Ústav fyzikální chemie J. Heyrovského, v.v.i. Praha
Akademie věd České Republiky

J. Heyrovský 1959

Nanomateriály

Ladislav Kavan
kavan@jh-inst.cas.cz

Richard P. Feynman (1918-1988), Nobelova cena 1965

“There’s Plenty of Room at the Bottom”

APS Meeting, Caltech, Dec. 29, 1959

13. Přednáška (18.5.2011) pozor 4 vyučovací hodiny

Nanomateriály na bázi uhlíku
Struktury elementárního uhlíku
Klasické struktury: Grafit, diamant, polyyny
Fullereny, grafen a uhlíkové nanotuby
Objev, příprava, elektronická struktura a vlastnosti
Další nanostruktury
Fullerenové lusky, dvojstěnné nanotuby, kompozity
Aplikace uhlíkových nanostruktur
Nanoelektronika, Li-ion baterie, superkondenzátory, palivové články, ukládání vodíku, nanomanipulace, nanomotory

14. Přednáška

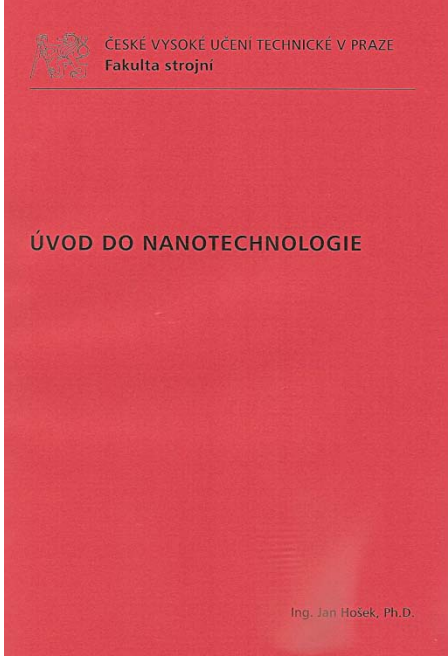
Aplikace nanomateriálů na bázi oxidů titaničitých
Fotokatalýza
Princip fotokatalýzy, samočistící a antibakteriální povlaky, odstraňování nečistot z vody a vzduchu (organické polutanty, NO_x a CO_2)
Konverze solární energie
Barvivem sensibilizované solární články: princip, funkce, možnosti profotovolatiku
Další aplikace
Elektrochromní displeje, ultrarychlé Li-ion baterie

Literatura

Nanocarbon

Z Weiss, G. Simha-Martynková, O. Šustai, Nanostruktura uhlíkových materiálů, VŠB TU Ostrava, 2005.
S. Reich, C. Thomsen, J. Maultzsch, Carbon Nanotubes, Wiley, Darmstadt, 2003.
A. Krueger, Carbon Materials and Nanotechnology, Wiley, 2008.

TiO_2
A. Fujishima and K. Hashimoto, T. Watanabe, TiO_2 fotoakatalýa a aplikace, Silikátový Svaz Praha, 2002
K. Kalyanasundaram, Dye Sensitized Solar Cells, Francis and Taylor, 2010.



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Jan Hošek, Úvod do nanotechnologie, skripta ČVUT 2010.
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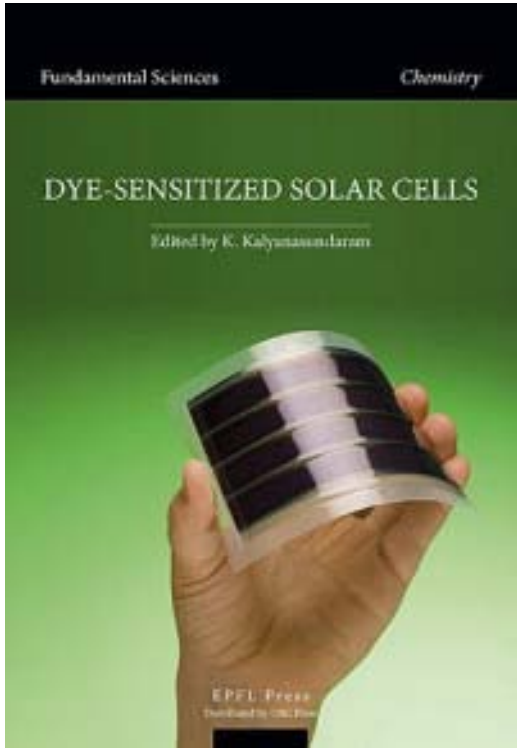
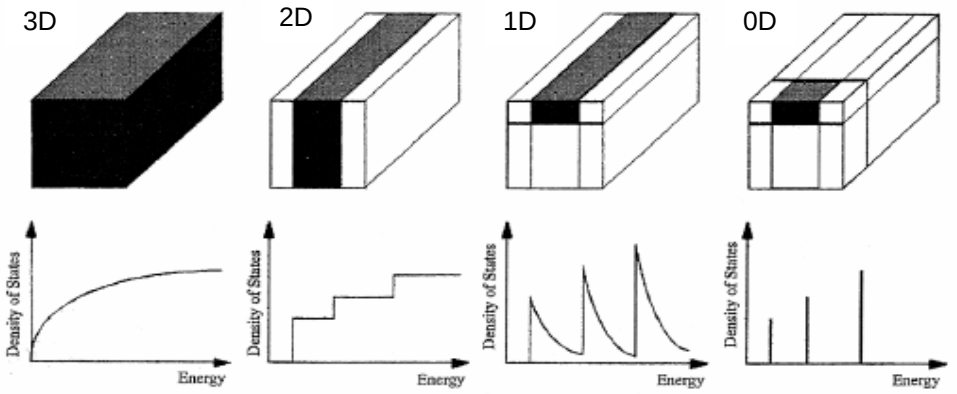
C.N.R. Rao, A. Muller, A.K. Cheetham, The Chemistry of Nanomaterials, Wiley 2003.
A. S. Edelstein and R. Cammarata, Nanomaterials, Synthesis, Properties and Application. Inst. of Physics Publishing, 1996.
G. A. Ozin, A.C. Arsenault, Nanochemistry, RSC Publ. Cambridge, 2005.
G. Q. Lu, X. S. Zhao, Nanoporous Materials Science and Engineering, Imperial College Press, London. 2004.



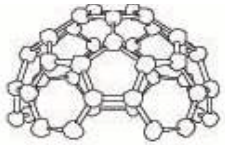
Hustota stavů *vs*. energie elektronů v krystalu

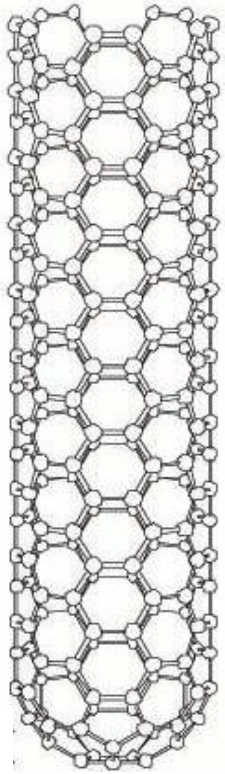


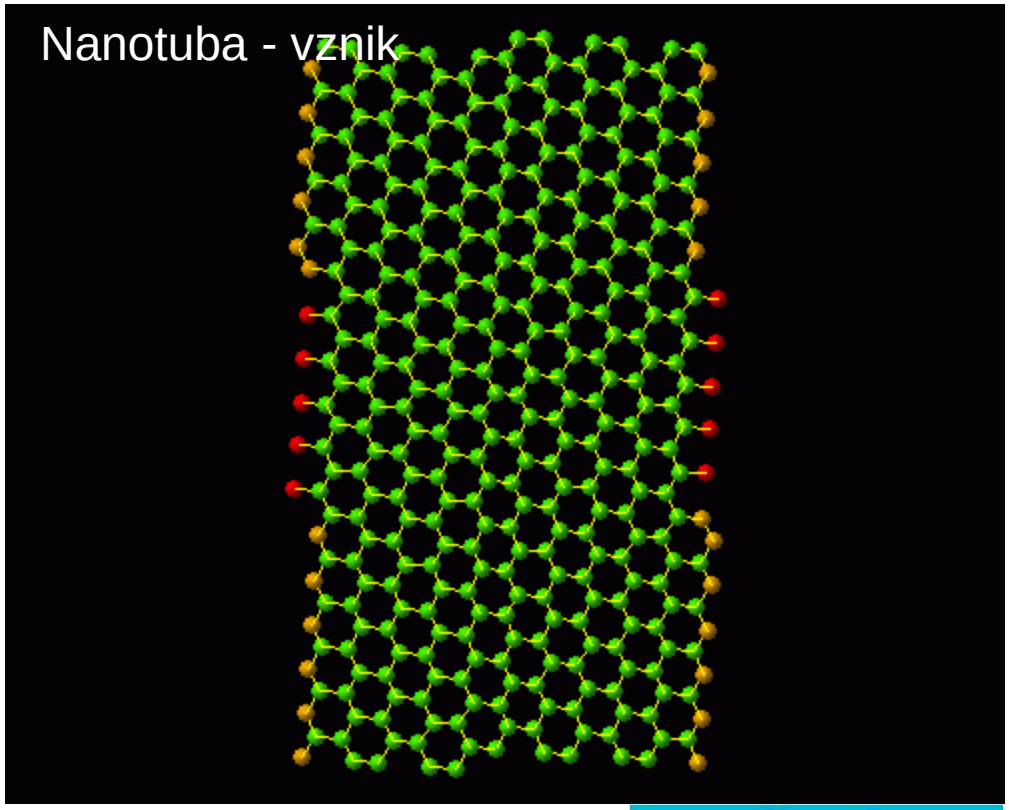
(„velký“) krystal | Kvantová Jáma/studna | Nanodrát | Kvantová tečka

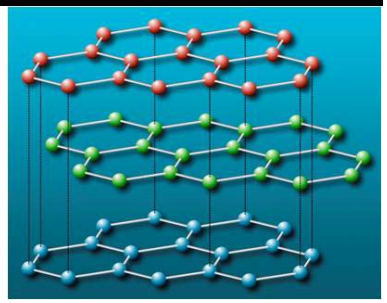
$$(DOS)_{3D} = c.E^{1/2} \text{ (Fermi-Dirac)}$$

Uhlíková nanotuba: SWNT



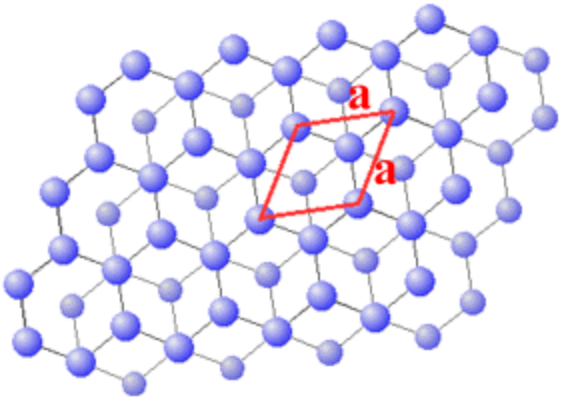


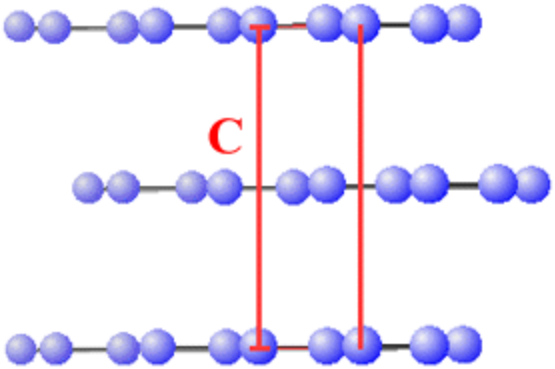




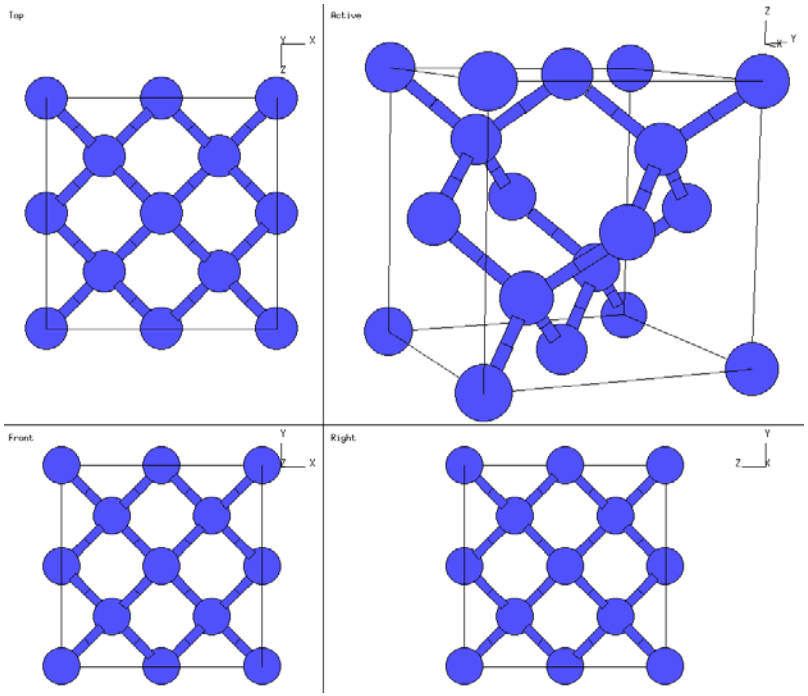
Elemental carbon: graphite, diamond and beyond

