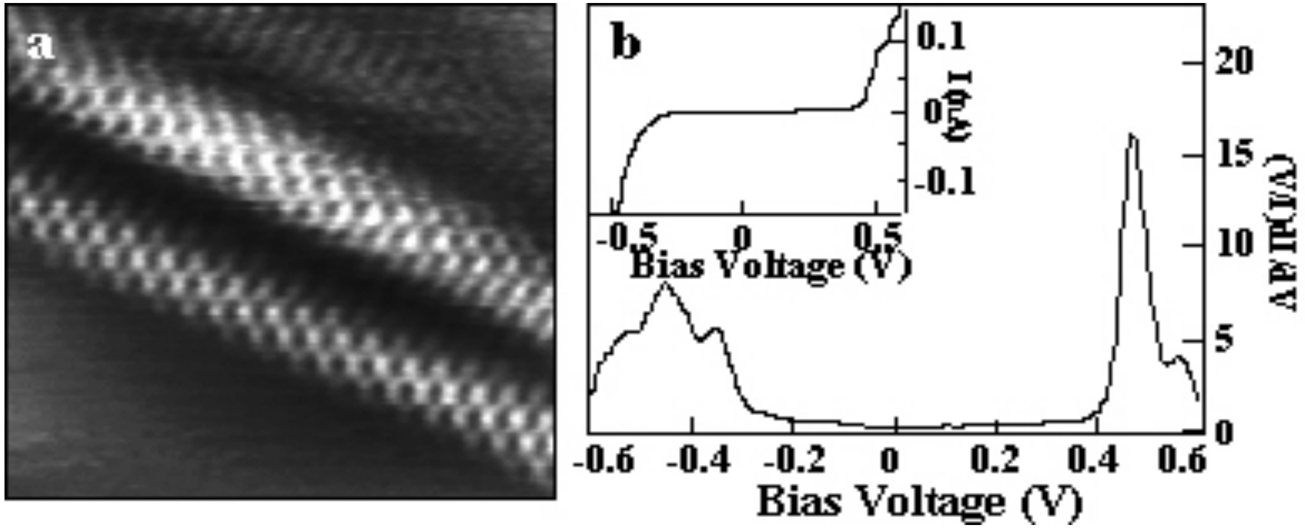
Topography „z (x, y, I=const)“



Spectroscopy „dI/dV“ (STS)



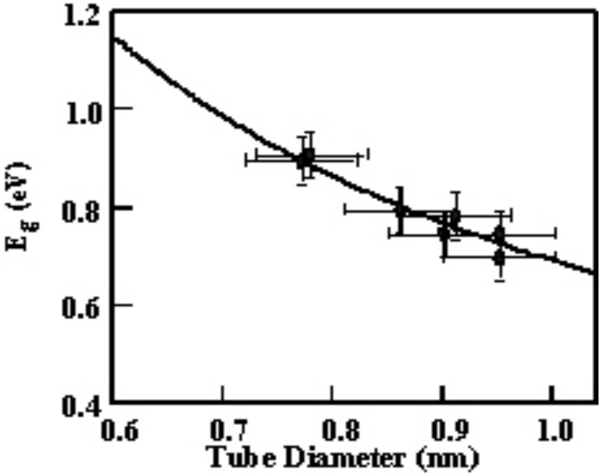
Scanning Tunneling Spectroscopy on SWCNTs



(14,-3) SWNT

⇒ **semiconducting**

Band gap as a function of tube diameter

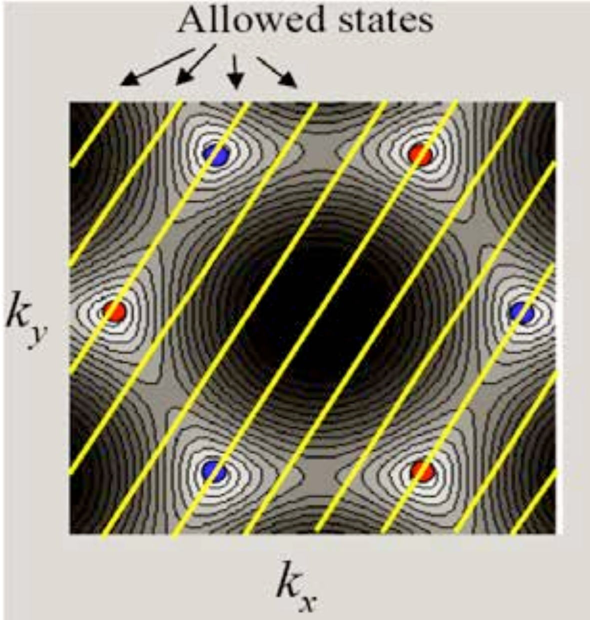


Carbon Nanotubes

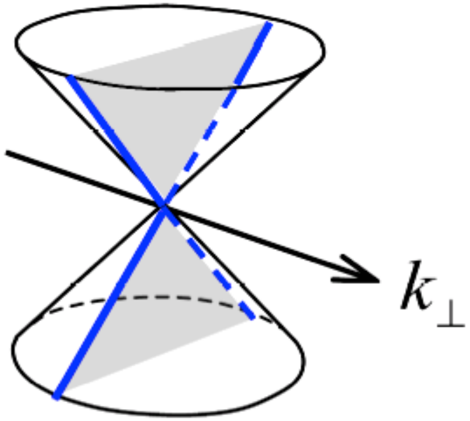
- introduction
- synthesis
- electronic structure
- electrical transport
- applications

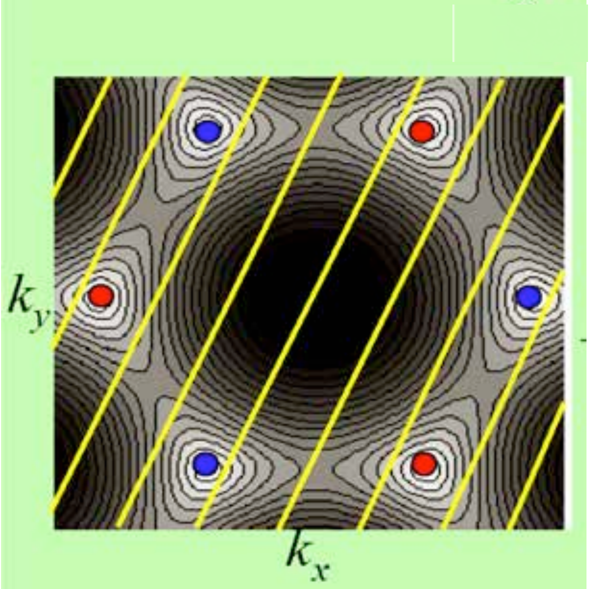
Ballistic transport in a 1D conductor

Carbon nanotubes (CNTs)

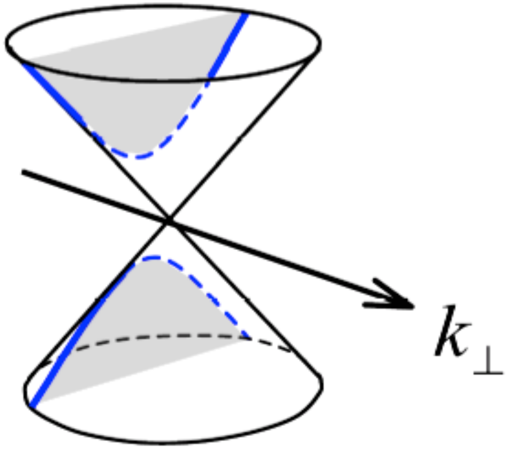


metallic tube

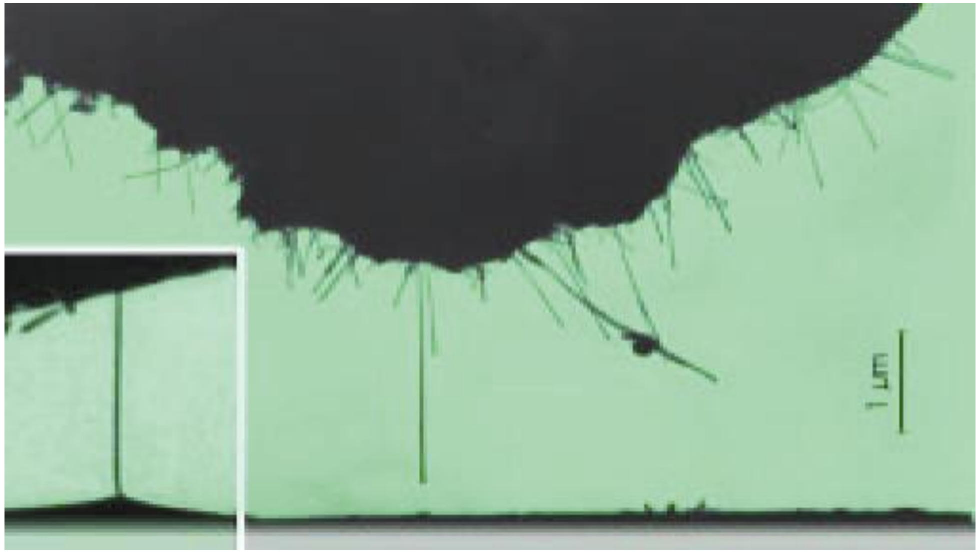


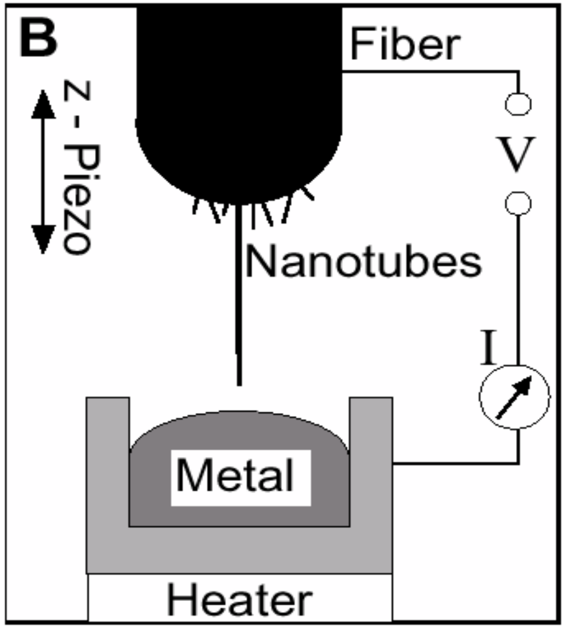


semiconducting tube



CNT – Quantum conductance



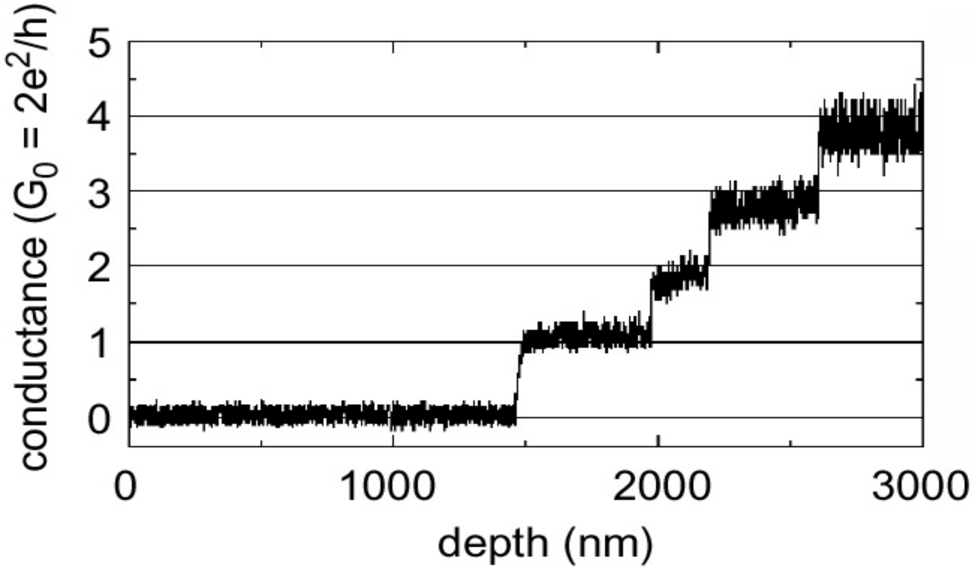


- MWCNT on a piezo-controlled tip

  → quantised conductance

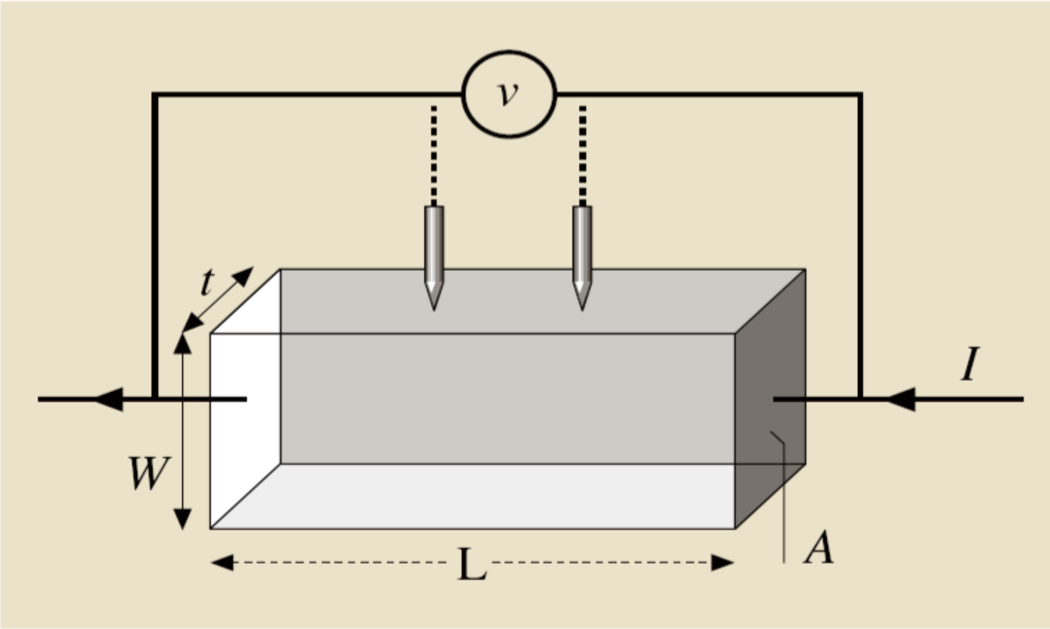
  $nG_0 = n\ (2e^2/h) = n\ ([12.9k\Omega]^{-1})$

- Ballistic electron transport
  - resistance independent of tube length
  - upto 25mA per nanotube



Frank et al., Science 280, 1744, (1998)

Resistance and resistivity



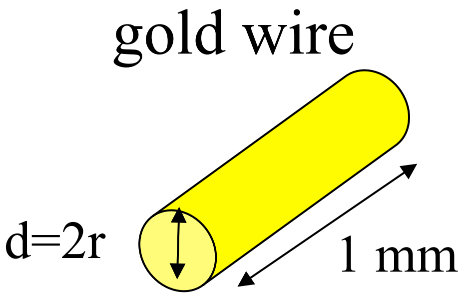
resistance $$\boxed{R = \frac{U}{I} = \frac{1}{G}}$$