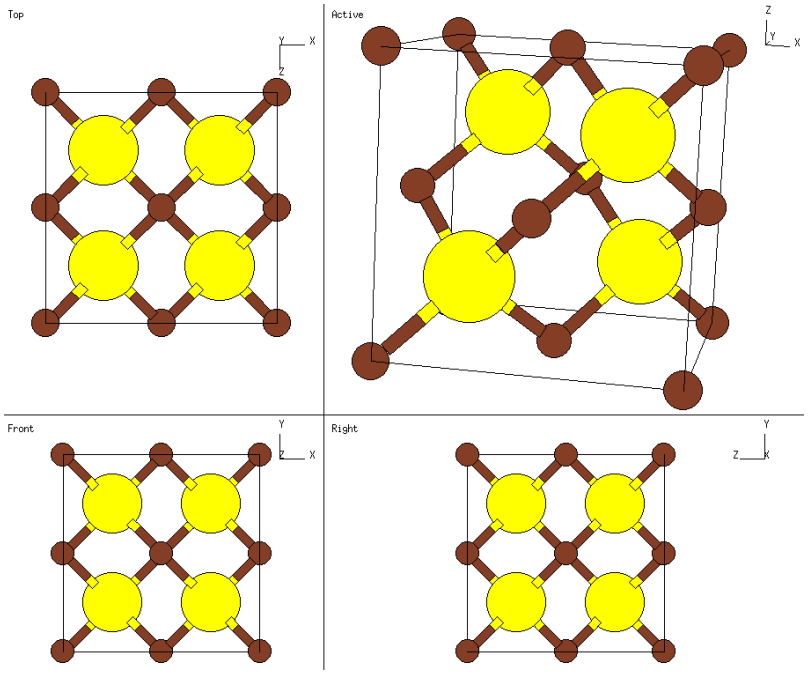
Hexagonal graphite – sp^2 bonding



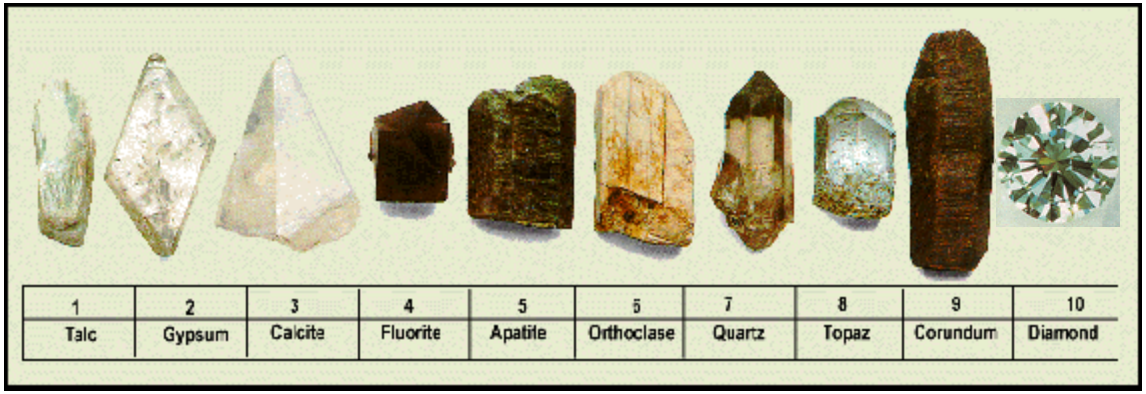


Cubic diamod-ZnS (sphalerite)





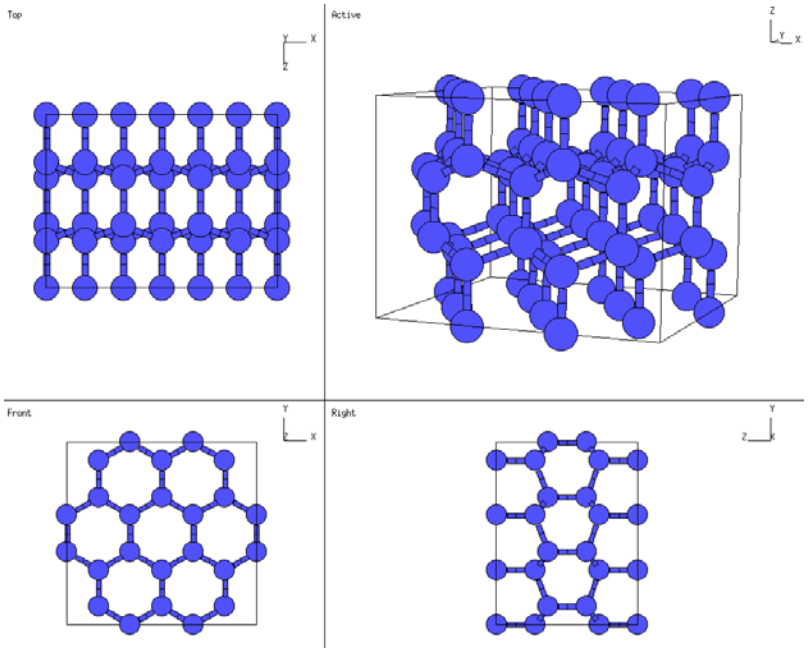
Hardness

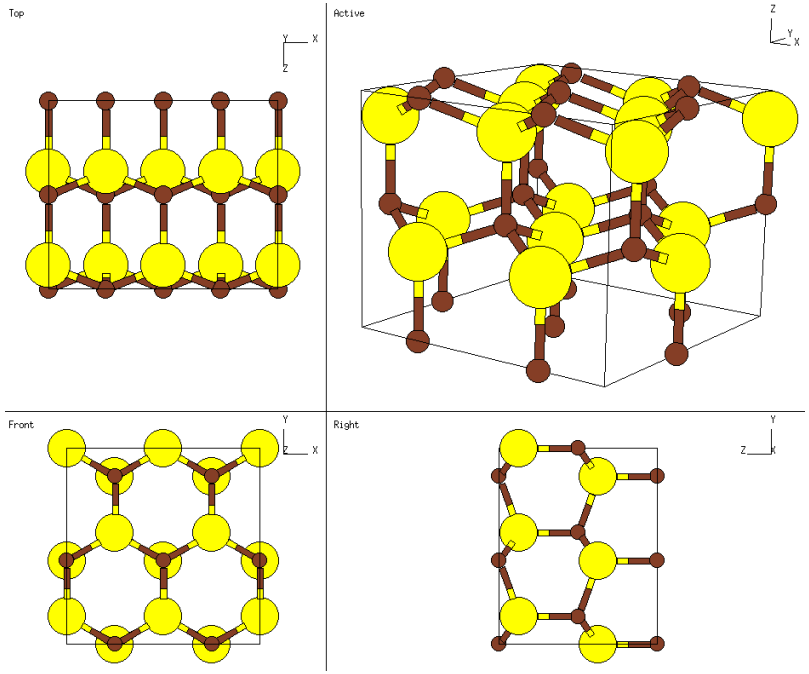


Mohs scale

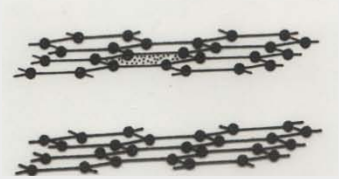
Thermal conductivity: 23.2 W/cm.K
(N.B. distinction of cubic zirconia)

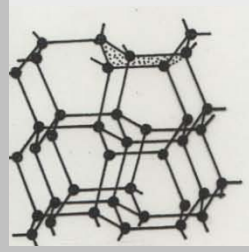
Lonsdaleite – ZnS (Wurtzite)



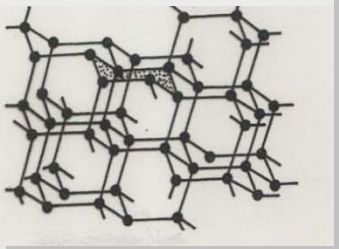


graphite

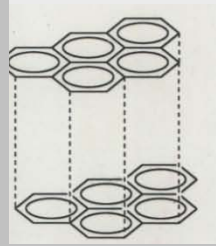




lonsdaleite



cubic

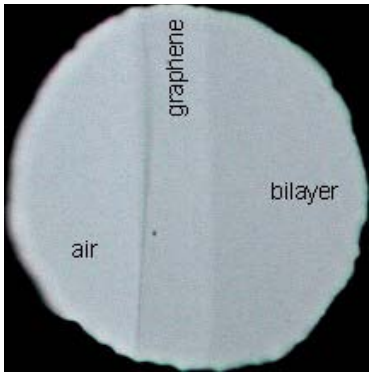


GRAPHENE


Andre Geim and Konstantin Novoselov
Nobel Prize 2010

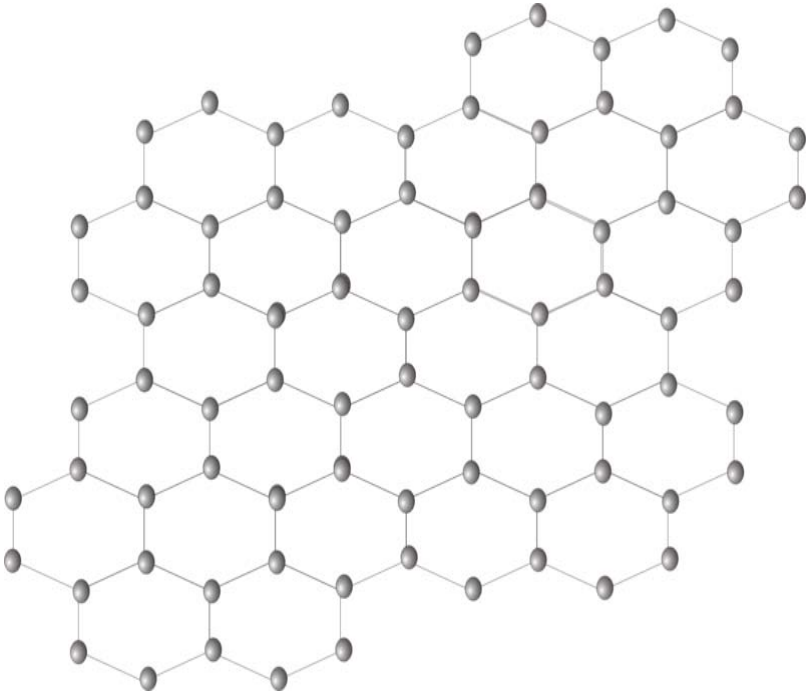
Novoselov, Geim* et al.,
Electric field effect in atomically thin carbon films.
Science **306**, 666-669 (2004)

Scotch tape
CVD on Cu support



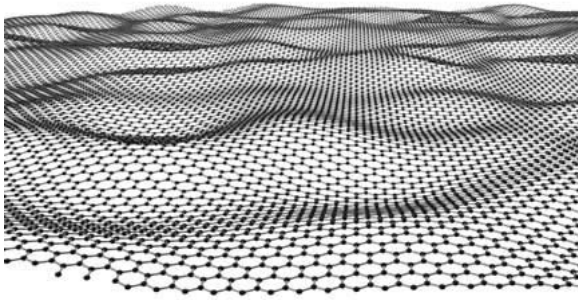
Opt. microscope: graphene on Si/SiO_2

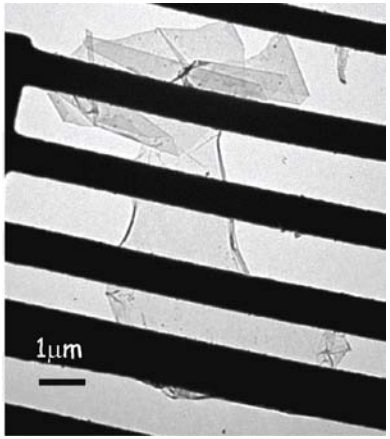
SEM of graphene sheet on Si wafer

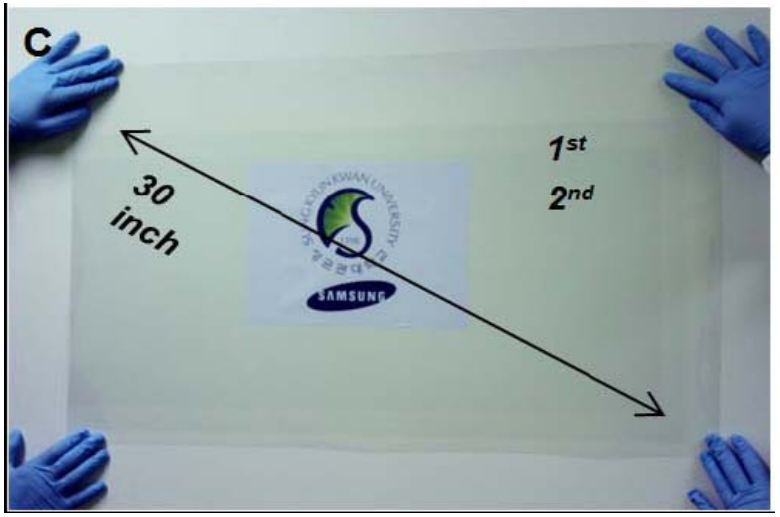


From graphite to graphene….

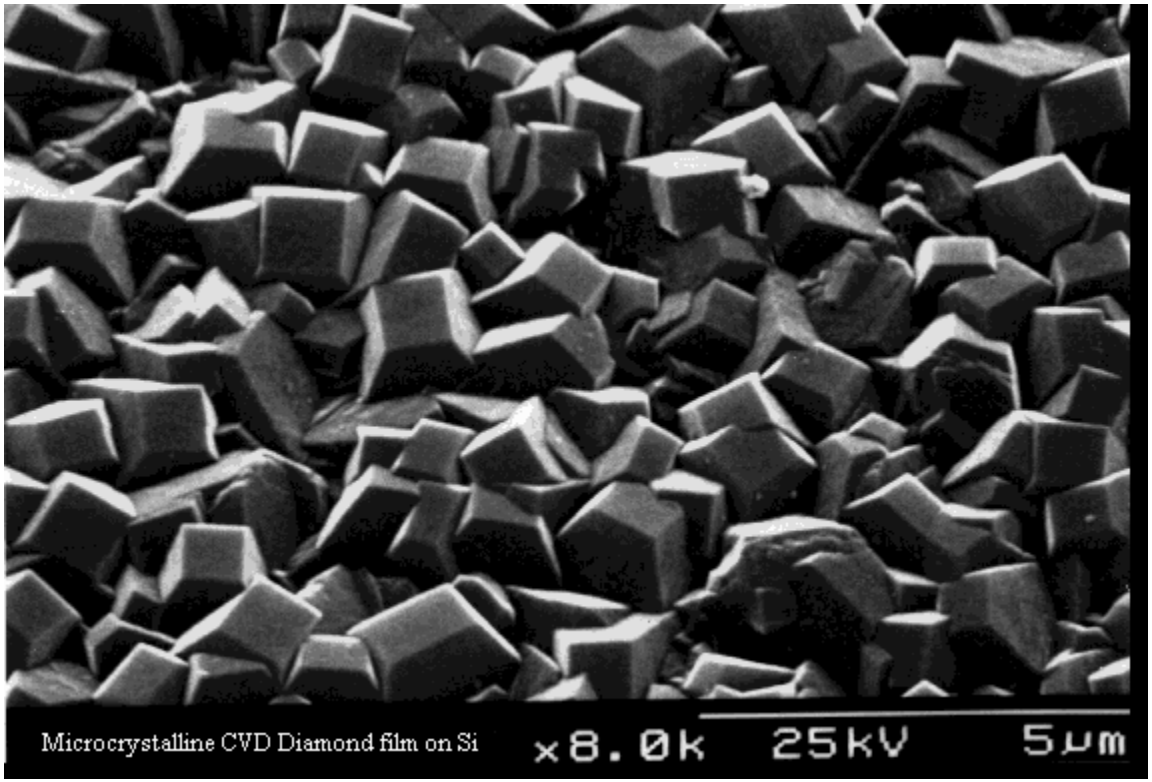
+







Diamond produced by CVD from CH_4 and H_2



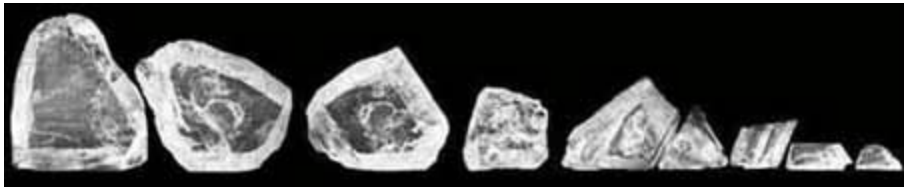
Famous diamonds: Cullinan (Star of Africa)

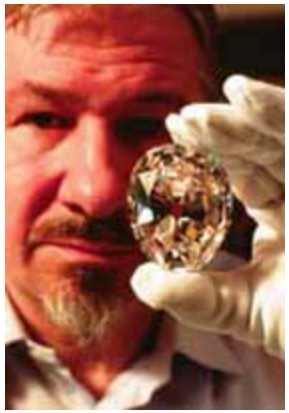
3106 carats (621 g): (1905) Transvaal

Thomas Cullinan Frederic Wells

Famous diamonds: Cullinan (Star of Africa)

3106 carats: Thomas Cullinan (1905) Transvaal

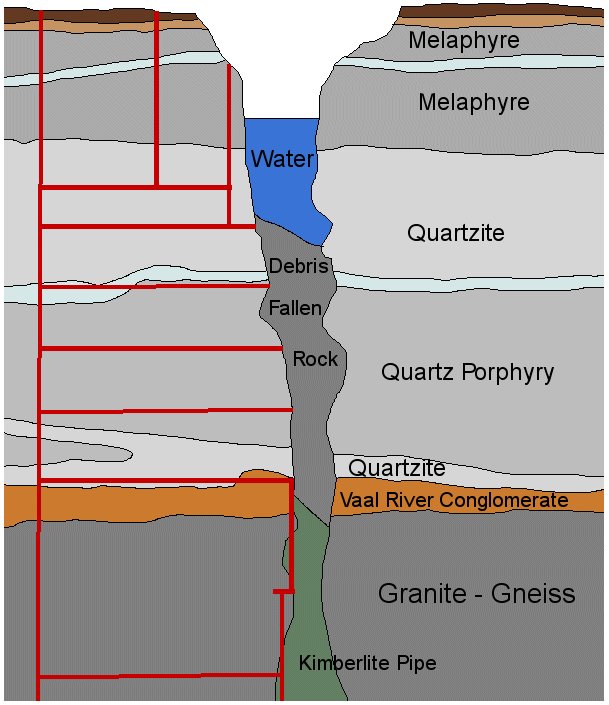




(1 carat = 0.2 g)

Cullinan I (Star of Africa, 530.20 carats)
54 x 44 x 29 mm

Cullinan II (317.40 carats)

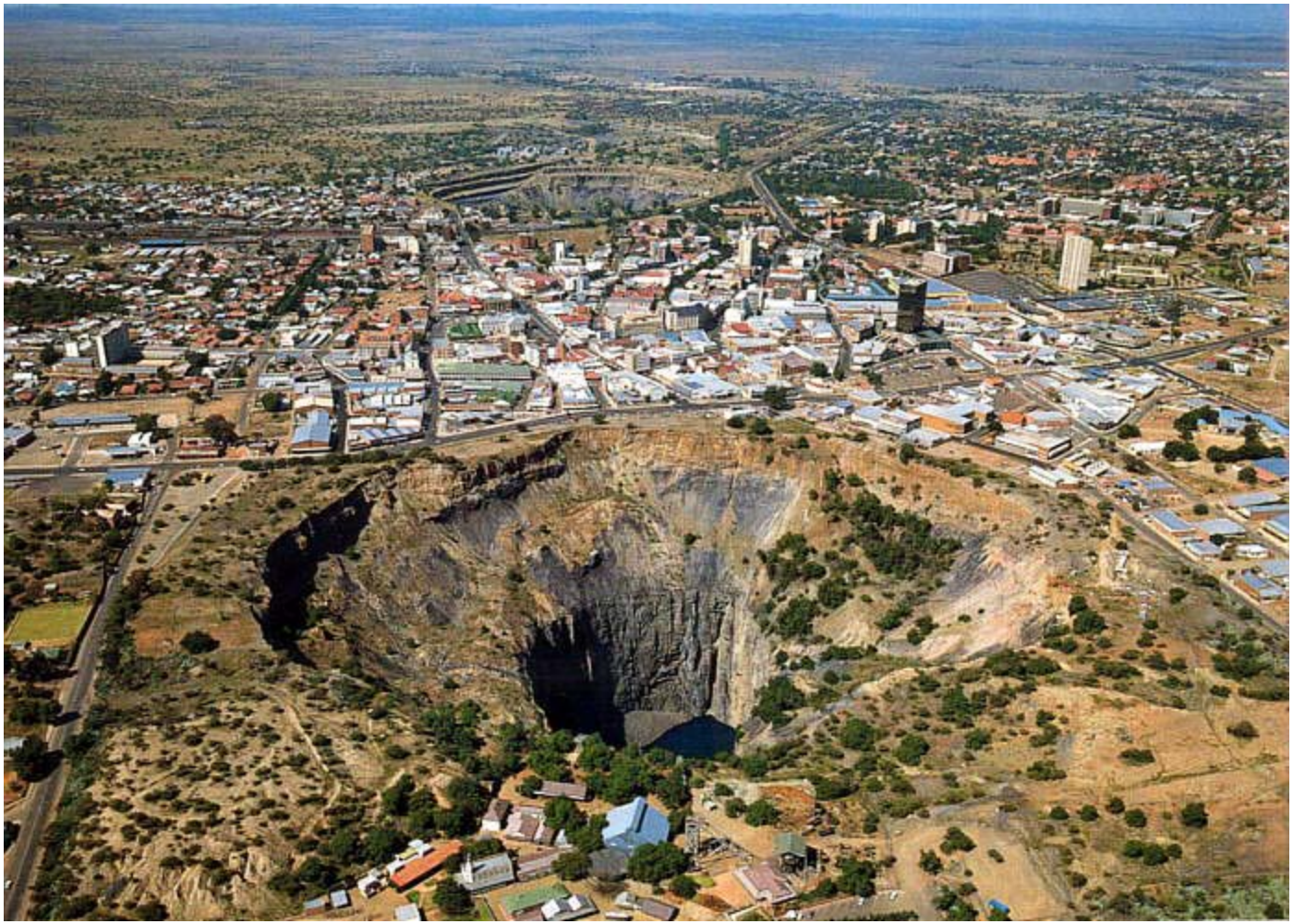


Kimberley's Big Hole
The biggest (?) man-made hole

Originally: 240m deep
Now: 215m deep
40m of ground water: 175m visible
Perimeter 1.6 km; Area: 17 hectares

Brief history
1866: first "Eureka" 21.25 carat
1871: Johannes Nicolaas and Diederik Arnoldus de Beer
1888: Cecil John Rhodes De Beers Consolidated Mines Ltd.
14.8.1914: The mine was suspended

22.5 million tons of earth => 2.722 tons of diamonds



Huge open pit mine near Mirny, Russia, East Siberia
525 m deep, 1200 meters in diameter.

This giant truck, BELAZ (200-220 ton payload)
Length 13,360 mm, Width 7,780 mm, Height 6,650 mm

Elemental carbon: hybridization state of C-atoms

sp^3 hybridization: diamond, lonsdaleite

sp^2 hybridization: graphite, fullerene

But carbon can also be hybridized sp^1

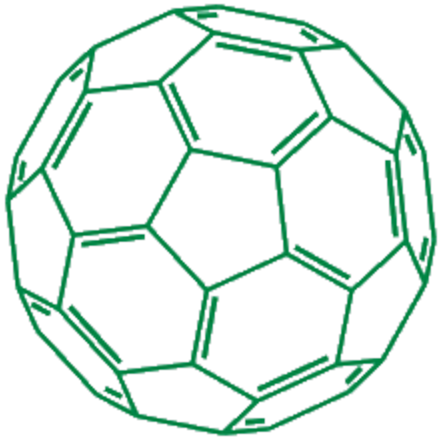
⇓

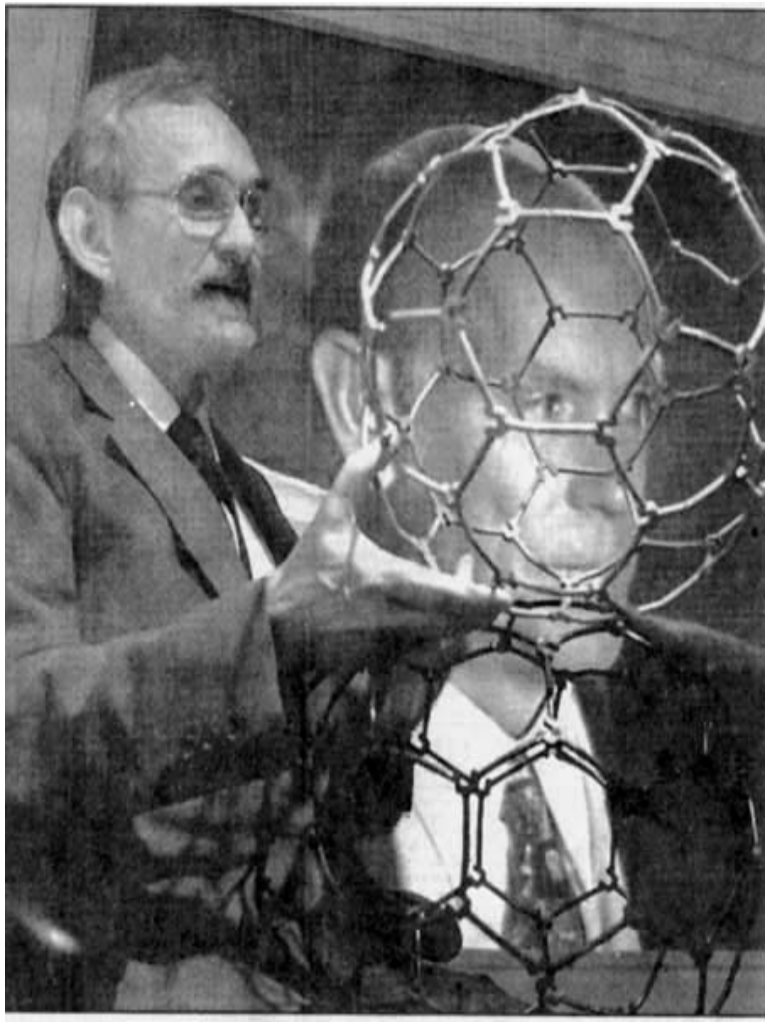
Carbynes

⇒ **Polyyne:** alternating single and triple bonds $-C \equiv C - C \equiv C -$

⇒ **Cumulene:** sole double bonds $= C = C = C =$

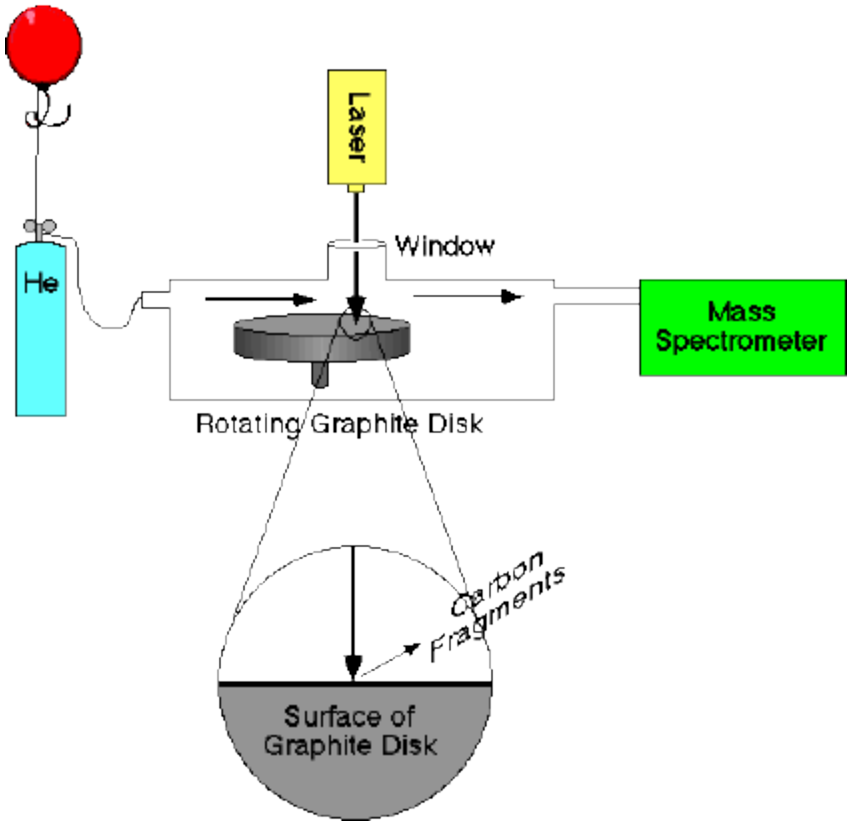
Fullerene: Nobel Prize Kroto, Smalley, Curl (1996)