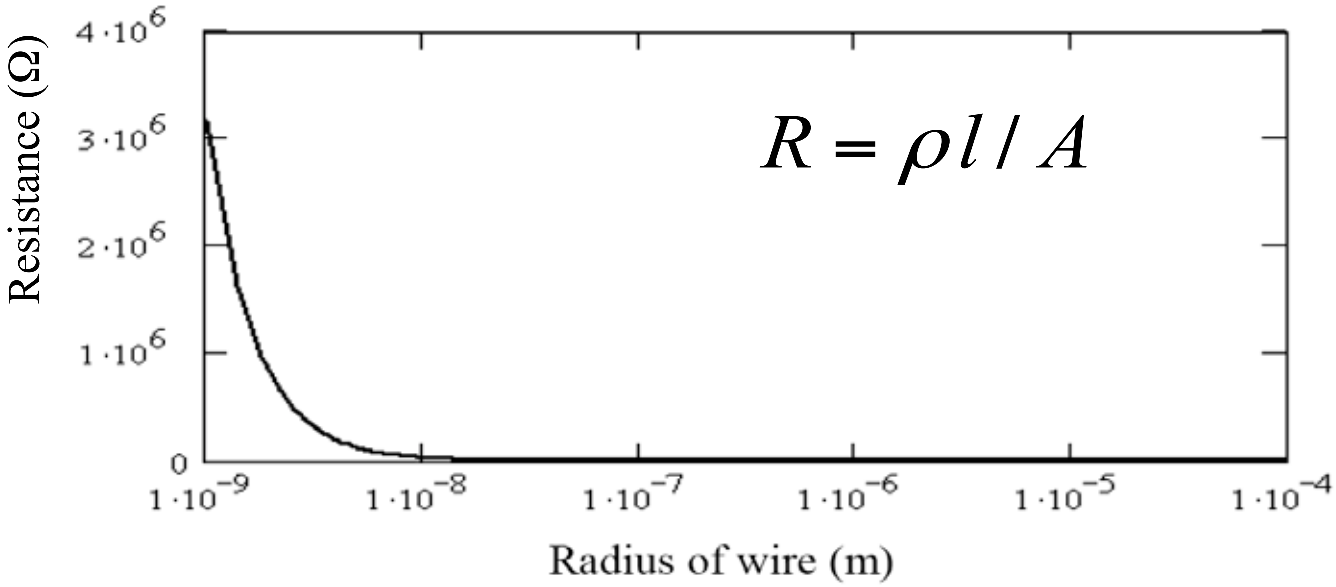
resistivity $$\boxed{\rho = \frac{1}{\sigma} = R\frac{A}{L}}$$

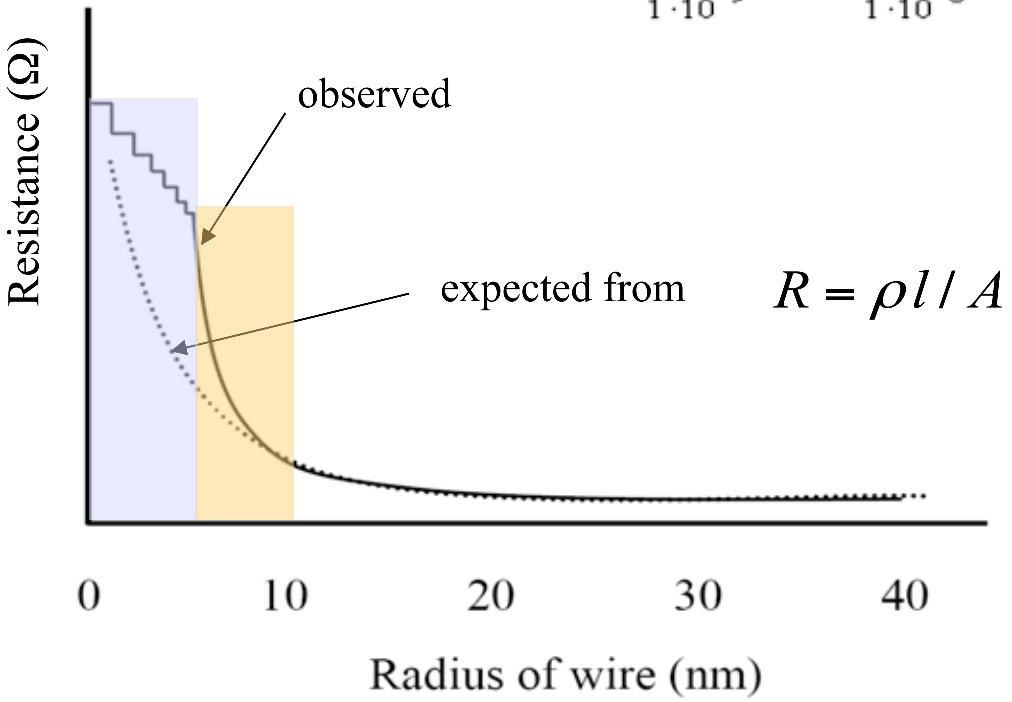
thin layers: sheet resistivity $$\rho_S = \frac{\rho}{t}$$ (t...film thickness)

$$\rho_S = \frac{R\,A}{L\,t} = \frac{R\,W t}{L\,t} = R\frac{W}{L}$$

Size effects





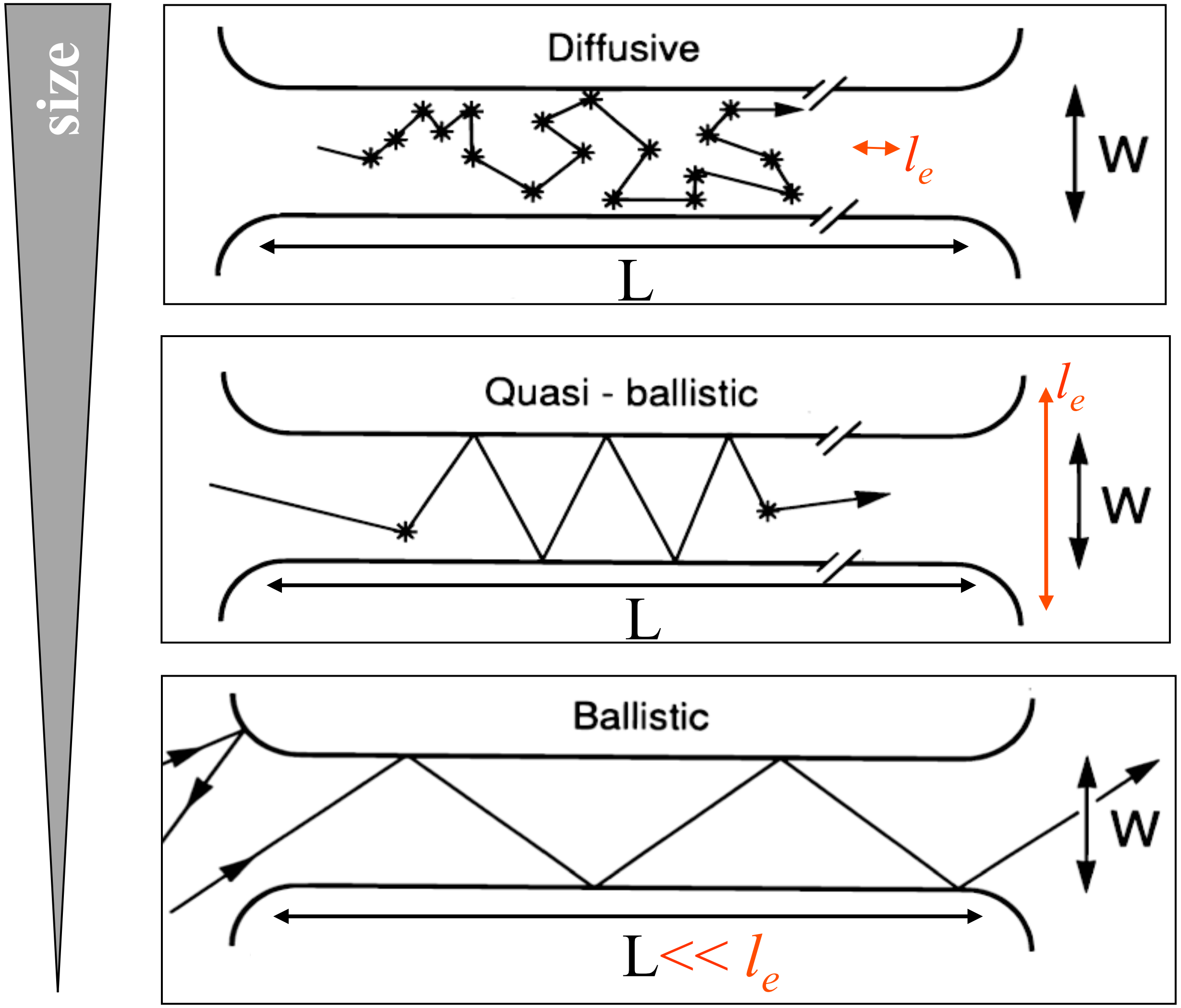


mesoscopic effects
- surface scattering

quantum effects

Electron transport regimes

l_e … mean free path (between elastic or inelastic scattering events)



$W, L > l_e$

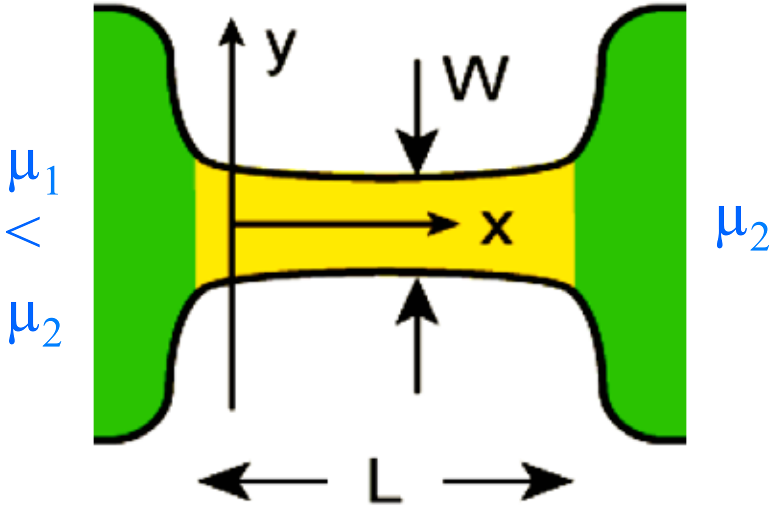
$W < l_e < L$

$W, L < l_e$

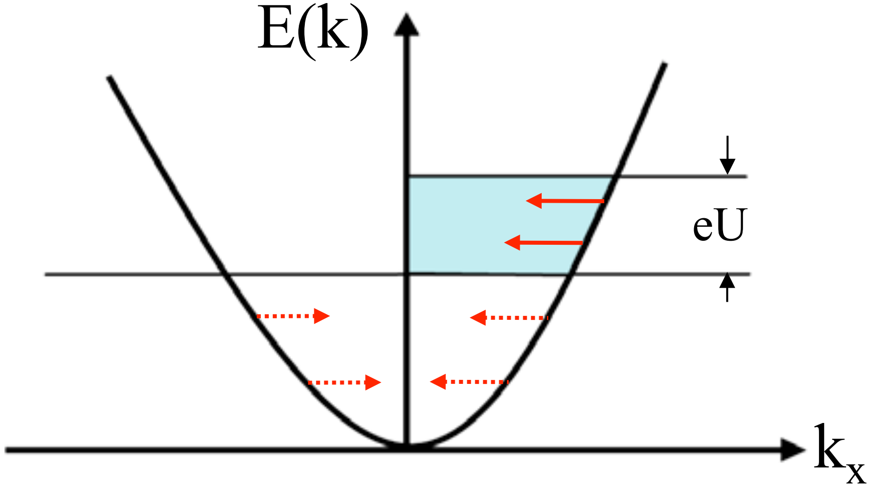
Ballistic transport in a 1D conductor

Electron waveguide

$W, L < l_e$



only one subband occupied



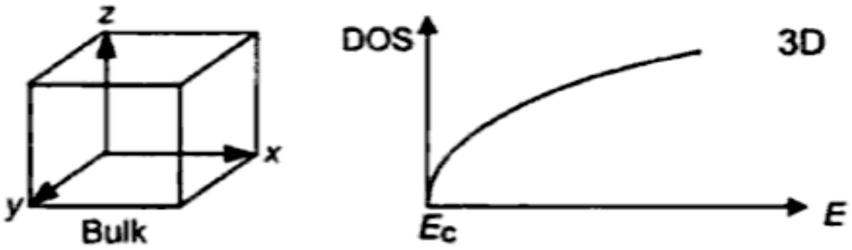
in 3D:

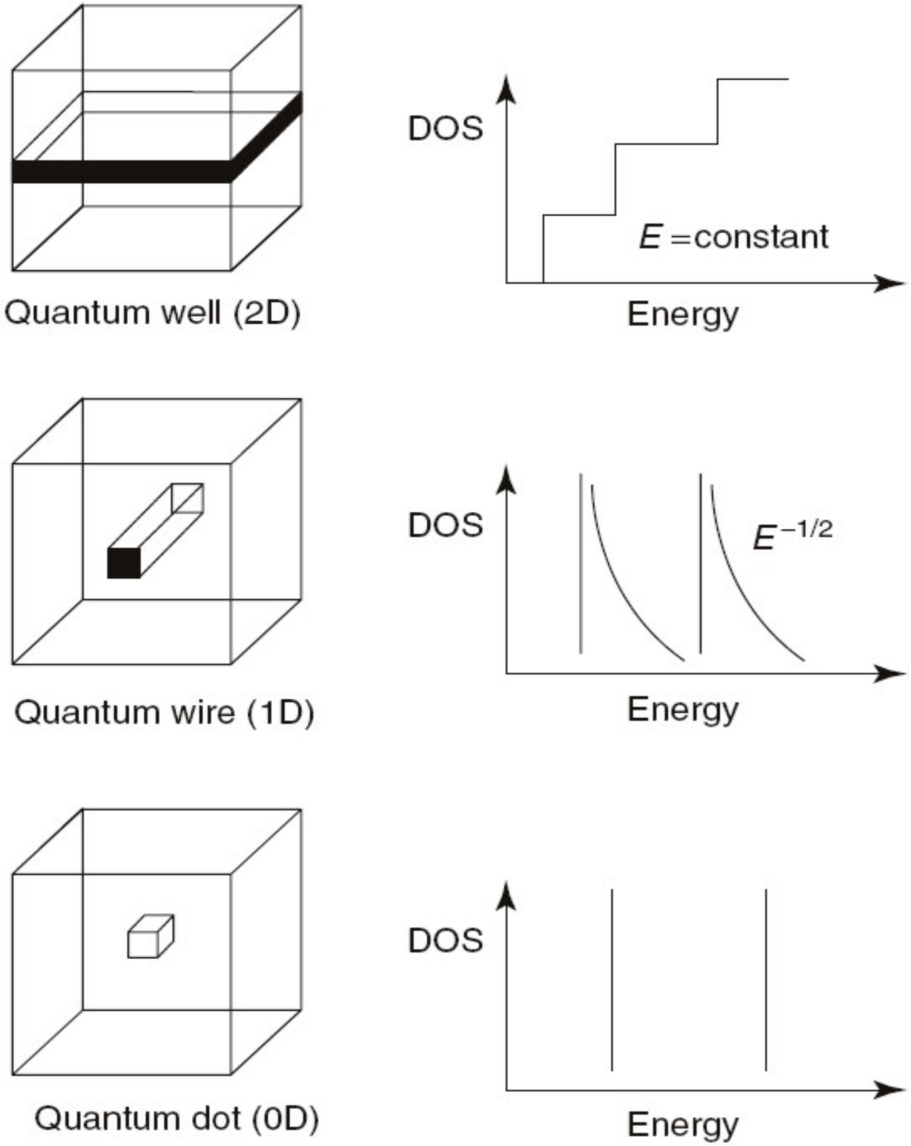
$$\mathbf{j} = eN\,\mathbf{v}$$

in 1D:

$$I = e\int_{E_F}^{E_F+eU} \rho_{1D}(E)\,v(\mathrm{E})\,dE$$

Electronic density of states (EDOS)





Ballistic transport in a 1D conductor

Electron waveguide

$$\boxed{I = e \int_{E_F}^{E_F + eU} \rho_{1D}(E)\, v(E)\, dE}$$

with $\rho_{1D}(E) = \frac{1}{\pi\hbar}\sqrt{\frac{2m}{E}} = \frac{1}{\pi}\left(\frac{\partial E}{\partial k}\right)^{-1}$

and $v(E) = \frac{1}{\hbar}\frac{\partial E}{\partial k}$ (group velocity)

$$\Downarrow$$

$$v(E)\rho_{1D}(E) = \frac{1}{\pi\hbar}$$

$$\Downarrow$$

$$\boxed{I = \frac{2e}{h}(eU); \quad \mathrm{G} = \frac{\mathrm{I}}{\mathrm{U}} = \frac{2e^2}{h}}$$

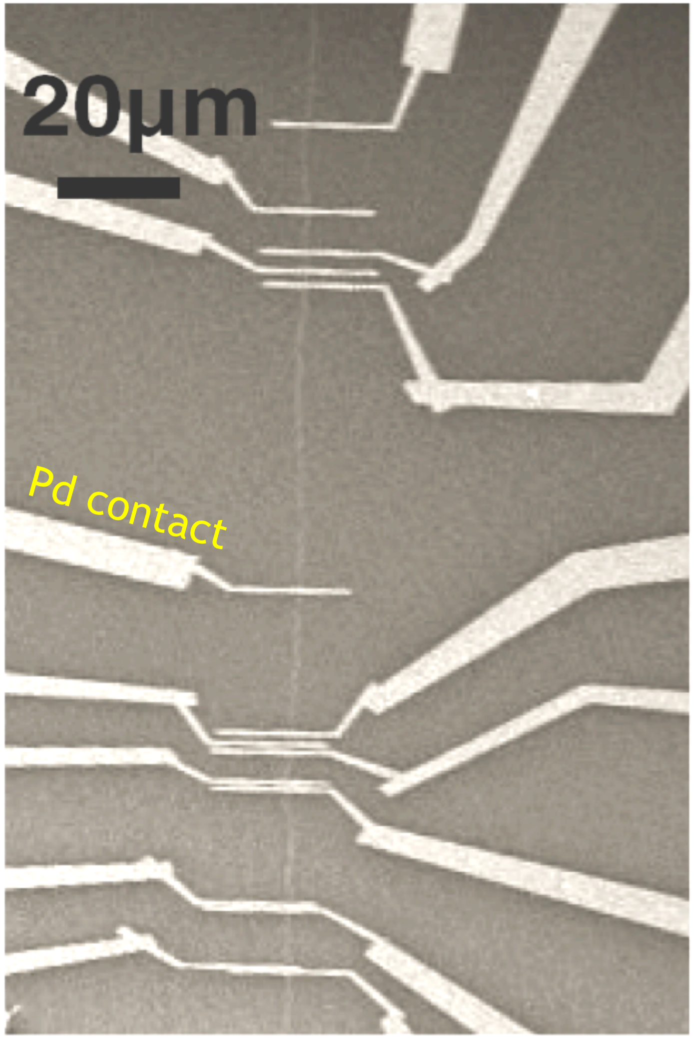
for N occupied subbands:

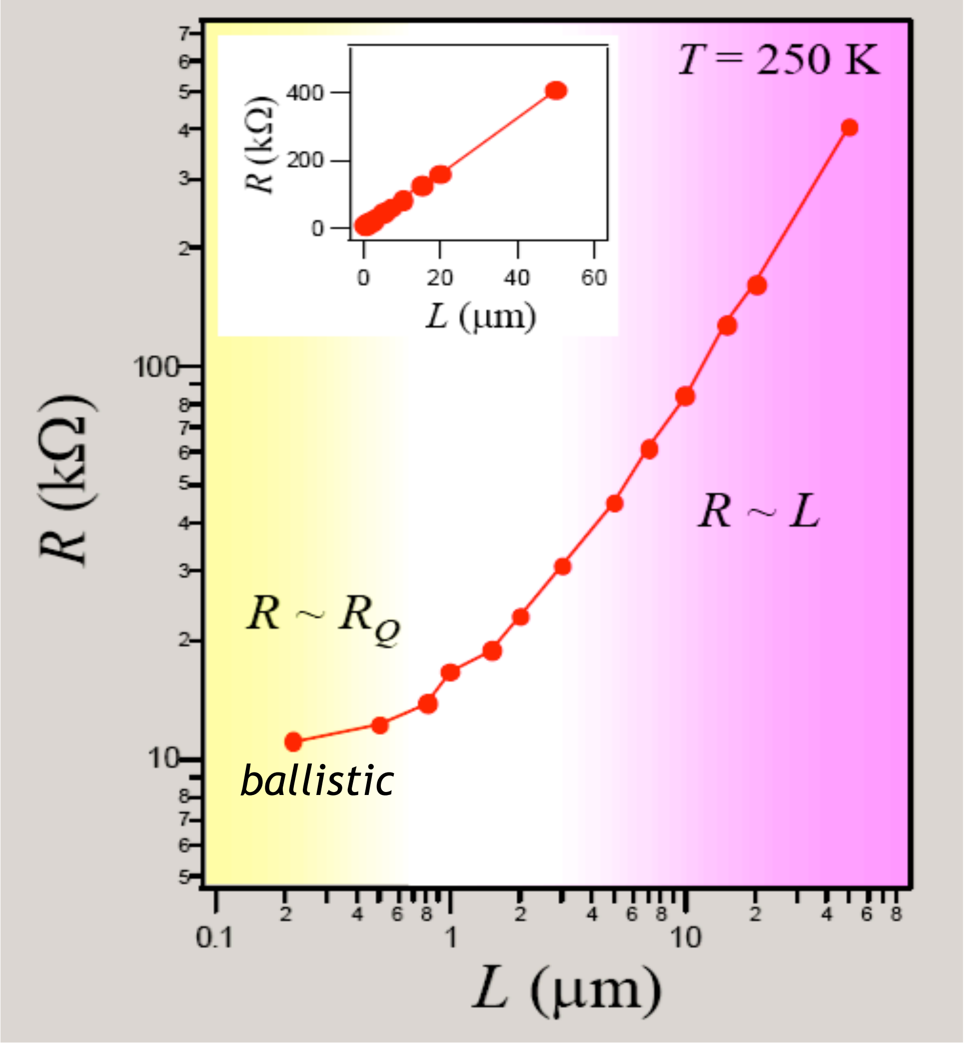
$$G = \frac{2e^2}{h} N$$

77.5 µS = (12.9 kΩ)$^{-1}$

Evaluation of mean free path in SWCNTs

Many contacts on long metallic tube:

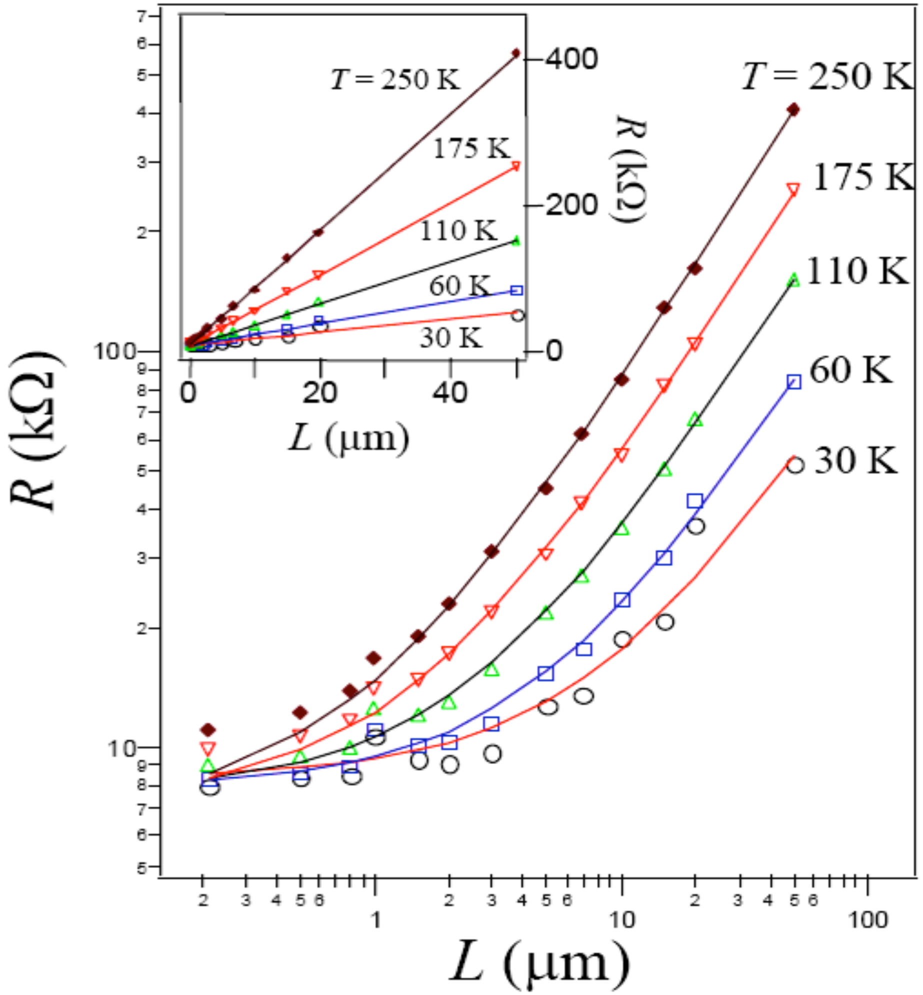




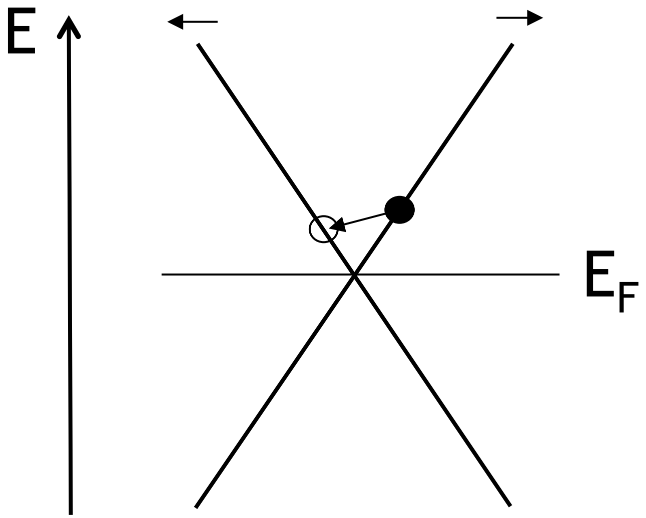
M.S. Purewal et al.; PRL 98 (2007), 186808.

Evaluation of mean free path in SWCNTs

Temperature dependence of resistance:

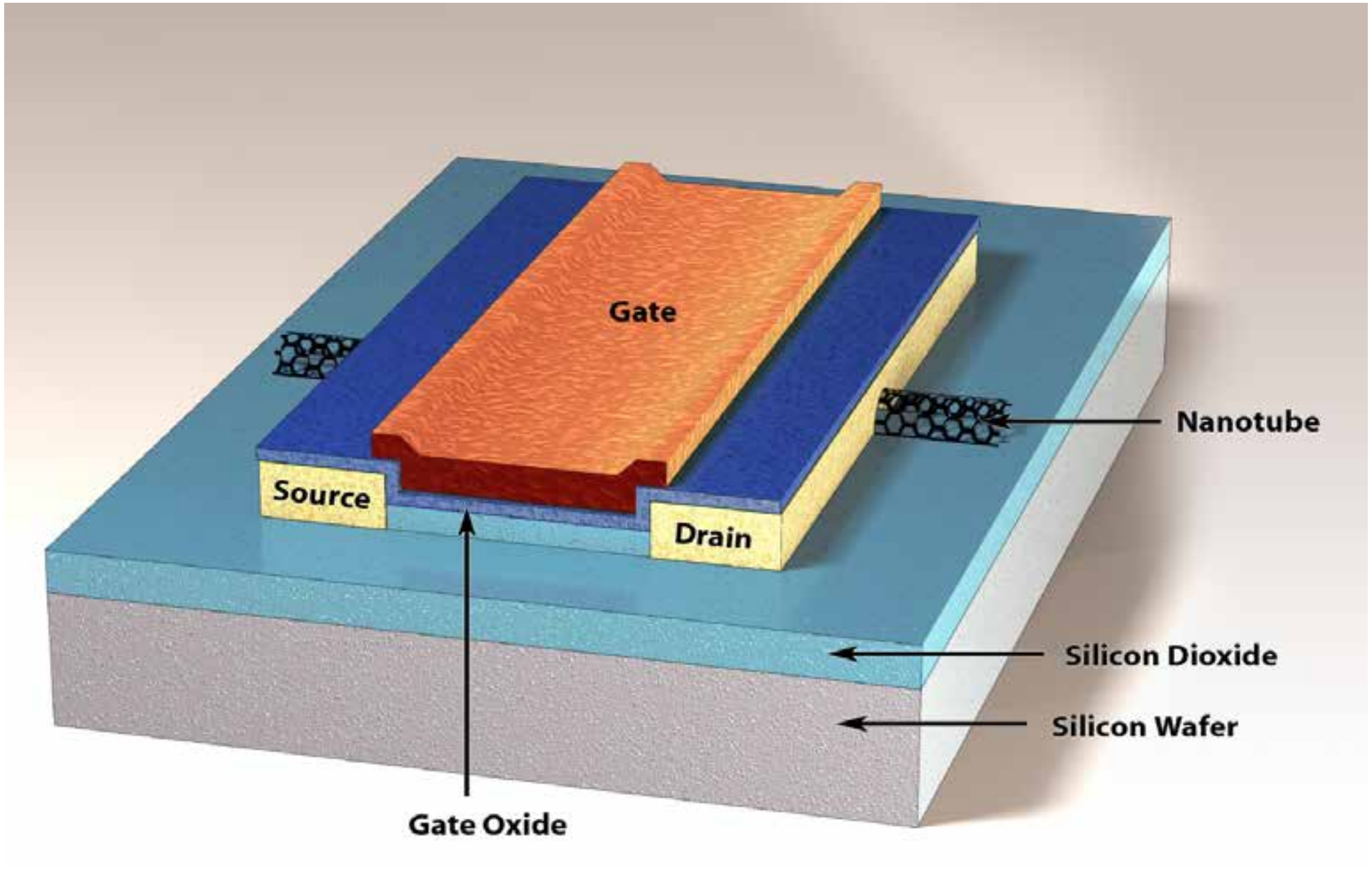


ballistic transport is limited by (acoustic) phonon scattering



M.S. Purewal et al.; PRL 98 (2007), 186808.