C_{60} fullerene
(buckminsterfullerene)

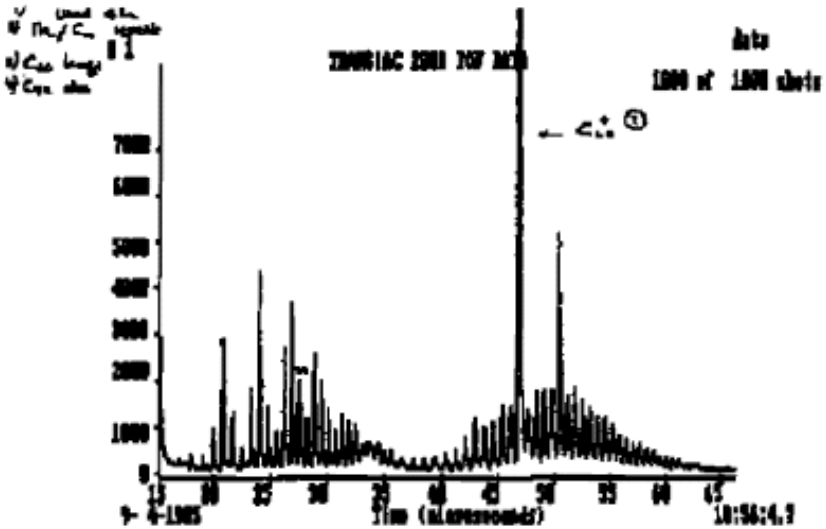
Apparatus for generating fullerene



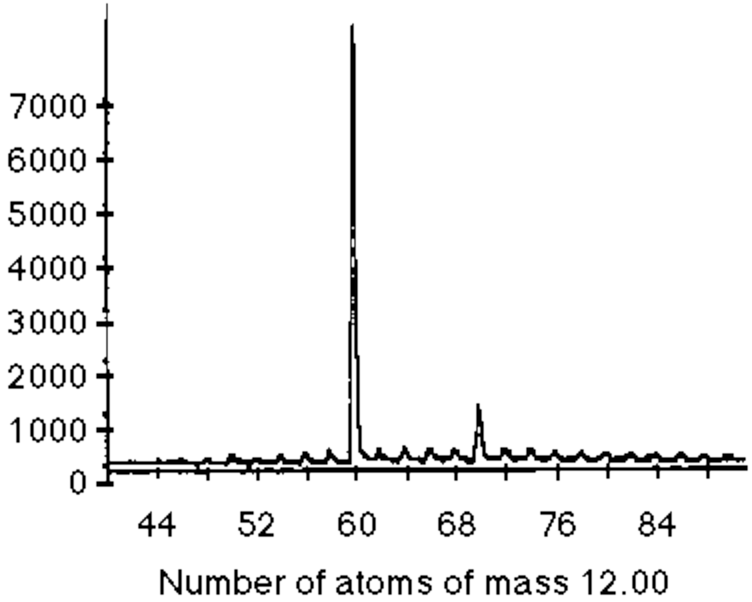
***Kroto* et al. (1985)**

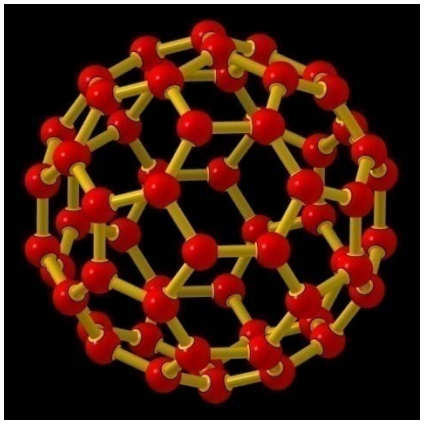
vaporization of graphite by laser (Nd-YAG 10 mJ/5ns)

supersonic beam of C-clusters in He

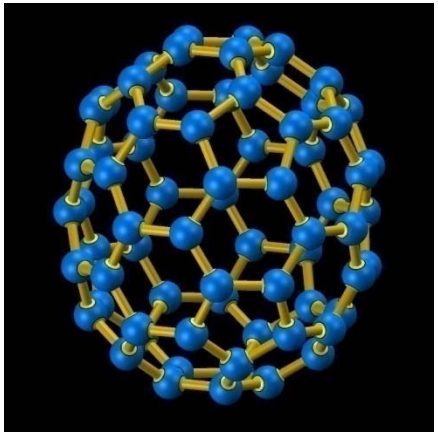


Mass spectrum

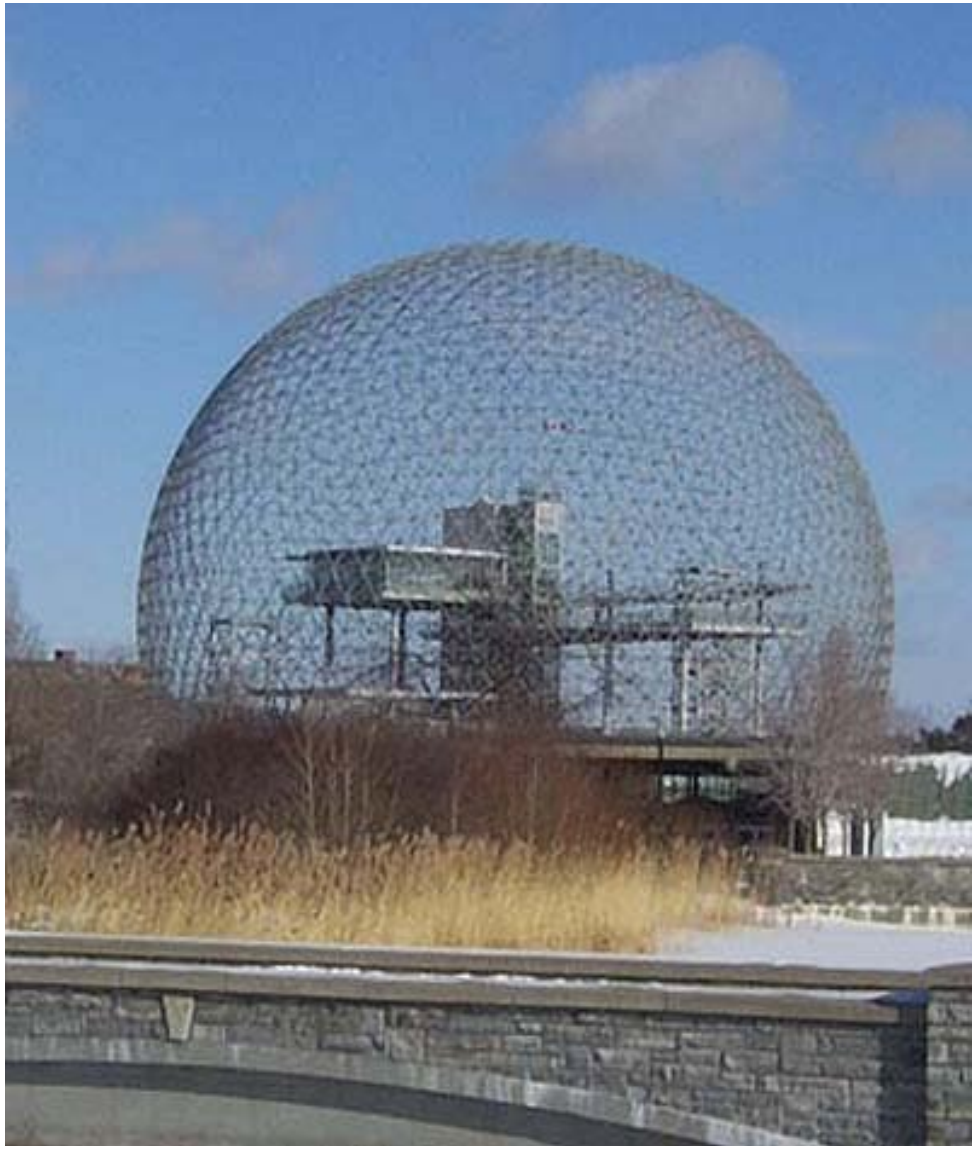




C_{60} fullerene

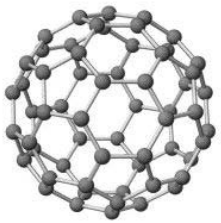


C_{70} fullerene

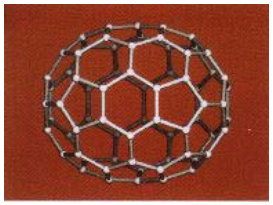


Expo '67 American Pavillion by R. Buckminster Fuller,
on Ile Sainte-Hélène, Montreal

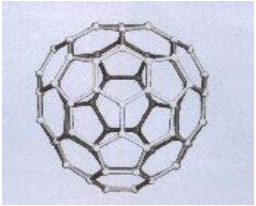
Fullerene gallery



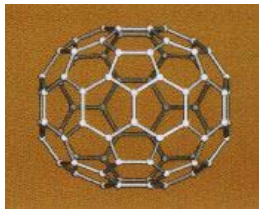
C_{60}



C_{70}



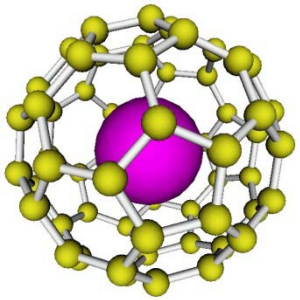
C_{76}



C_{78}

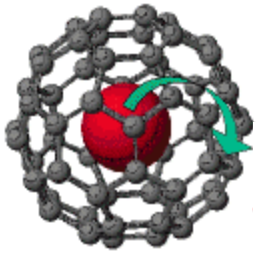
C_{82}

and many others.....

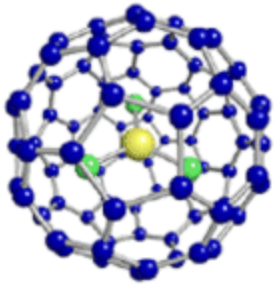


Endohedral fullerenes:

$La@C_{82}$



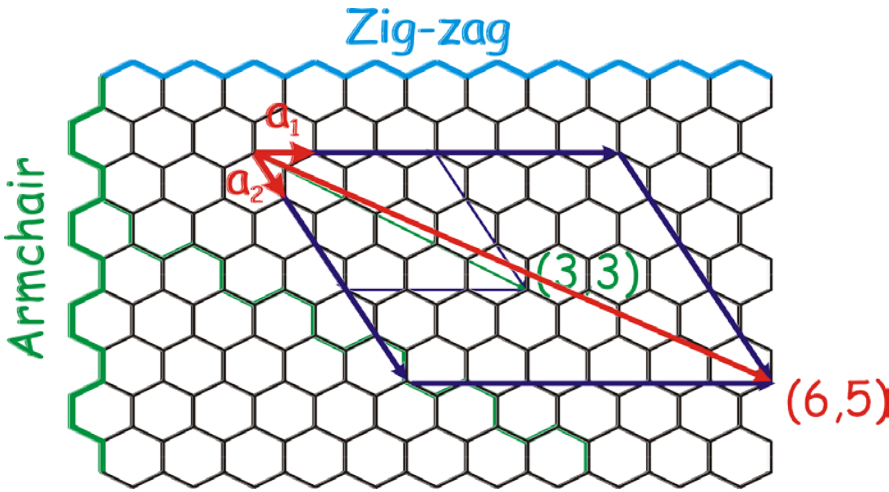
$Sc_3N@C_{82}$

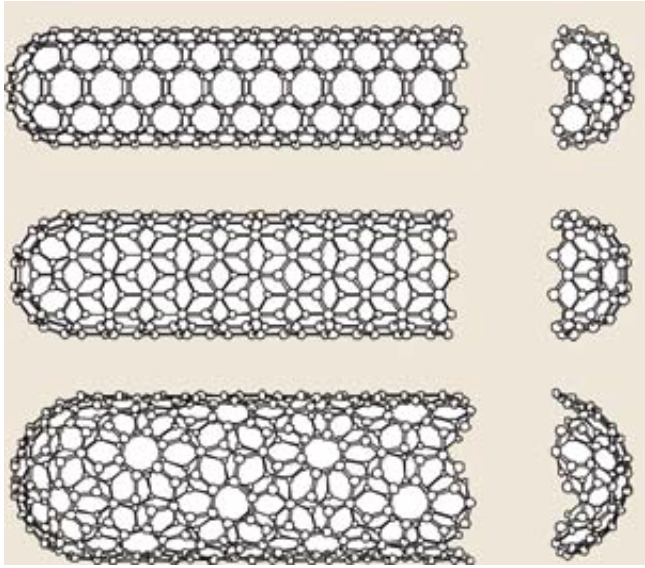


Chirality: (*n, m*)

chiral vector $C_h = na_1 + ma_2$
a_1 , a_2 …. unit vectors of the hexagonal structure

→ nanotube definition (n,m)





Armchair nT
(*n*=*m*) metal

Zig-zag nT
(*n*-*m*) = 3*i* metal
(*n*-*m*) ≠ 3*i* semi.