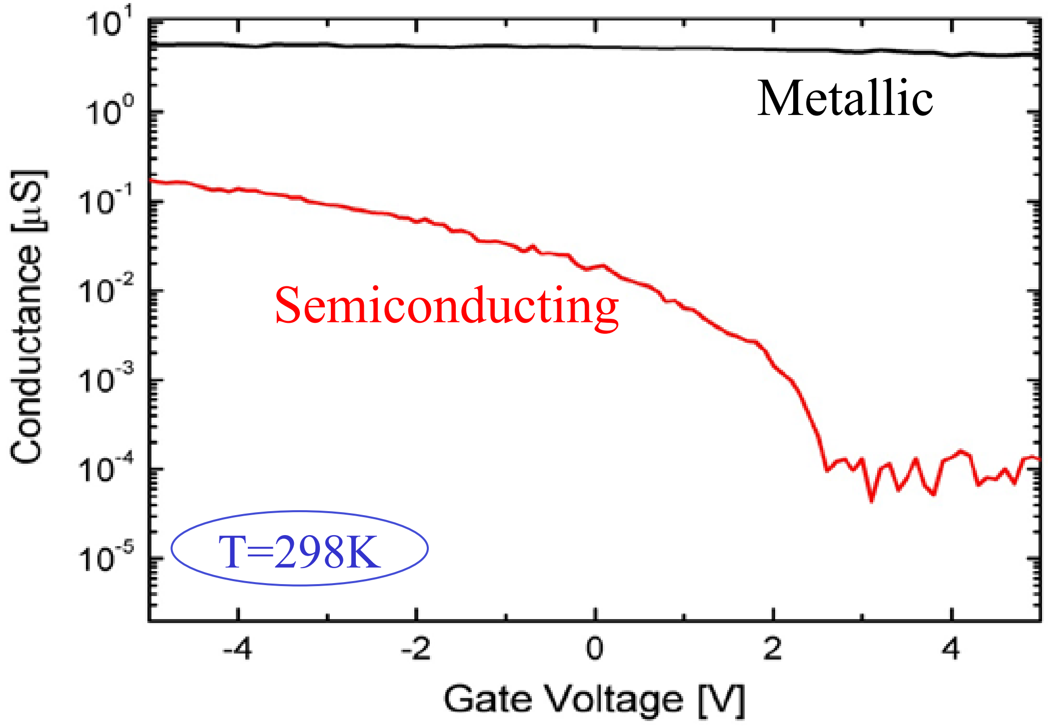
Carbon Nanotubes
for
electronic devices

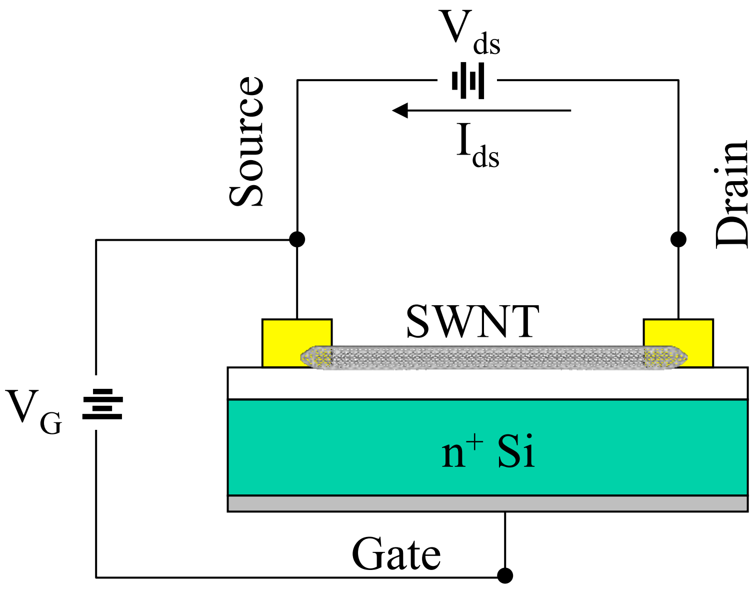


Electronic Transport in SWCNTs

(**room** temperature)

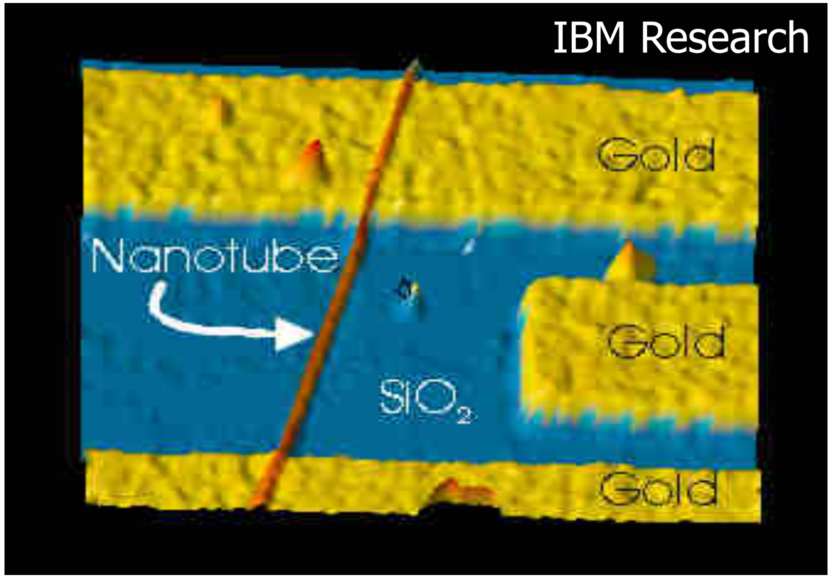
Gate Dependence of conductance

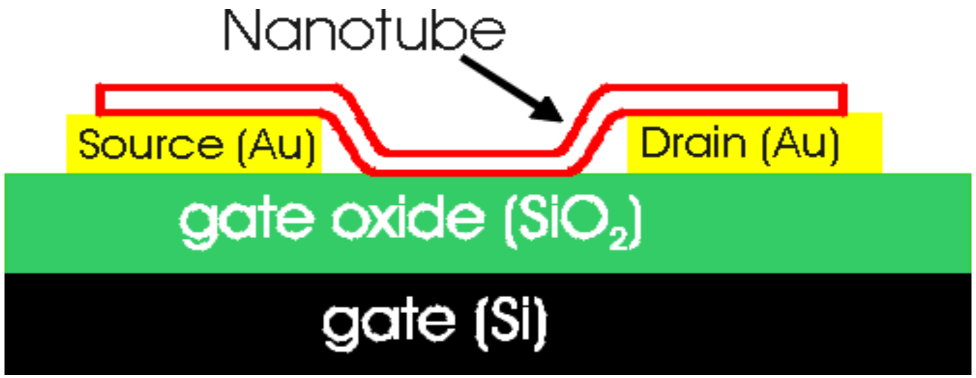




Conductance
I_{ds} / V_{ds}

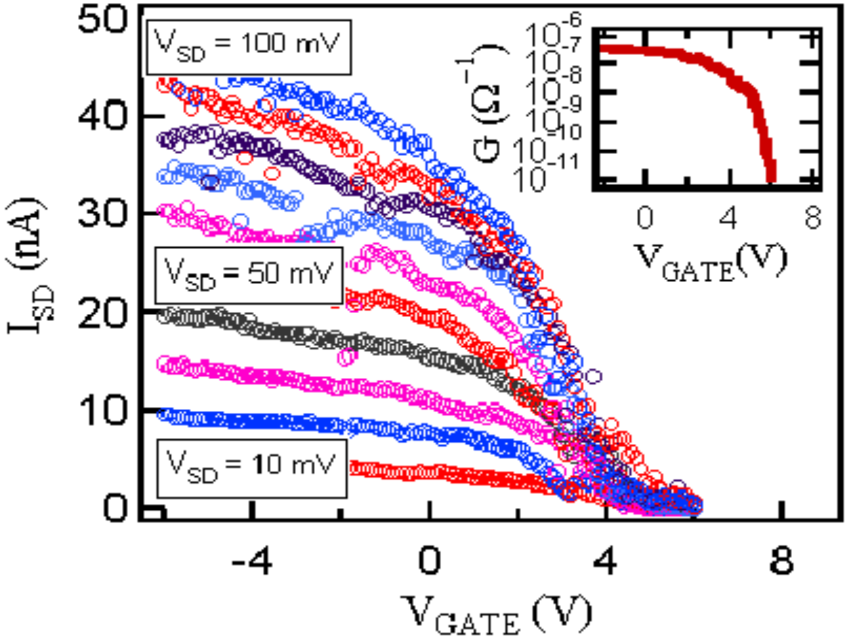
CNT Field-Effect Transistor





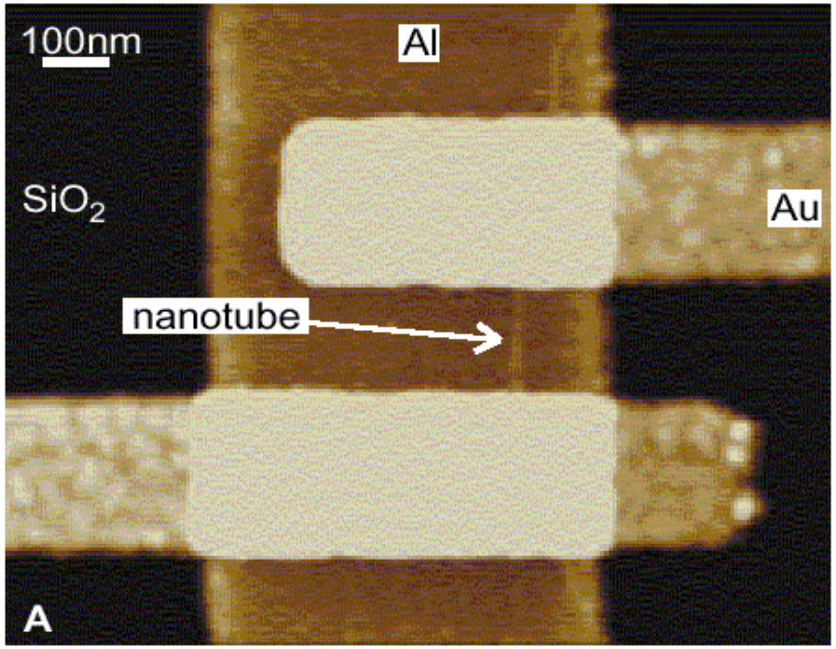
- ❑ FET with SWCNT or MWCNT
- ❑ Applying V_{gate}

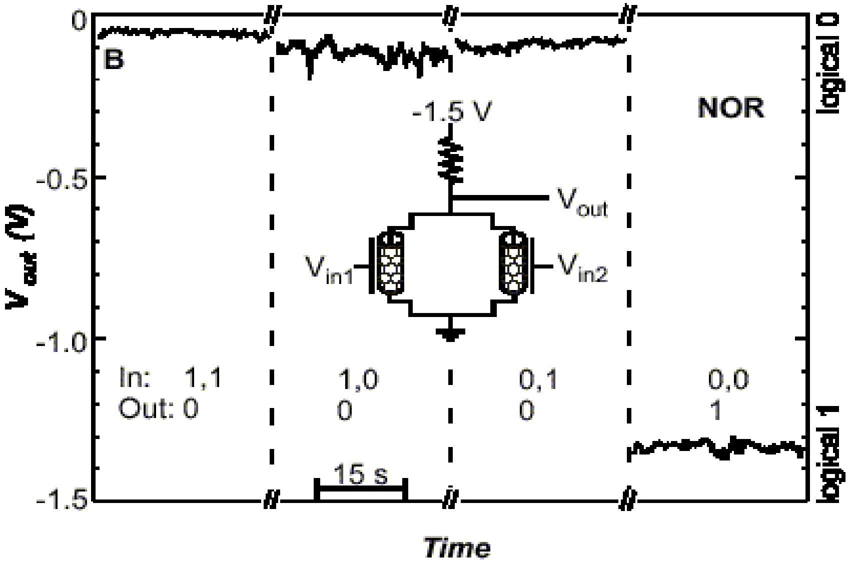
  $\Rightarrow$ Control of current I_{SD} through NT



Martel et al., Appl. Phys. Lett. 73, 2447, (1998)

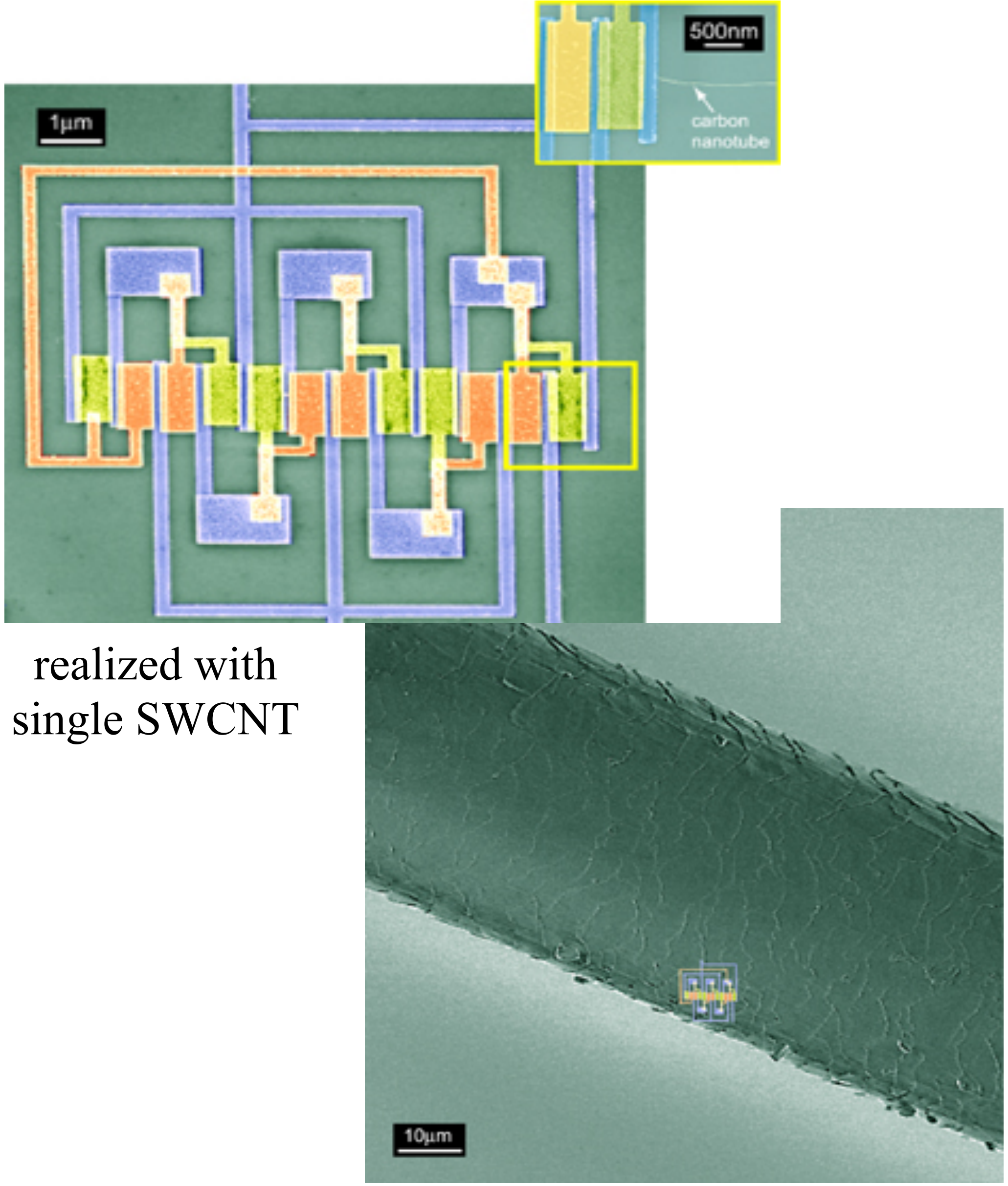
Carbon Nanotube Logic





Bachtold et al., Science 294, 1317, (2001)

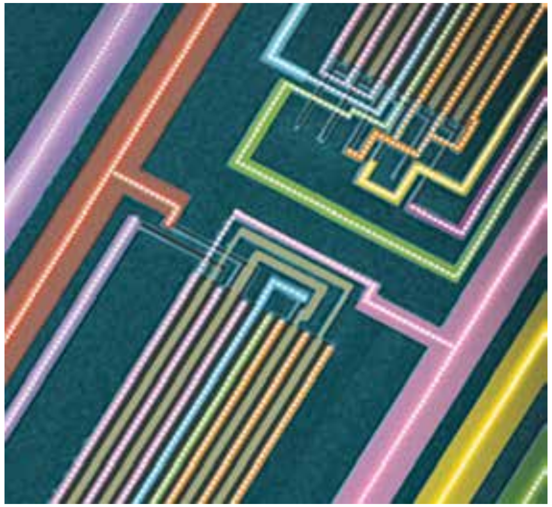
CNT-based electrical circuits

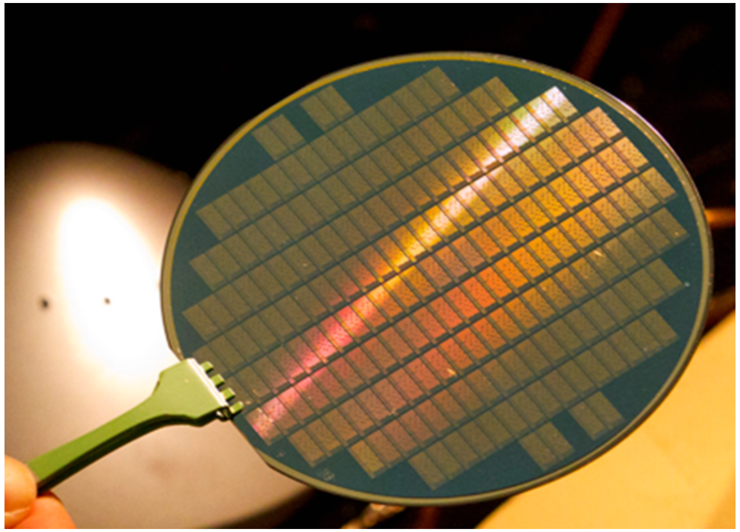


realized with
single SWCNT

Z. Chen et al., Science 311 (2006), 1735

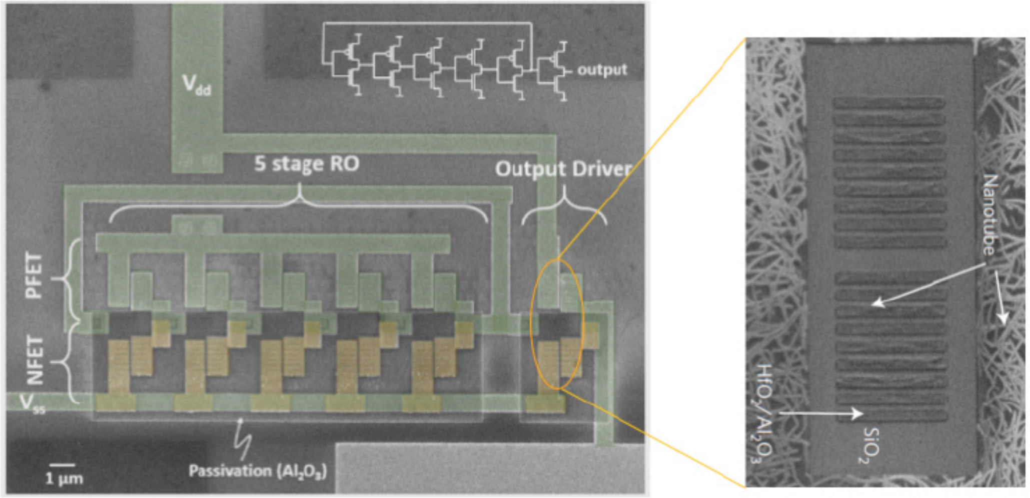
first CNT computer

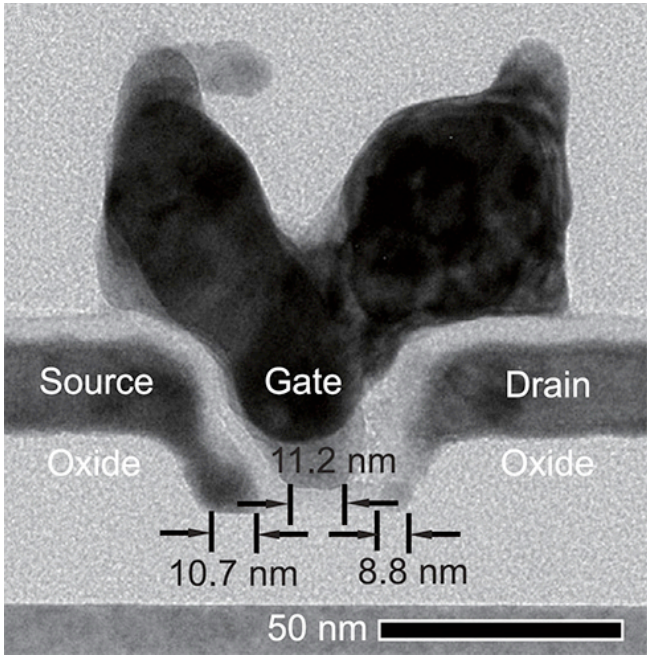




M. Shulaker et al., Nature 501 (2013), 526

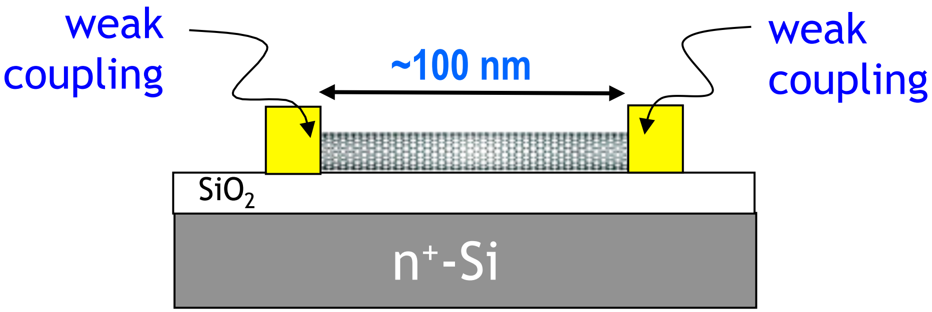
IBM - High-speed logic integrated circuits with solution-processed self-assembled carbon nanotubes



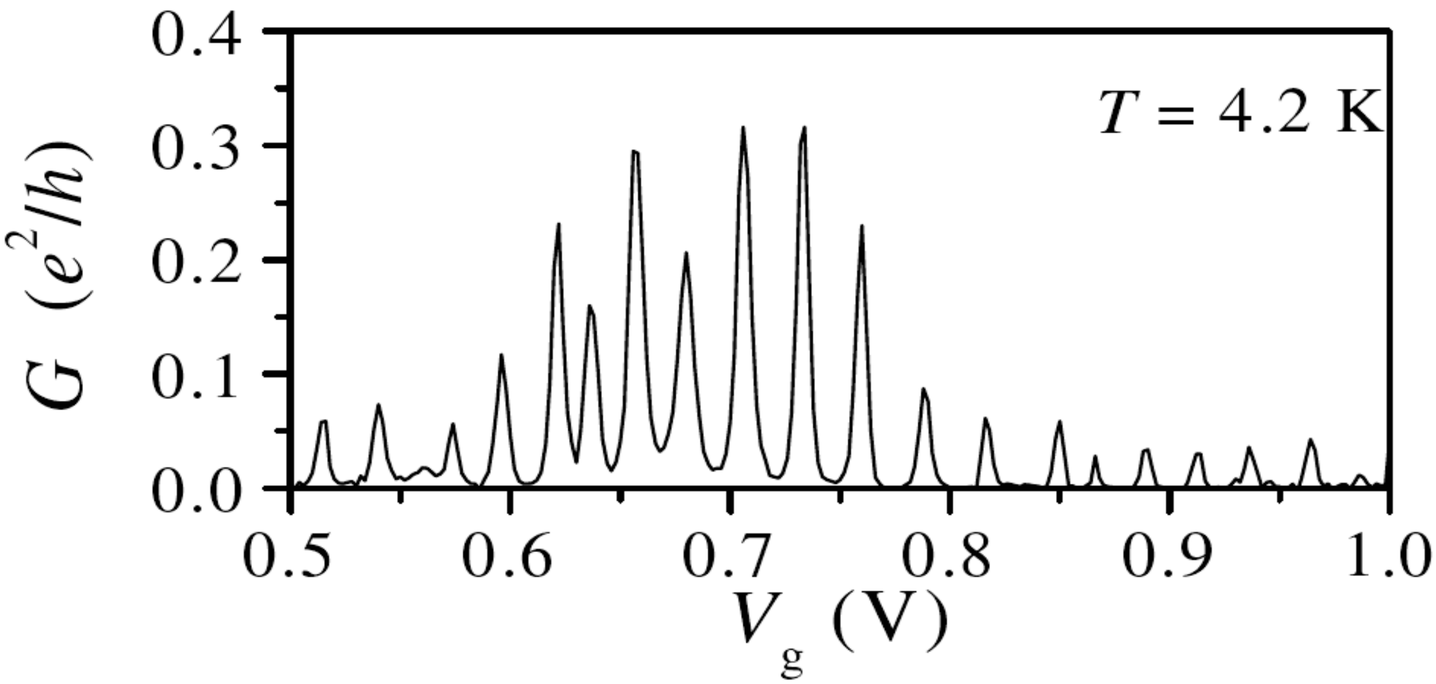


Nature Nanotechnology 12, 861 (2017)
Science 356, 1369 (2017)

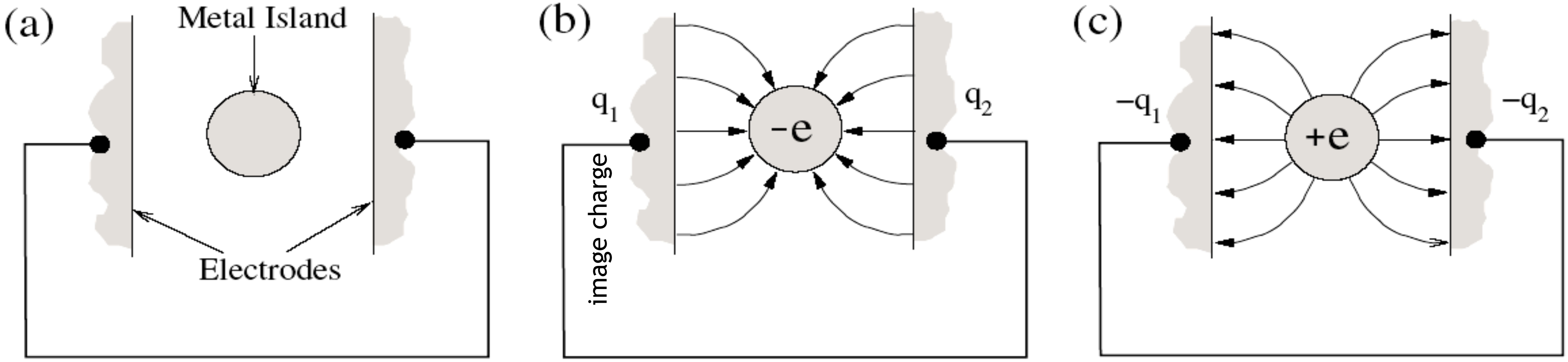
Short CNTs: Quantum dots



Coulomb blockade (CB)



Single-electron charging energy

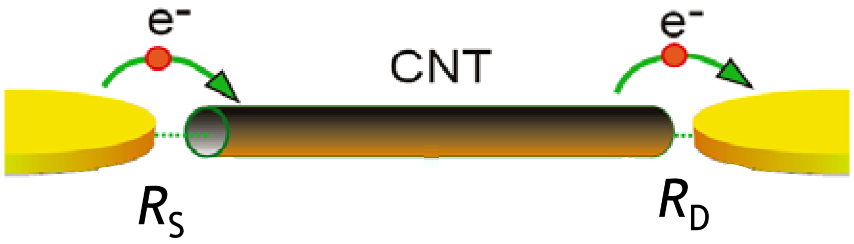


$$\boxed{E_C = \frac{e^2}{2C_{tot}}}$$

100 nm long SWCNT (r = 1 nm, d_{ox} = 300 nm):

$$E_C = \frac{e^2}{2C'_g \cdot 100\,\mathrm{nm}} = \frac{e^2}{2 \cdot 2 \cdot 10^{-18}\,\mathrm{F}} \approx 40\,\mathrm{meV}$$