Chiral nT
(*n*-*m*) = 3*i* metal
(*n*-*m*) ≠ 3*i* semi.

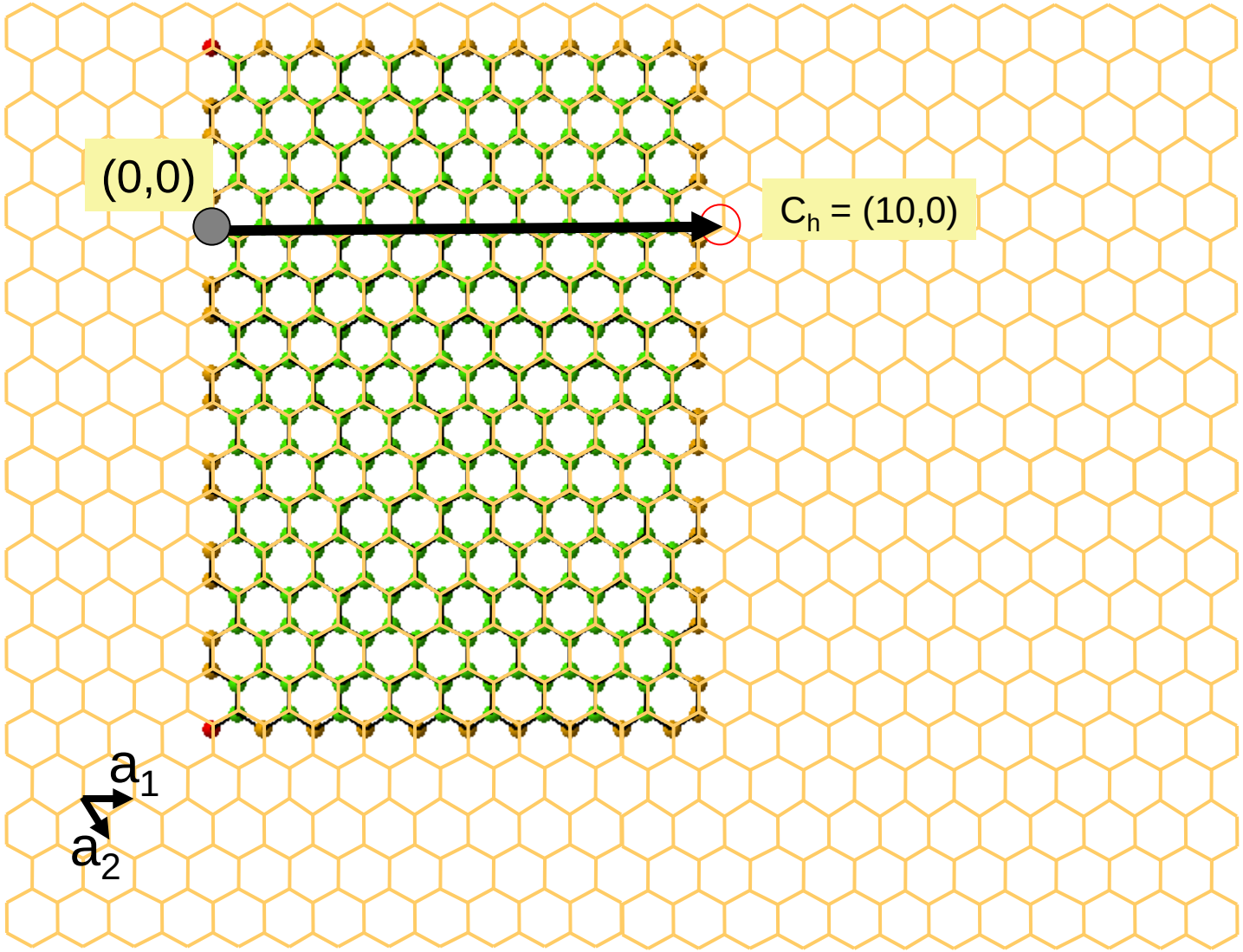
nanotube diameter d_0

$$d_0 = \frac{a_{c-c}\sqrt{3}}{\pi}\sqrt{N}$$

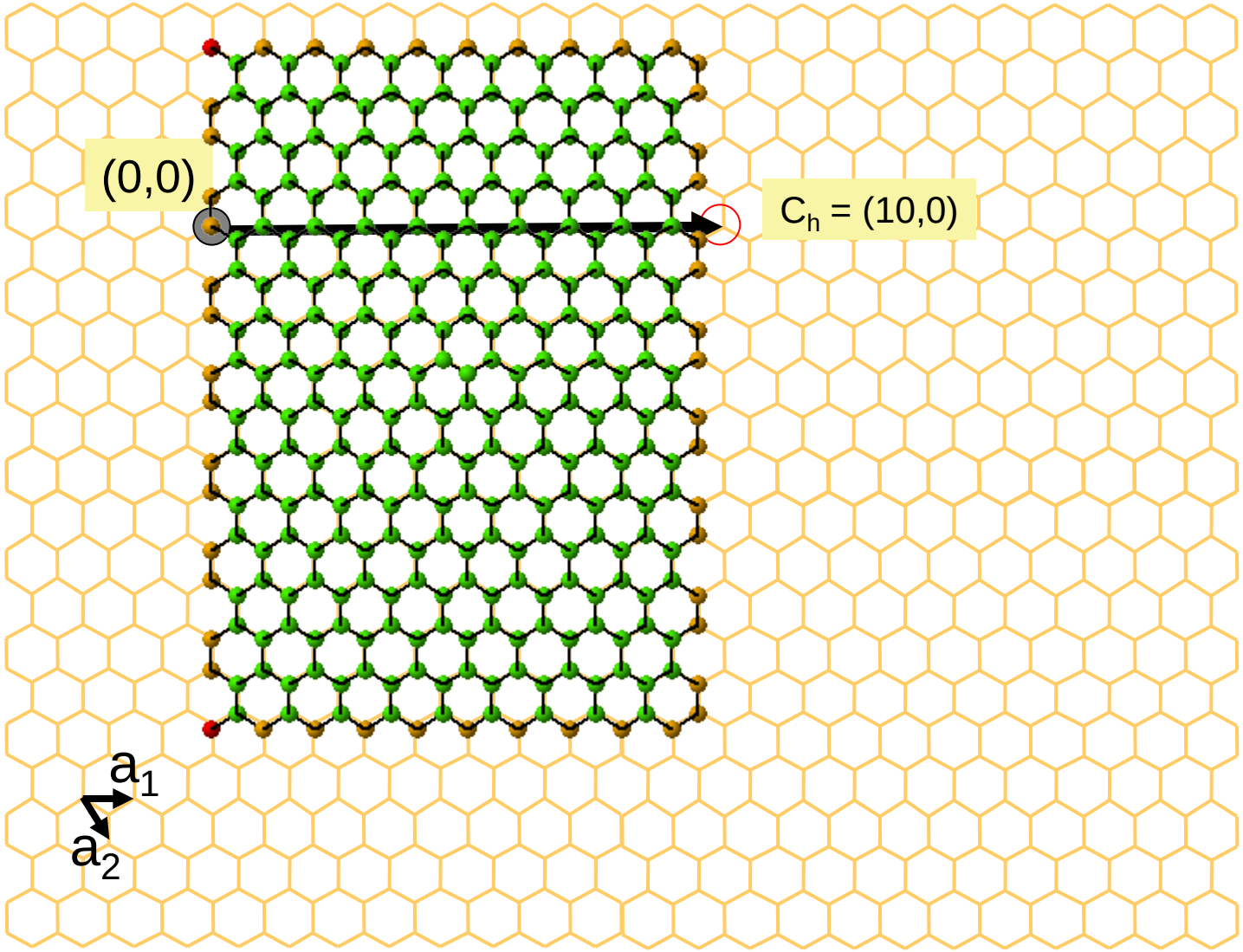
$a_{C\text{-}C}$ = 1.42 Å

$N = n^2 + nm + m^2$

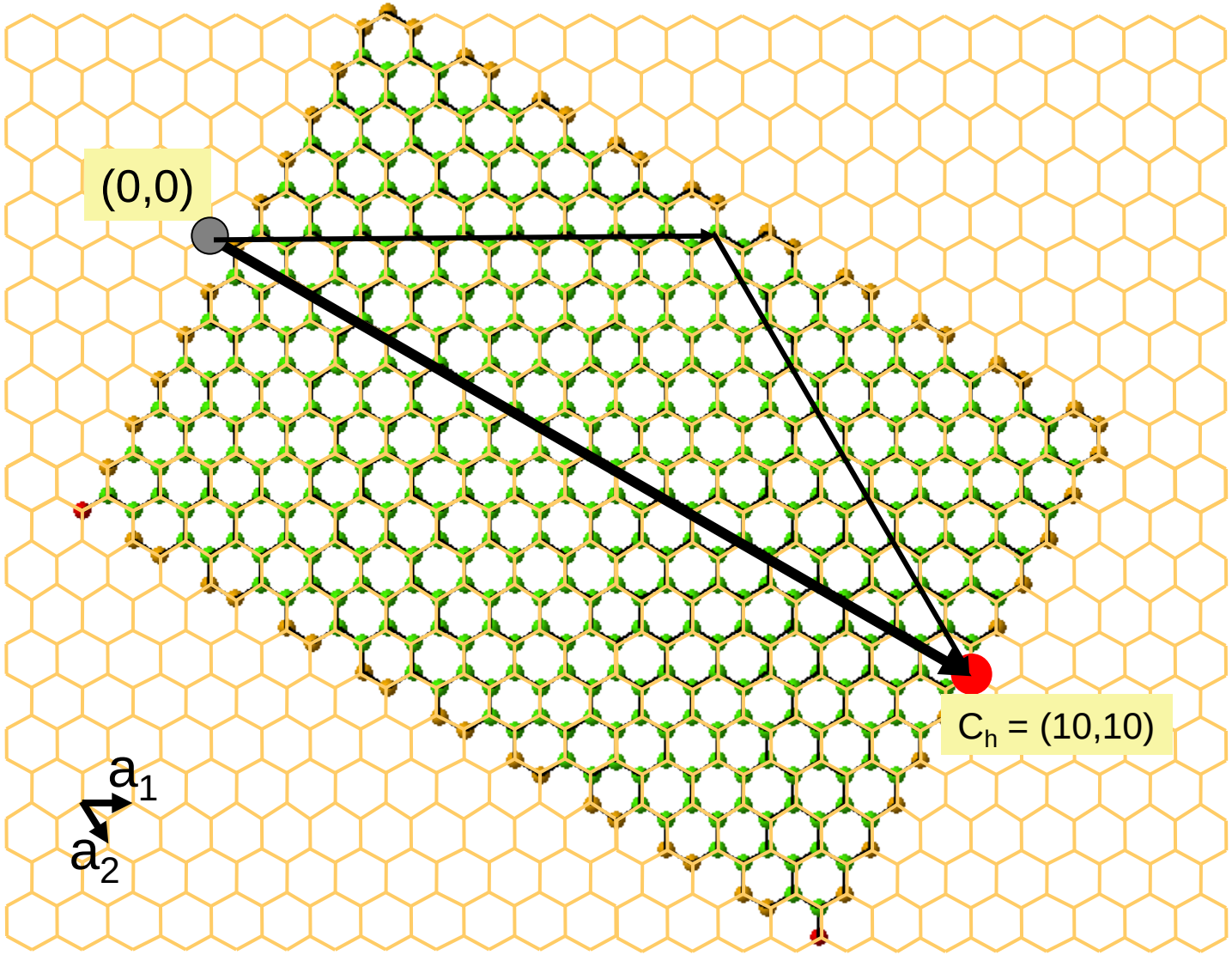
Rolování (10,0) SWNT (zig-zag)



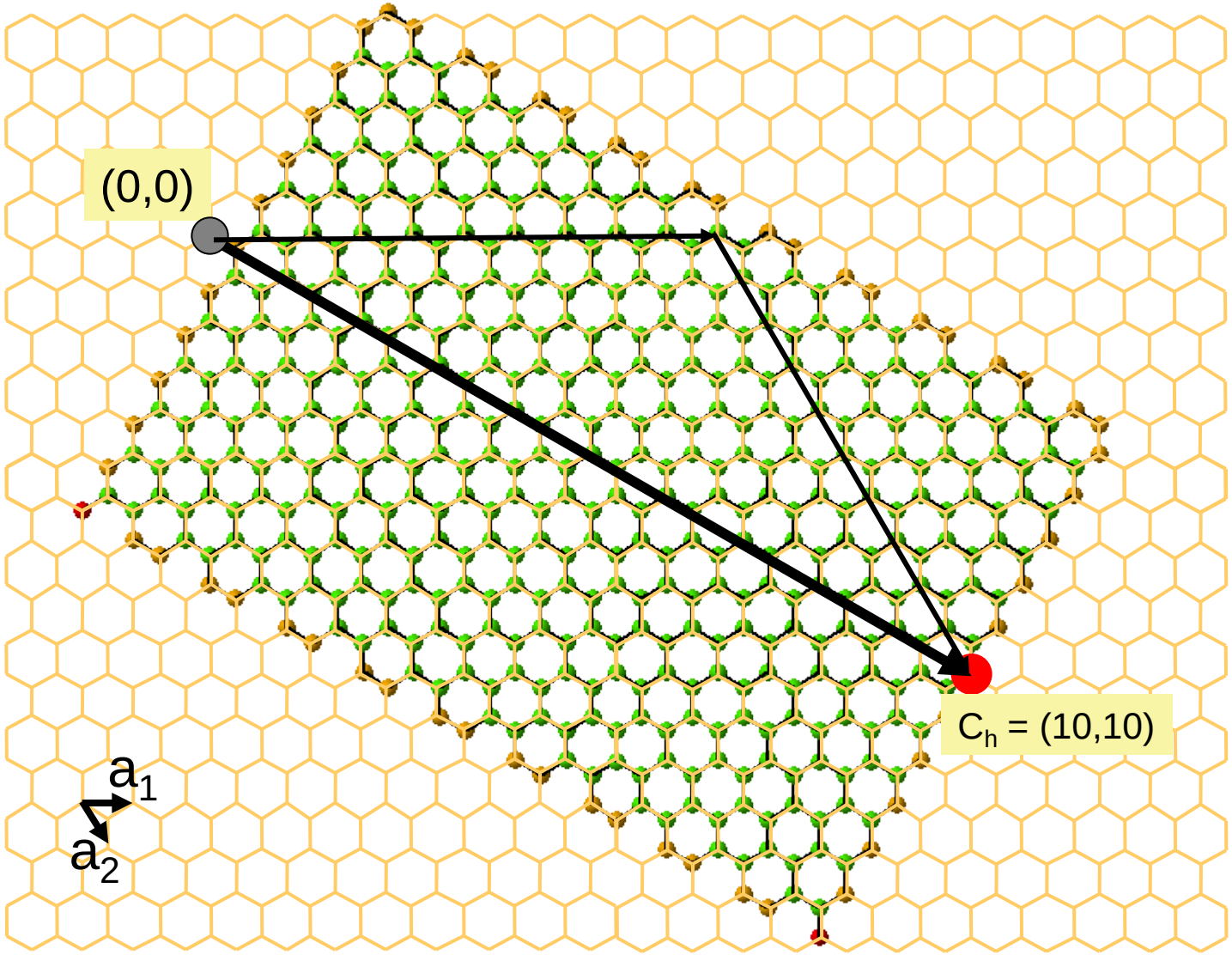
Rolování (10,0) SWNT (Animace)