Conditions for observing CB



1 $\boxed{k_BT << e^2/2C_{tot}}$

2 $\Delta E\cdot\Delta t > \hbar/2$

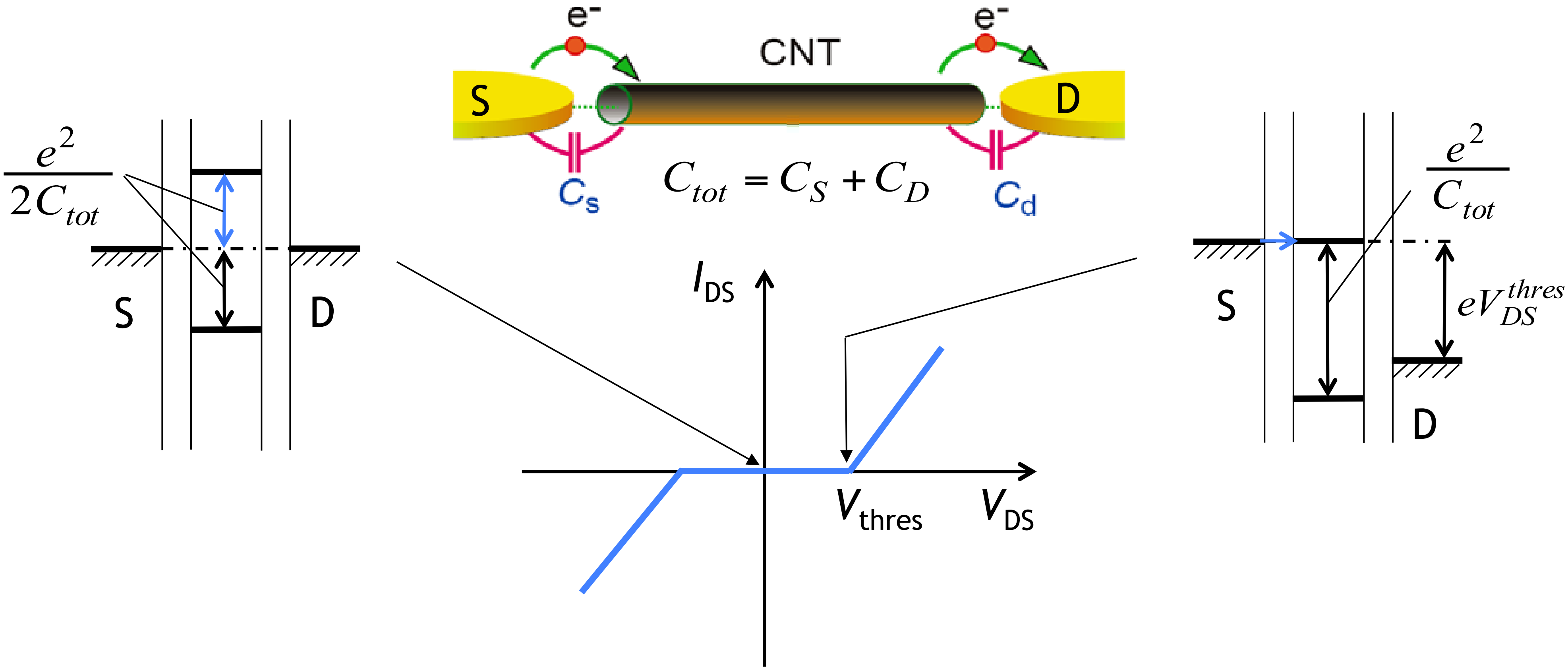
$\Delta E = e^2/2C;\ \Delta t = R_{tunnel}\cdot C$

$\boxed{R_{tunnel} > \hbar/e^2 \approx 4\ k\Omega}$

<u>lifting of CB via</u>

- V_{DS}
- V_{gate}

Threshold bias for tunneling



asymmetric case ($C_S >> C_D$ or $C_D >> C_S$):

$$V_{DS}^{thres} = \min\left(\frac{e}{2C_S};\frac{e}{2C_D}\right)$$

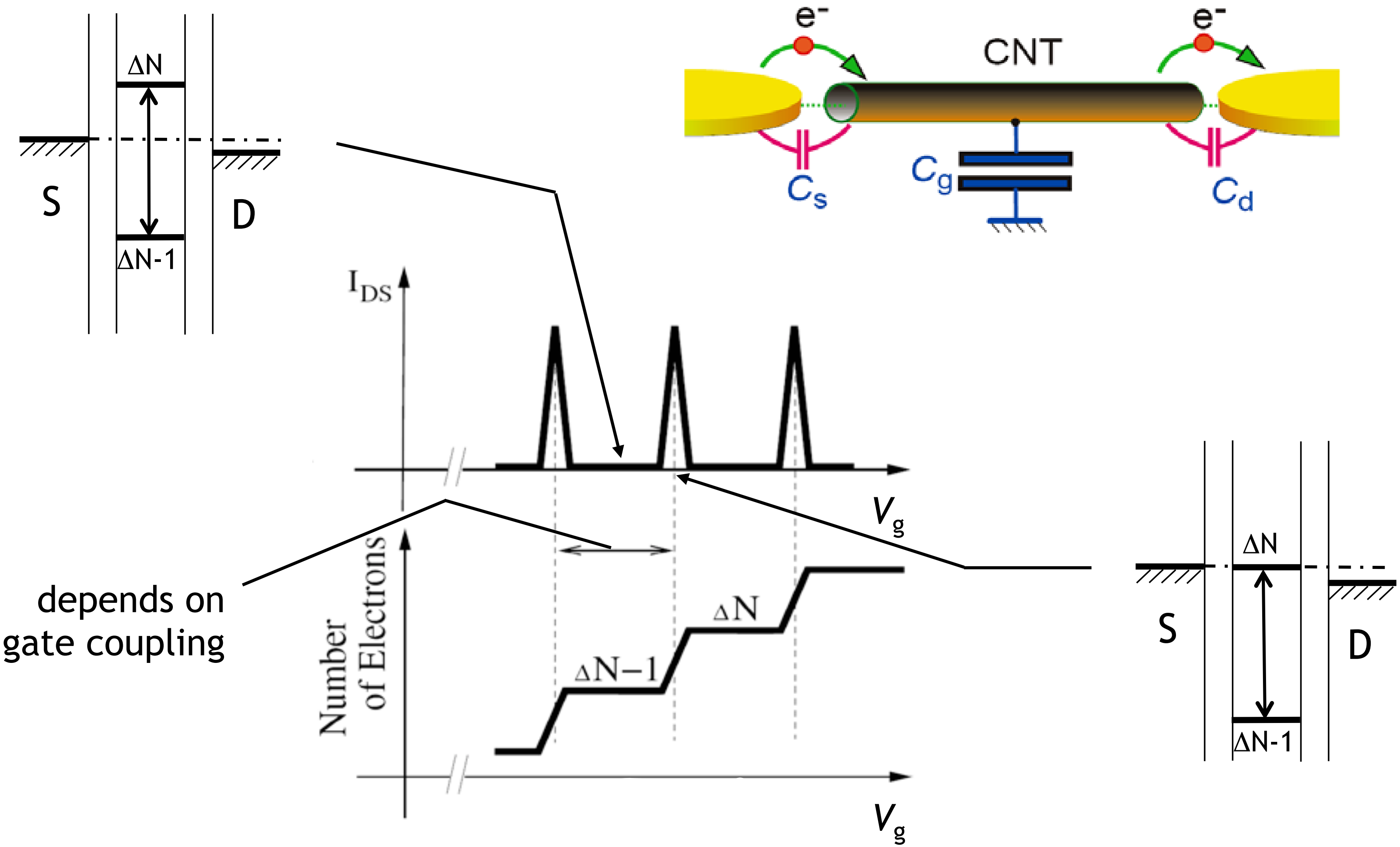
<u>symmetric case</u> ($C_S = C_D = C_{tot}/2$):
(relevant for CNTs)

$$V_{DS}^{thres} = \frac{e}{2C_S} = \frac{e}{2C_D} = \frac{e}{C_{tot}}$$

Single-electron transistor (SET)

Coulomb blockade oscillations

$$C_{tot} = C_S + C_D + C_g$$

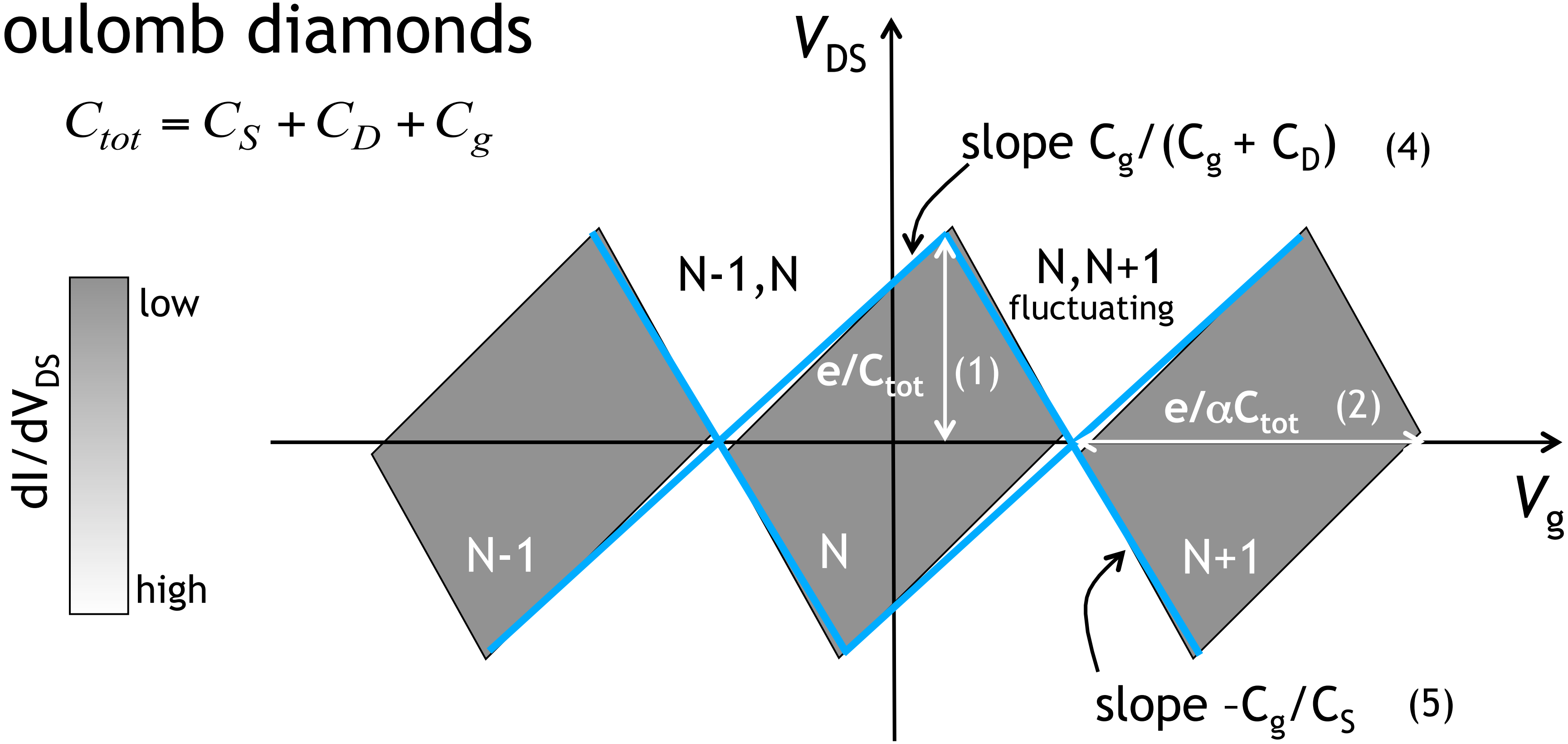


depends on
gate coupling

Single-electron transistor (SET)

Coulomb diamonds

$$C_{tot} = C_S + C_D + C_g$$



gate coupling factor
("electrostatic lever arm")

$$\boxed{\alpha = C_g/C_{tot}} \quad (3)$$

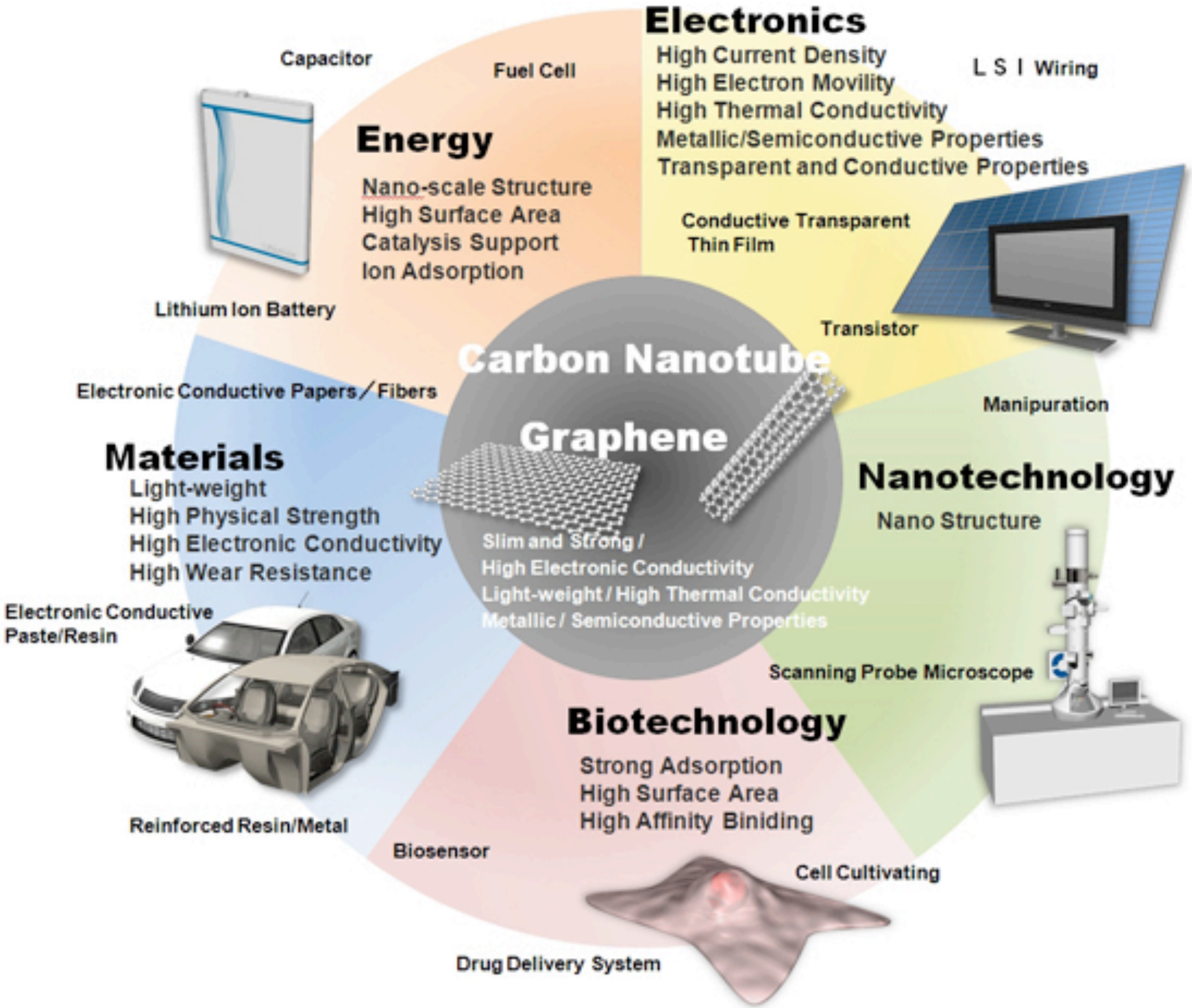
→ access to C_{tot} (1), α (2), C_g (3), C_D (4) and C_S (5)