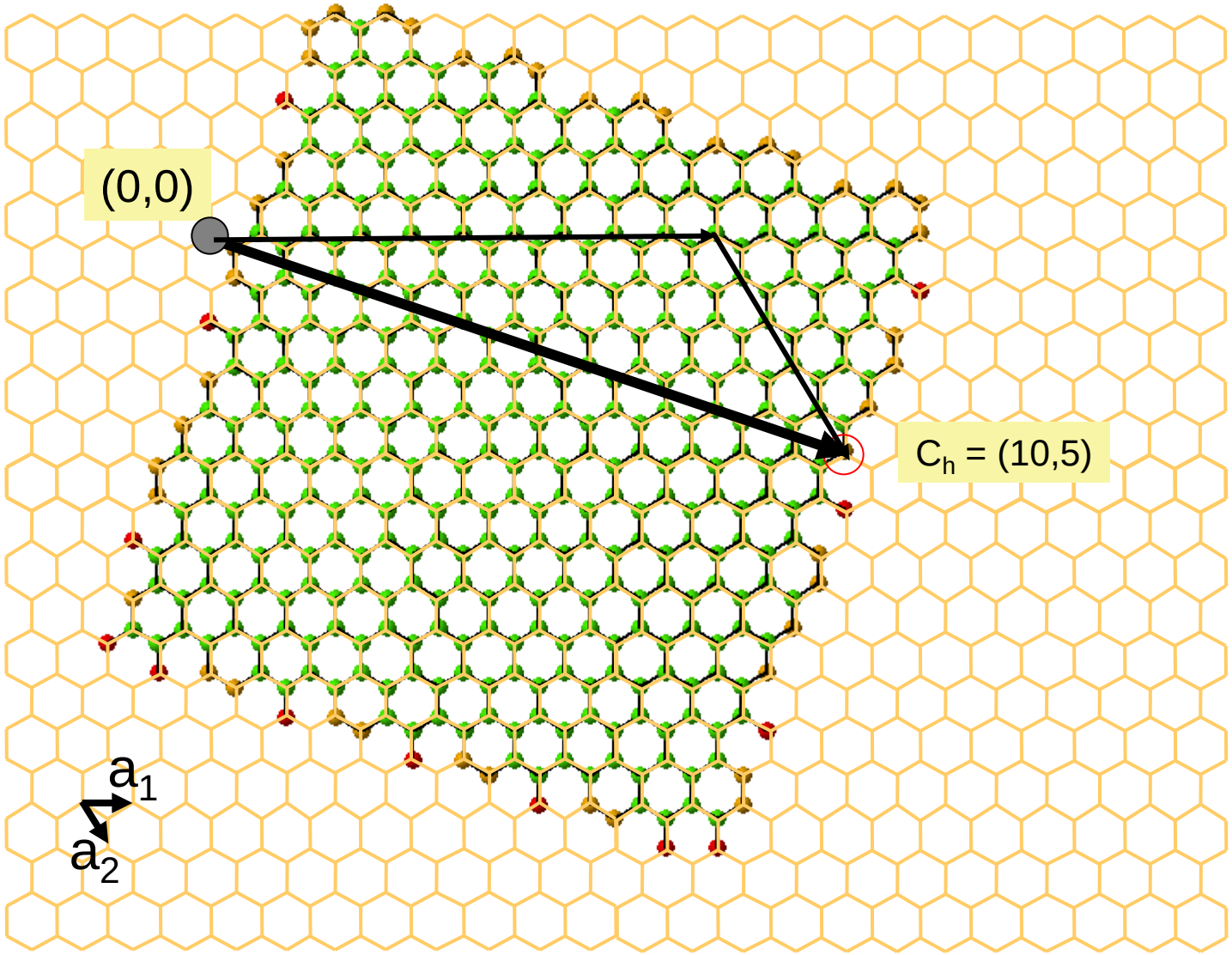
Rolování (10,10) SWNT (židlička)



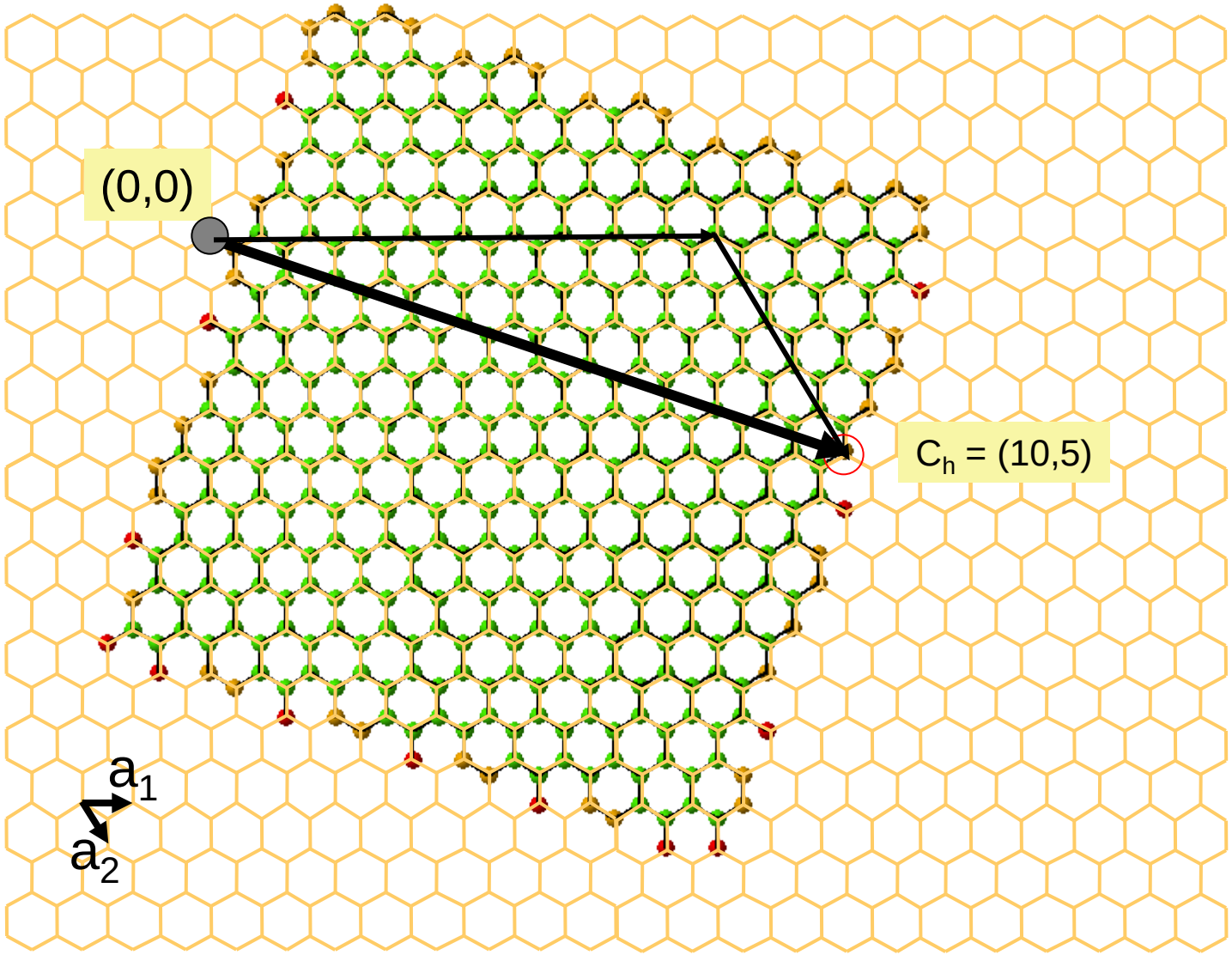
Rolování (10,10) SWNT (Animace)



Rolování(10,5) SWNT (chirální)

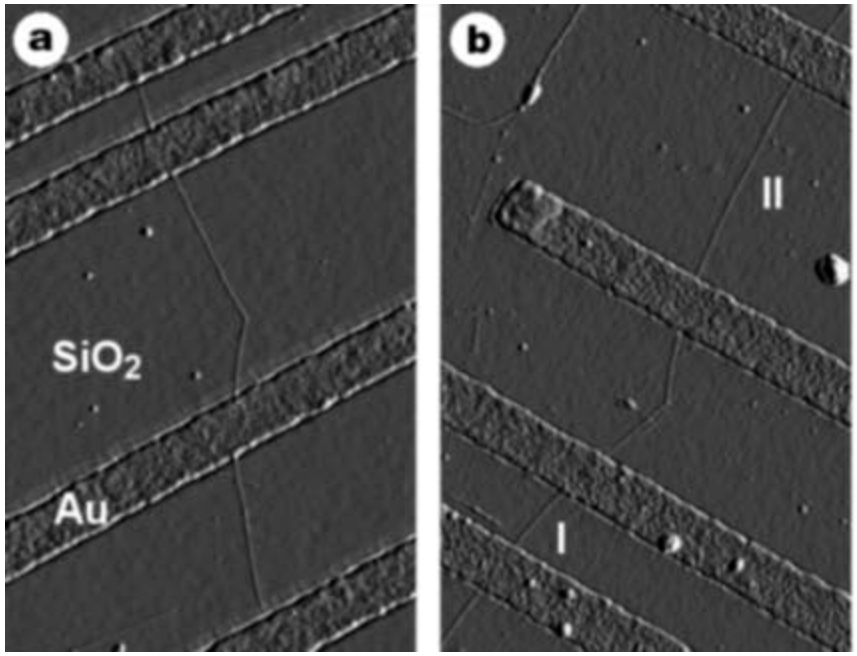


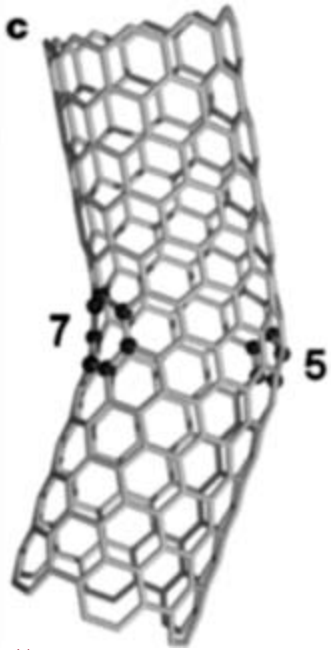
Rolování (10,5) SWNT (Animace)



NANO-DIODA: přechod kov-polovodič v nanotubě

Cik-cak (polovodič)





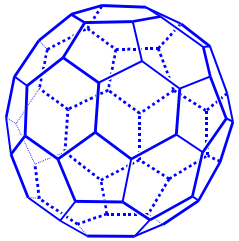
Místo zlomu
(5- & 7-úhelník)

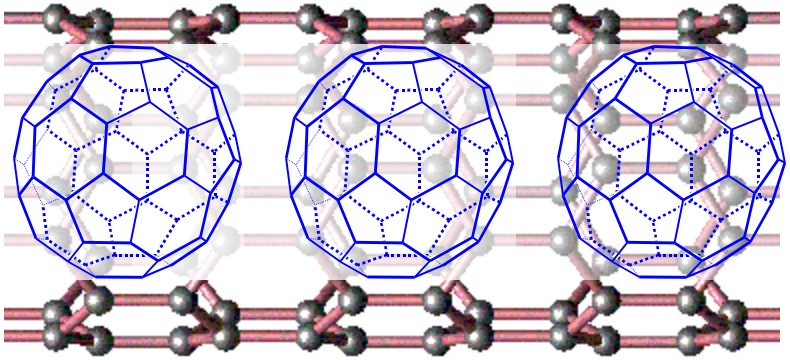
Židlička (kov)

AFM “zlomené” nanotuby na křemíku s Au kontakty

Yao, Z. et al. *Nature* **402**, 273 (1999)

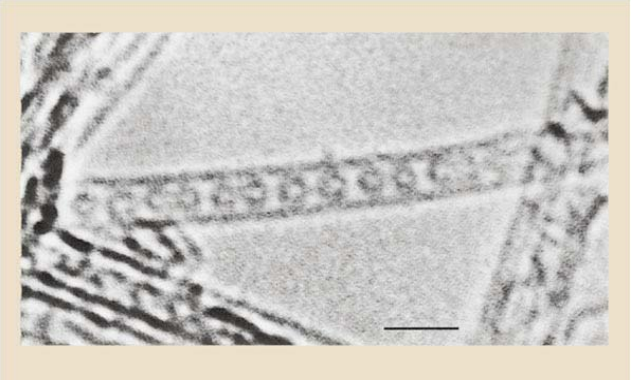
Formation of fullerene peapod (C_{60}@SWCNT)