$\searrow$ $E_C = e^2/2C_{tot}$

Carbon Nanotubes

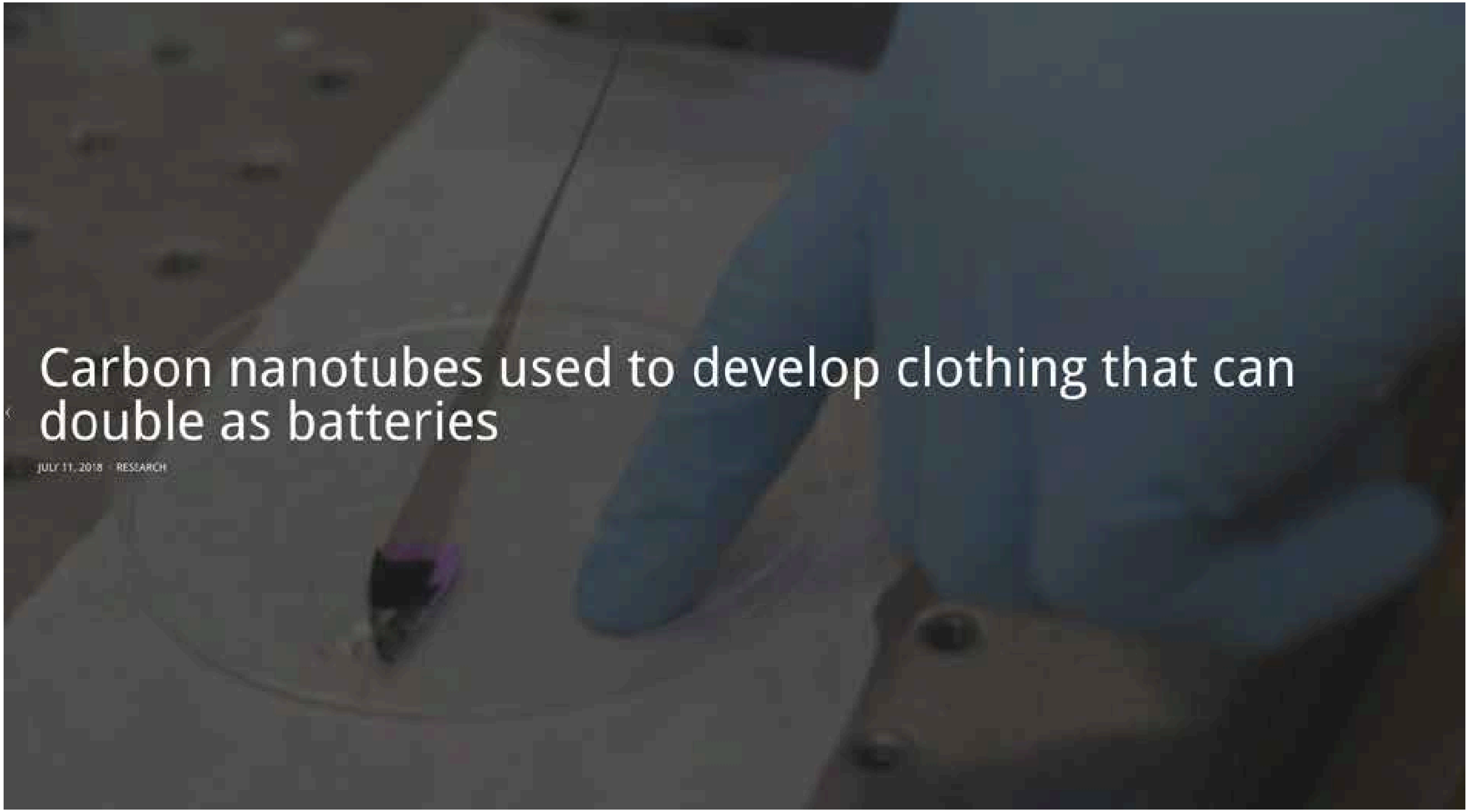
- introduction
- synthesis
- electronic structure
- electrical transport
- applications

Applications:



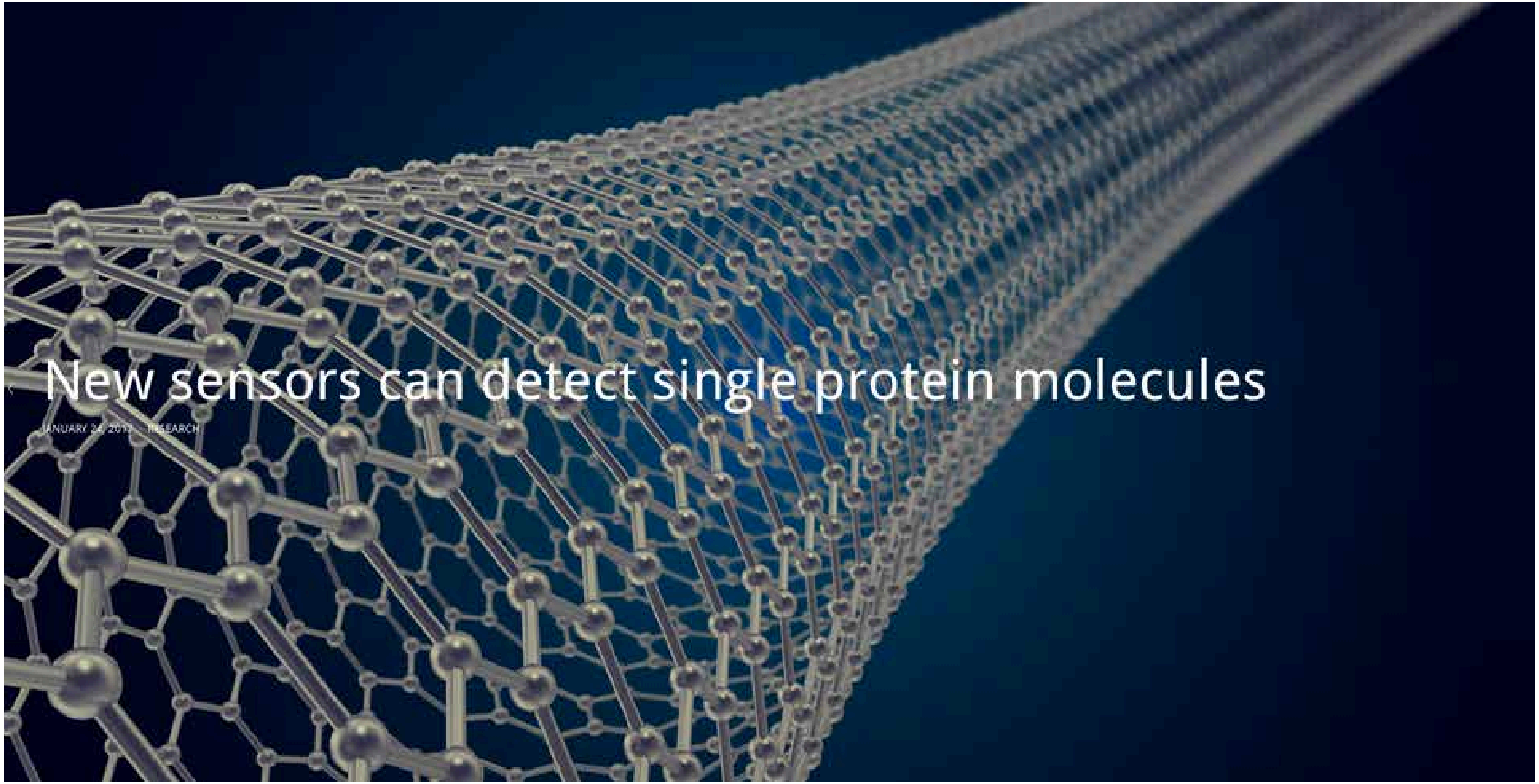
NASA Awards Contract for Carbon Nanotube Technology

SEPTEMBER 29, 2018 · RESEARCH



Carbon nanotubes used to develop clothing that can double as batteries

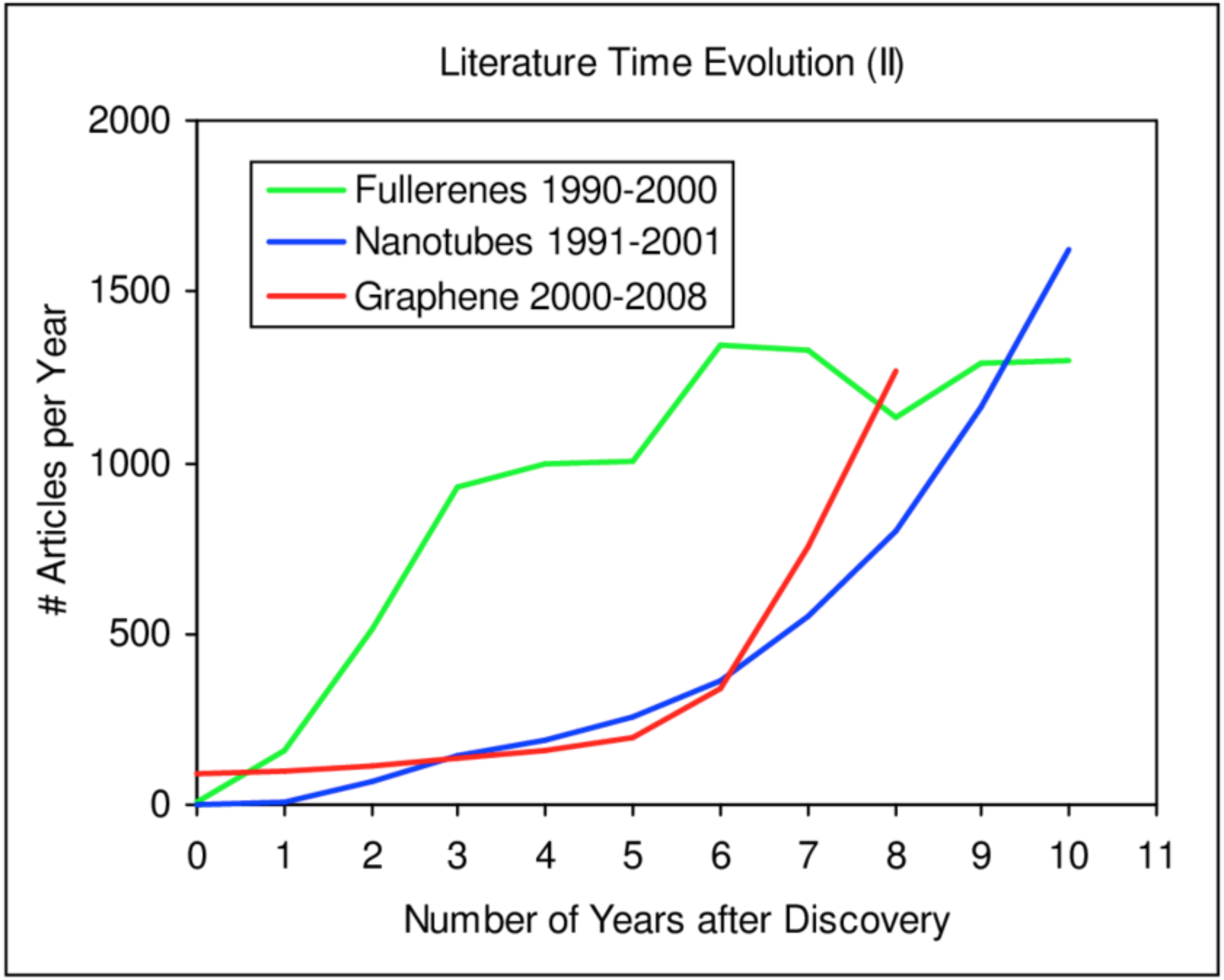
JULY 11, 2018 · RESEARCH



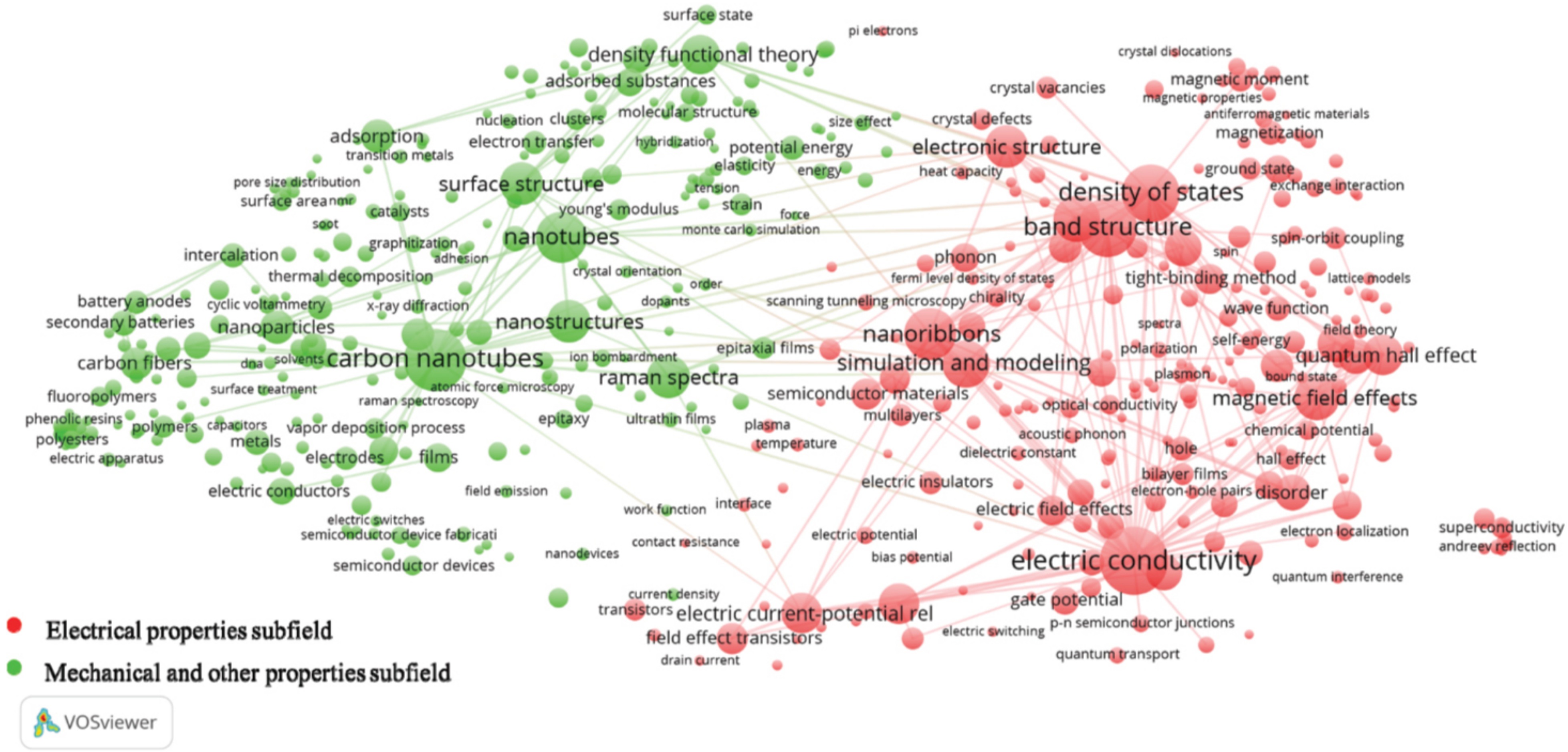
New sensors can detect single protein molecules