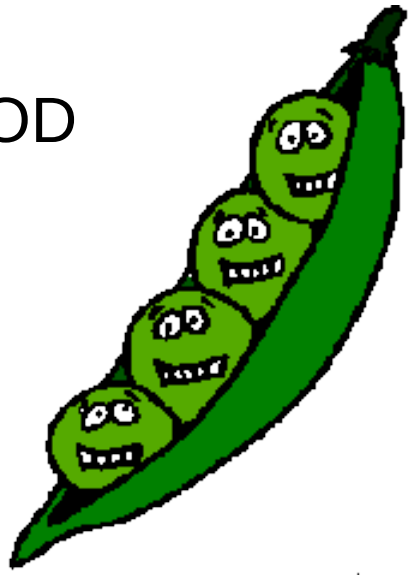




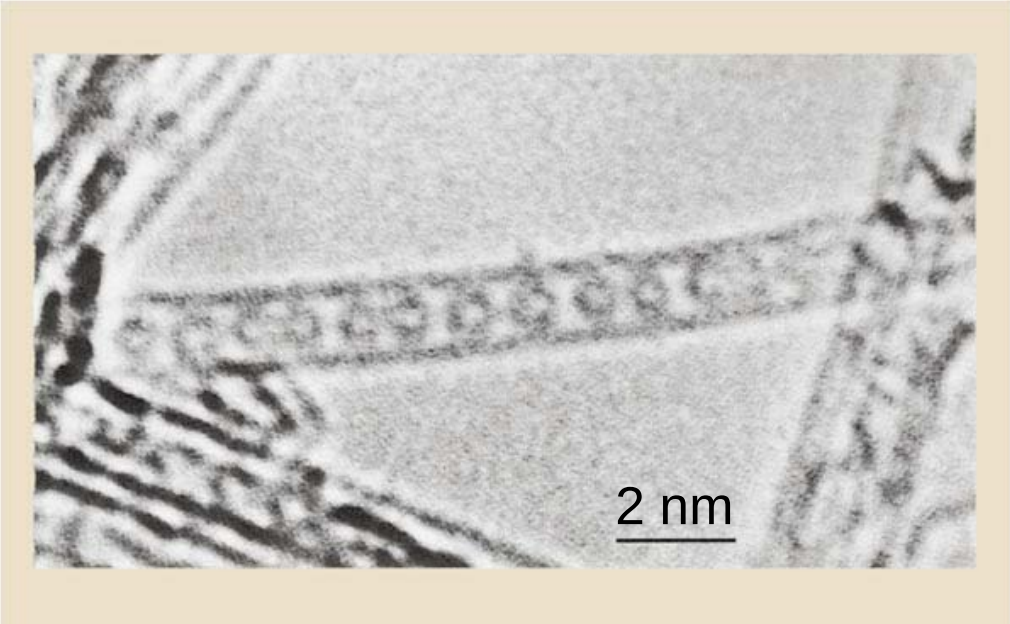
C_{60} (g)

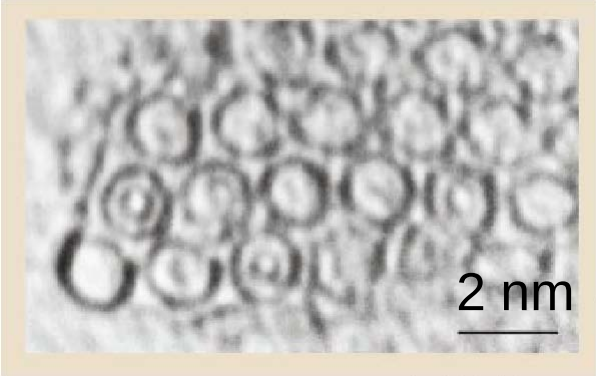
FULLERENE PEAPOD



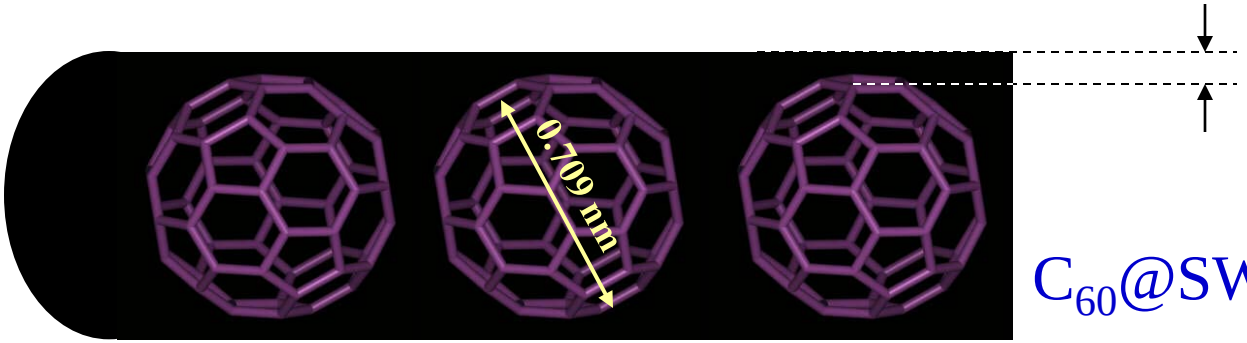


Fullerenový lusk C_{60}@SWCNT



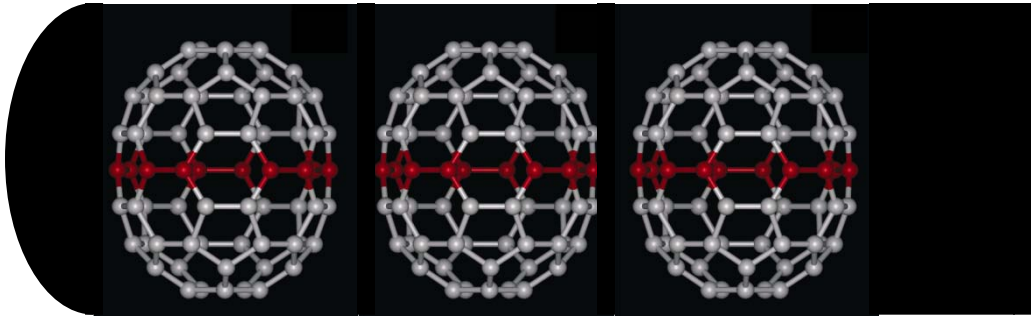


Smith,B.W.; Monthioux,M.; Luzzi,D.E., *Nature* **396**, 323 (1998)



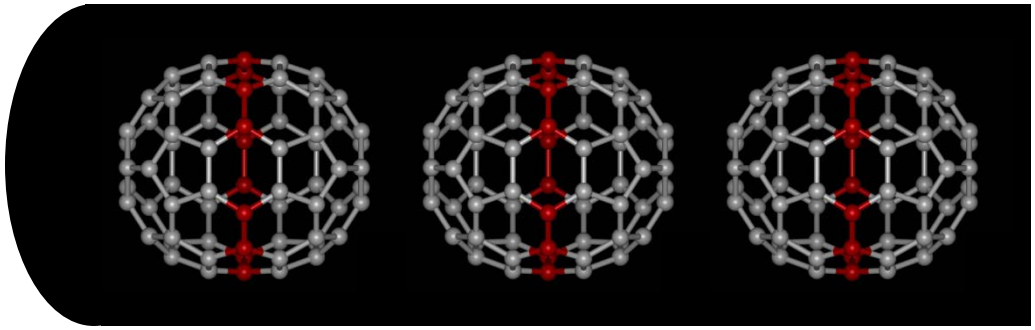
0.3 nm

C_{60}@SWCNT, d = 0.97 nm



C_{70}@SWCNT, d = 1.0 nm

2 allotropické 2-D fáze

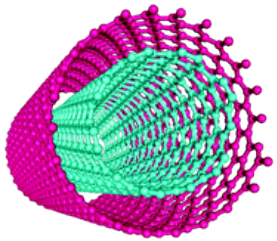


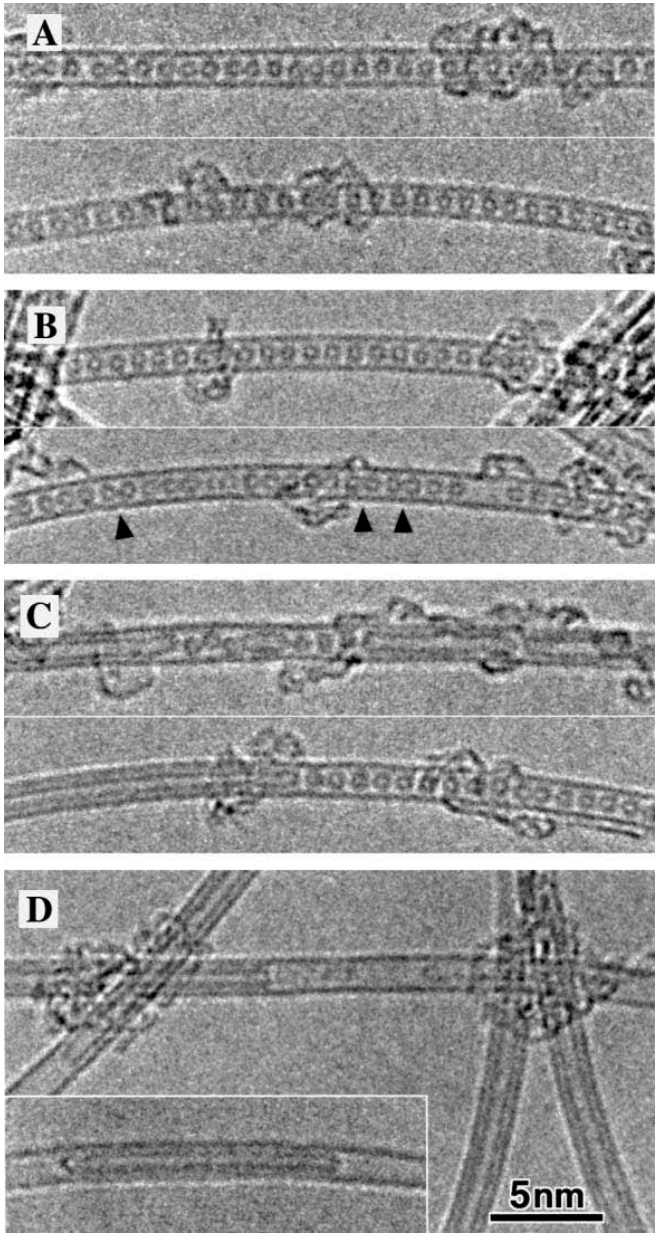
C_{70}@SWCNT, d = 1.1 nm

Dvojstěnné nanotuby

C_{60}@SWCNT

DWCNT





RT

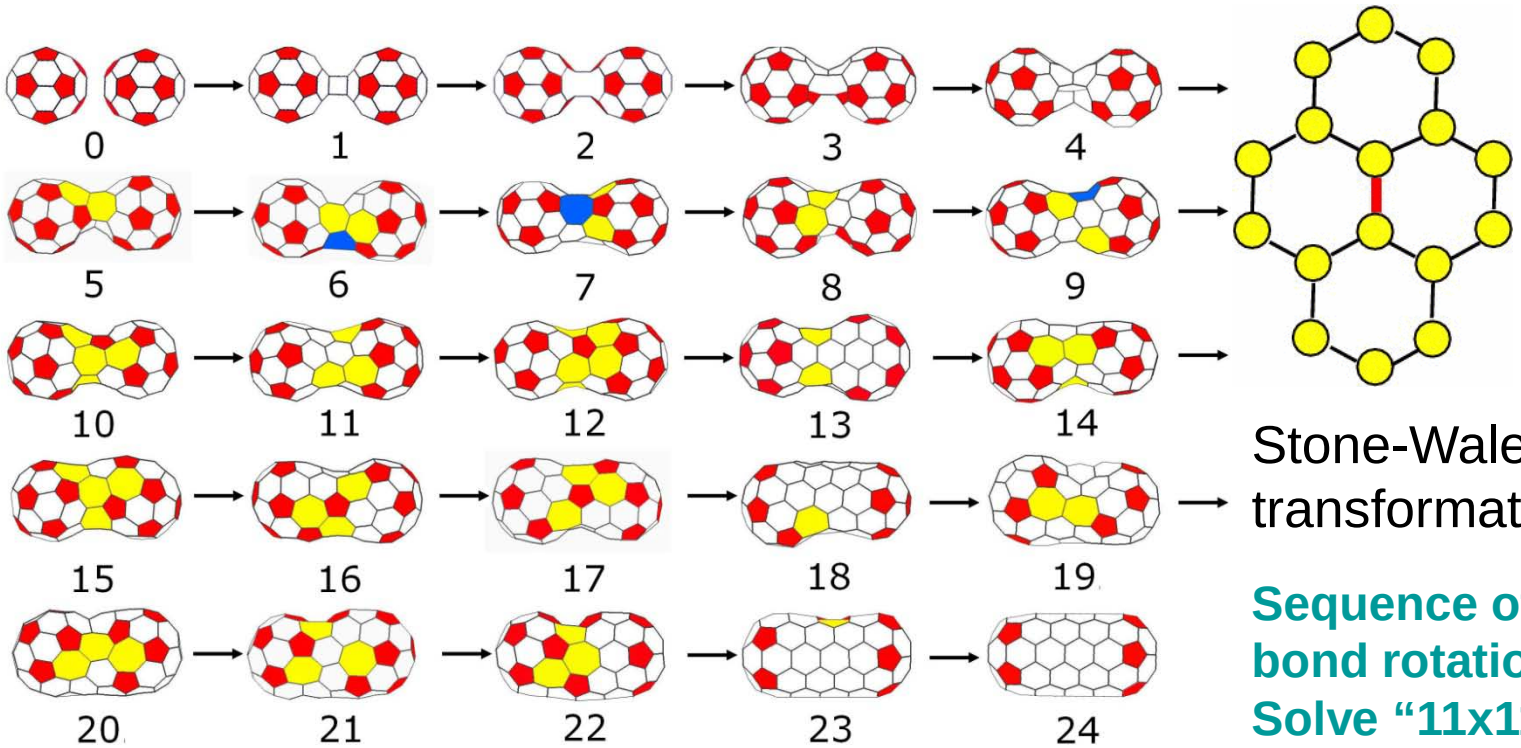
800 °C

1000 °C

1200 °C

Stone-Wales rearrangement pathway for fusion of fullerenes

[Hiroshi Ueno, Shuichi Osawa, Eiji Osawa, and Kazuo Takeuchi, Fullerene Science And Technology **6**, 319-338 (1998)]

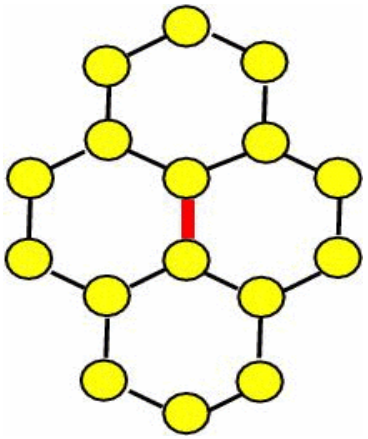


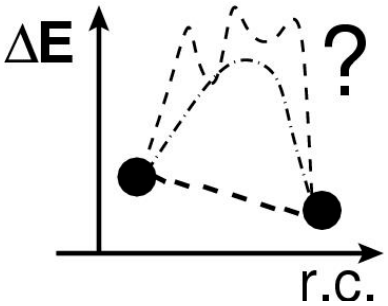
Stone-Wales transformation

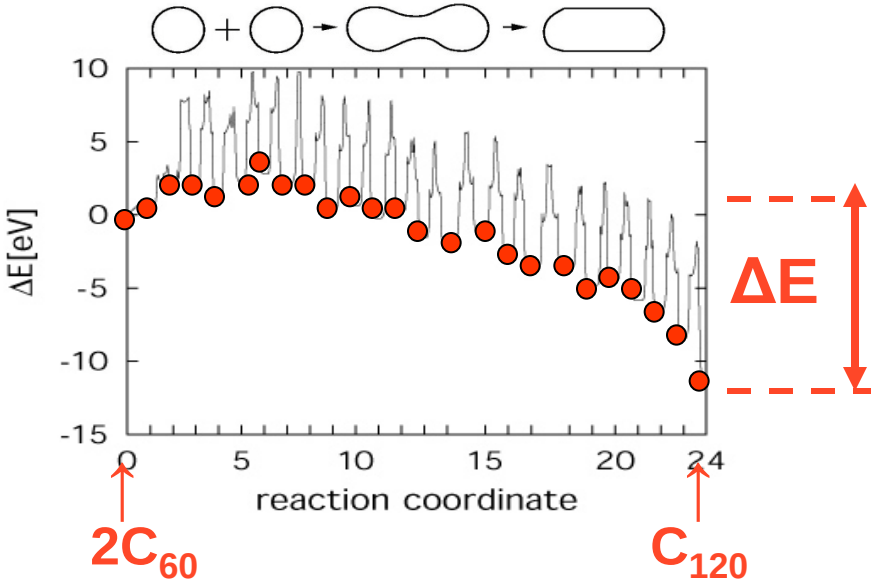
Sequence of bond rotations: Solve "11x11x11 Rubik's Cube" puzzle

- Do we understand the energetics?

Do we understand the Stone-Wales process?



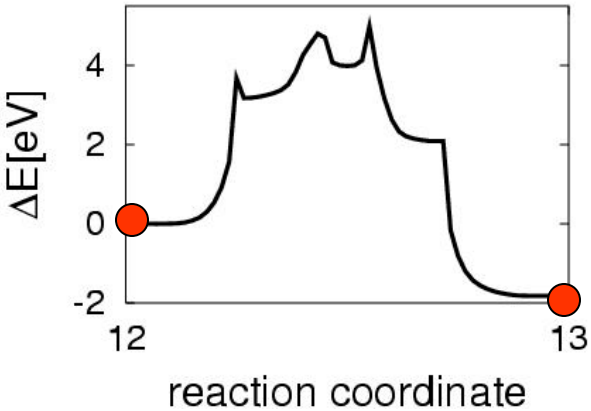




Search in 360-dimensional configuration space using string method:

Stone-Wales
is a multi-step process
•Activation barriers
do not exceed ≈ 5eV

Multi-step process



Aplikace uhlíkových nanotub

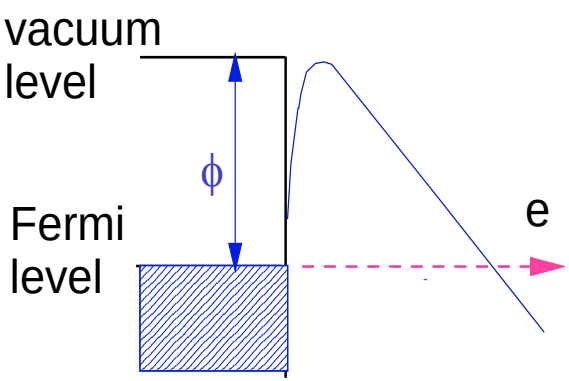
- Ukládání vodíku ?
- Mikroelektronika
- Autoemise: display (Samsung)
- Mech. vlastnosti, C/C kompozity
- Superkondenzátory

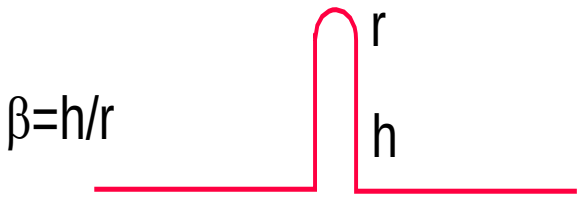
Uniqueness of CNTs

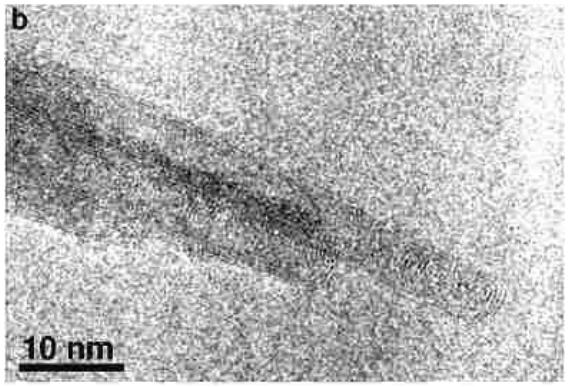
Unique properties of

- Sharp - aspect ratio – field emission, electrical composites
- Highest current density 10^9 A/cm^2 – Vias, FE,
- Ballistic electron transport - FETs
- Highest Youngs modulus, ~1TPa - composites
- Highest thermal conductivity, 4000 W/m.K - composites
- Electrode potential range/surface area – sensors, supercaps

Field Emission







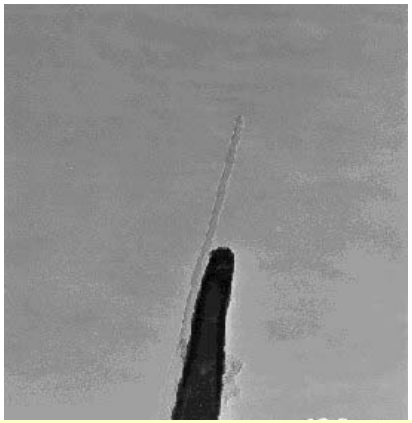
- Field emission is electron tunnelling from solids under very high local field (10^8 V/m)
- Obeys Fowler-Nordheim eqn

$$J = aE^2 \exp\left(-\frac{b\phi^{3/2}}{\beta E}\right)$$

CNTs good because -

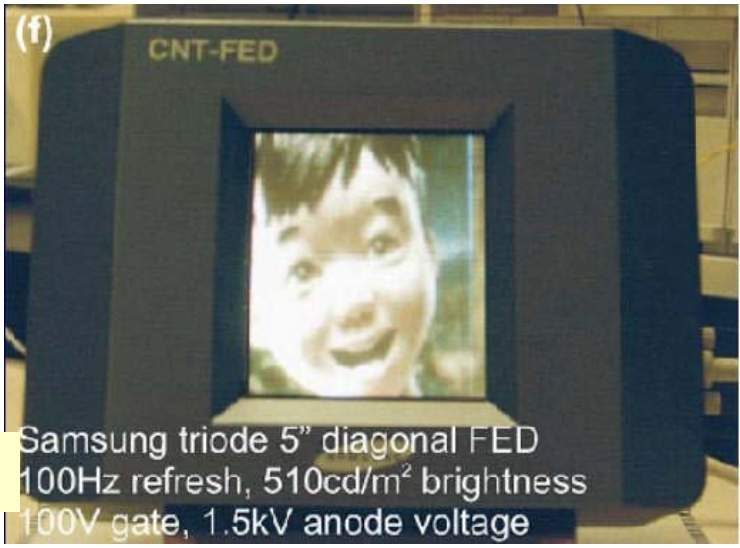
- Large $\beta = h/r$
- High physical stability of carbon vs. sputtering /erosion
- Good chemical stability vs. poisoning
- High max current density before electromigration (10^9 A/cm^2, 1uA per CNT)

Field Emission Applications



E-gun for SEM

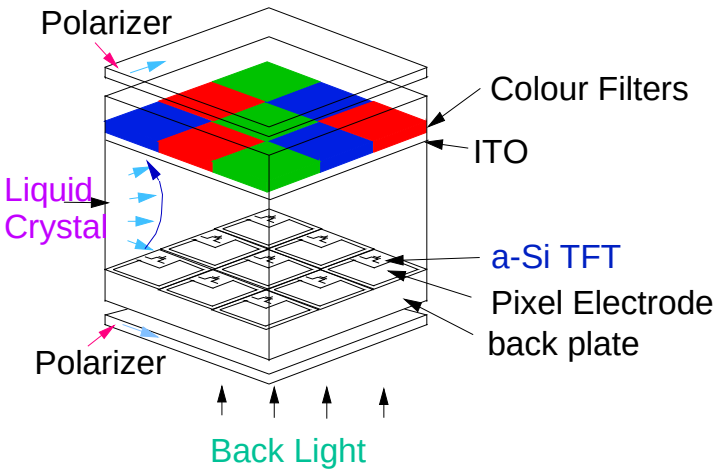
Microwave Amplifier

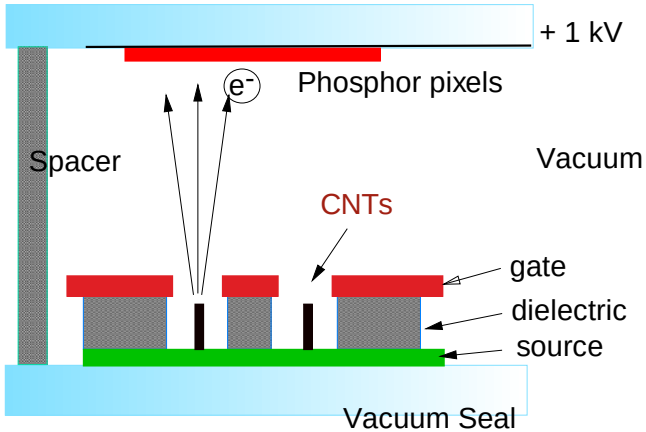


Displays

X-ray sources

Field Emission Displays



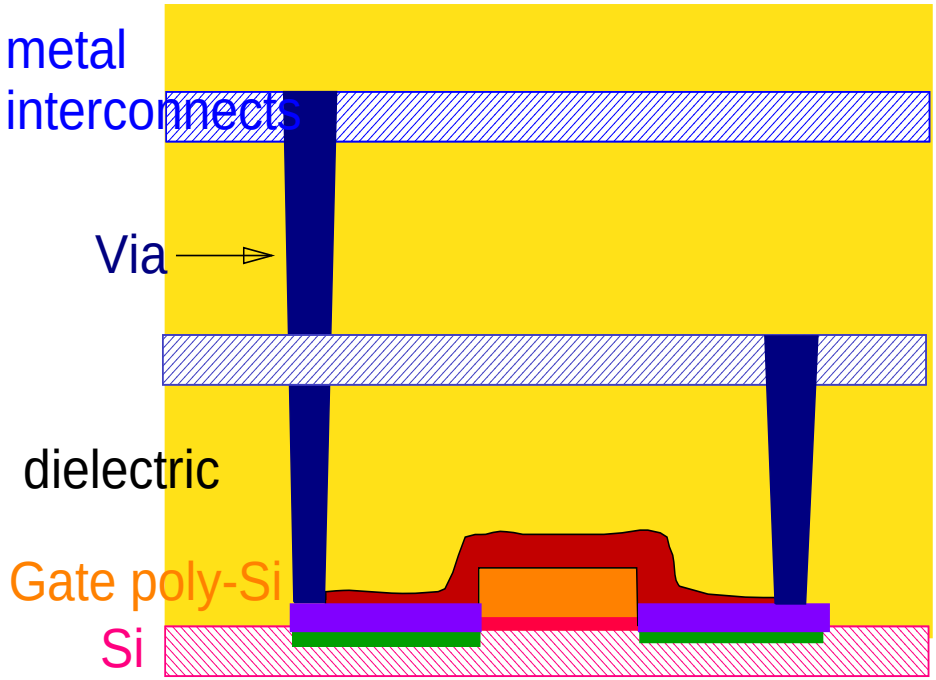


- **Displays = $40 bn market**

- Field emission from a CNT tip arrays

- Advantages compared to LCD
  - *Video rate*
  - *Brightness*
  - *Power efficiency* *LCD=6%*
  - Viewing angle
  - Temp range

Electronics – Interconnects in ICs