JANUARY 24, 2017 · RESEARCH

Nature Nanotechnology 12, 368 (2017)

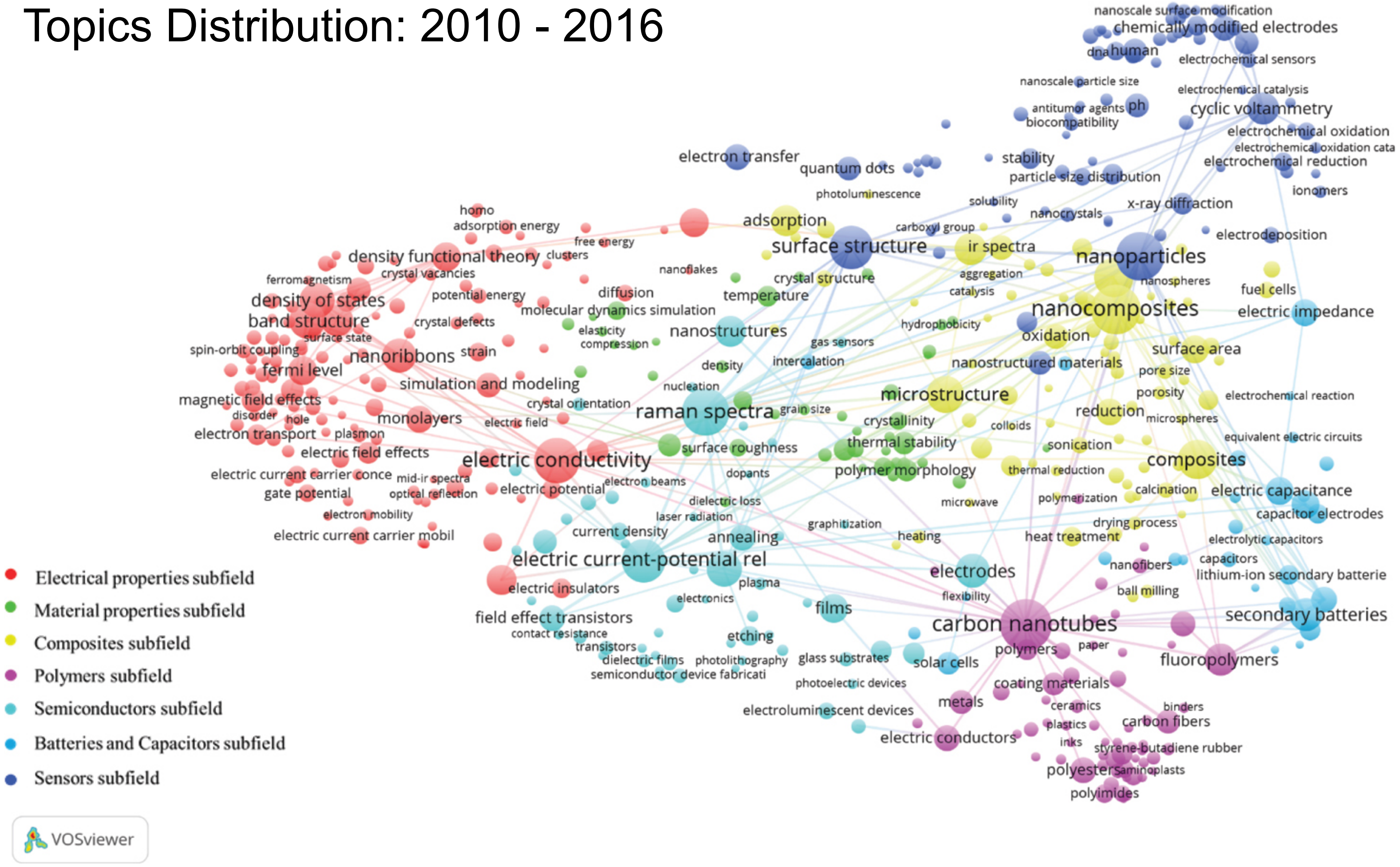

Literature Time Evolution (II)
Fullerenes 1990-2000
Nanotubes 1991-2001
Graphene 2000-2008
Articles per Year
2000
1500
1000
500
0
0
1
2
3
4
5
6
7
8
9
10
11
Number of Years after Discovery

Topics Distribution: before 2009



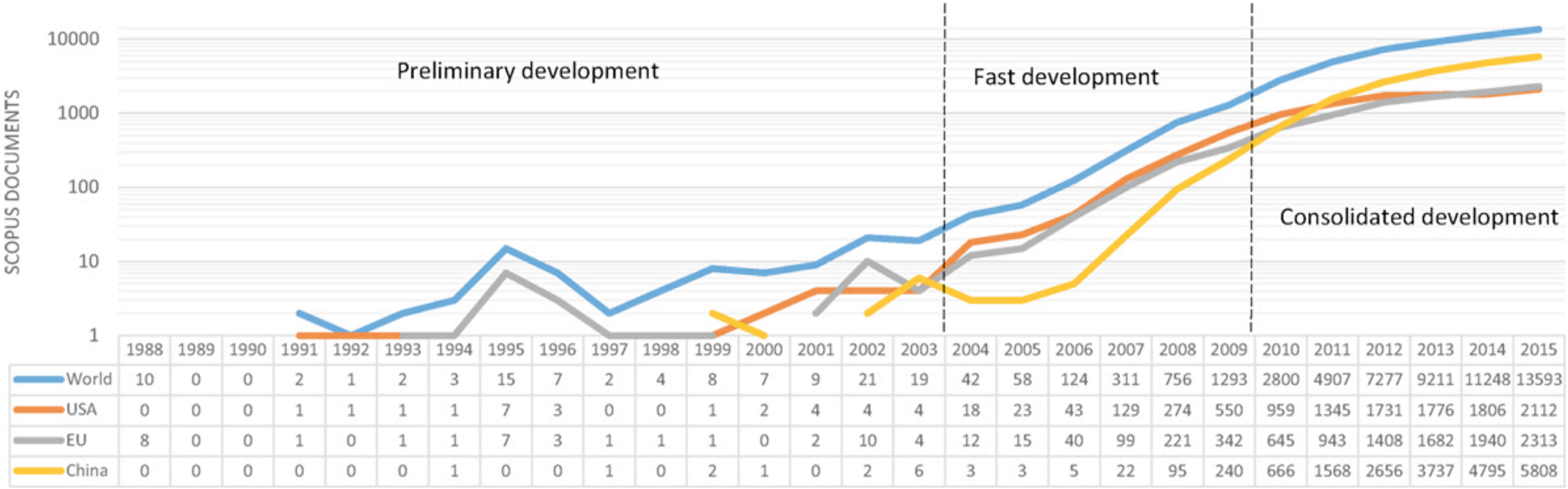
https://doi.org/10.2478/jdis-2018-0005

Topics Distribution: 2010 - 2016



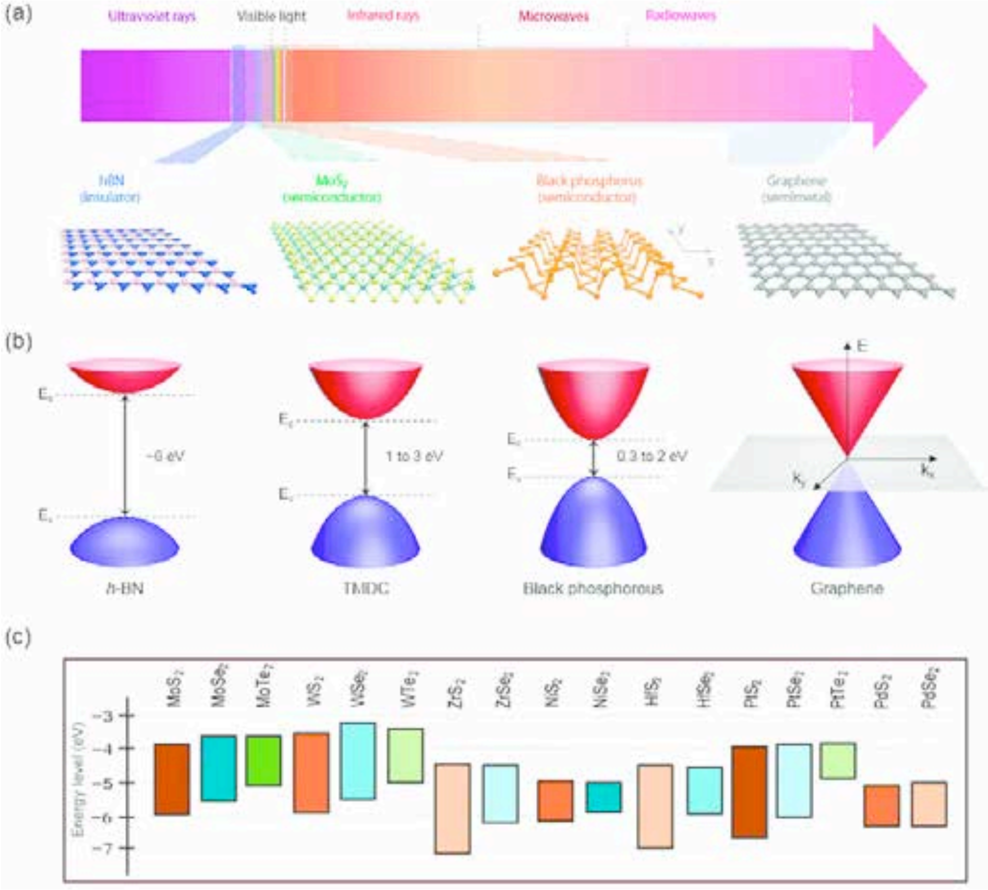
https://doi.org/10.2478/jdis-2018-0005

Carbon-Nano Publications and Patents



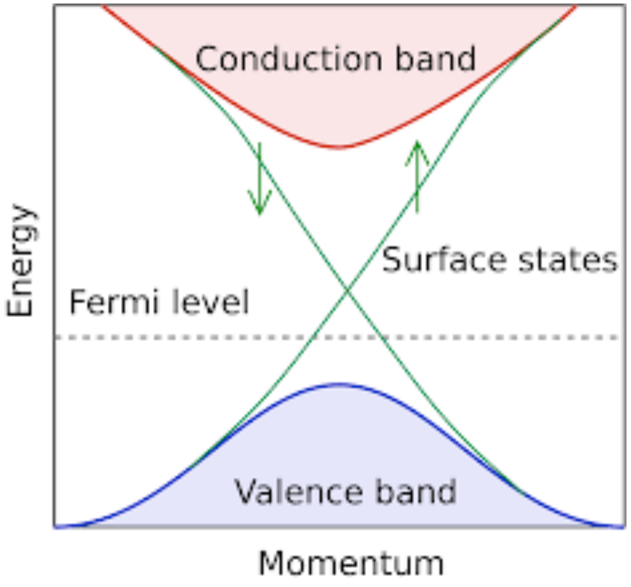
	1988	1989	1990	1991	1992	1993	1994	1995	1996	1997	1998	1999	2000	2001	2002	2003	2004	2005	2006	2007	2008	2009	2010	2011	2012	2013	2014	2015
▬ World	10	0	0	2	1	2	3	15	7	2	4	8	7	9	21	19	42	58	124	311	756	1293	2800	4907	7277	9211	11248	13593
▬ USA	0	0	0	1	1	1	1	7	3	0	0	1	2	4	4	4	18	23	43	129	274	550	959	1345	1731	1776	1806	2112
▬ EU	8	0	0	1	0	1	1	7	3	1	1	1	0	2	10	4	12	15	40	99	221	342	645	943	1408	1682	1940	2313
▬ China	0	0	0	0	0	0	1	0	0	1	0	2	1	0	2	6	3	3	5	22	95	240	666	1568	2656	3737	4795	5808

Two-dimensional Materials

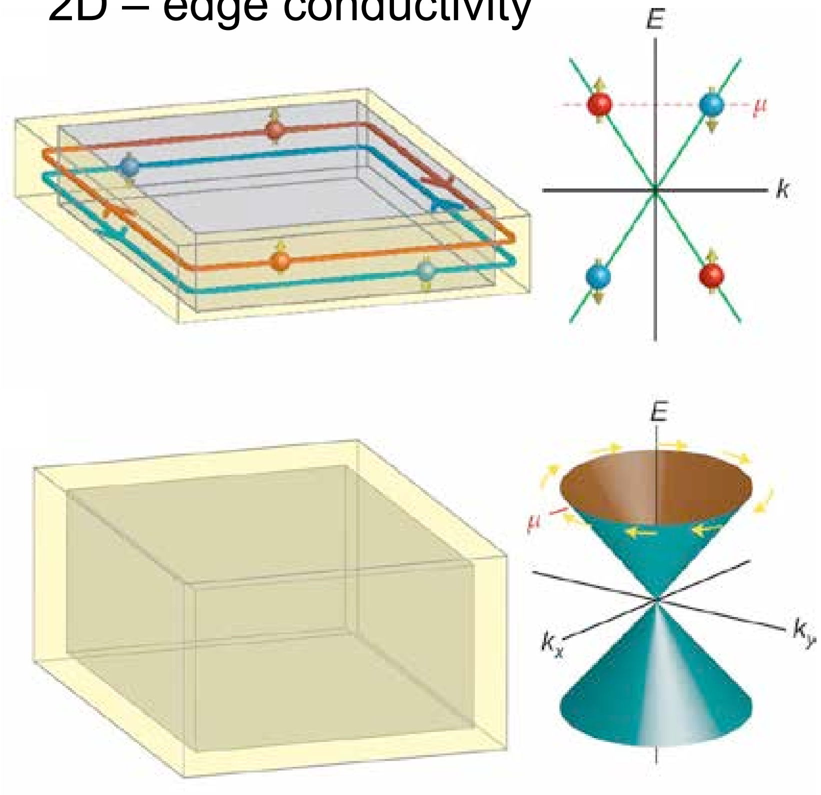


Nanomaterials 6, 193 (2016)

Topological Insulators:



2D – edge conductivity



3D – surface conductivity

2D Dirac Materials: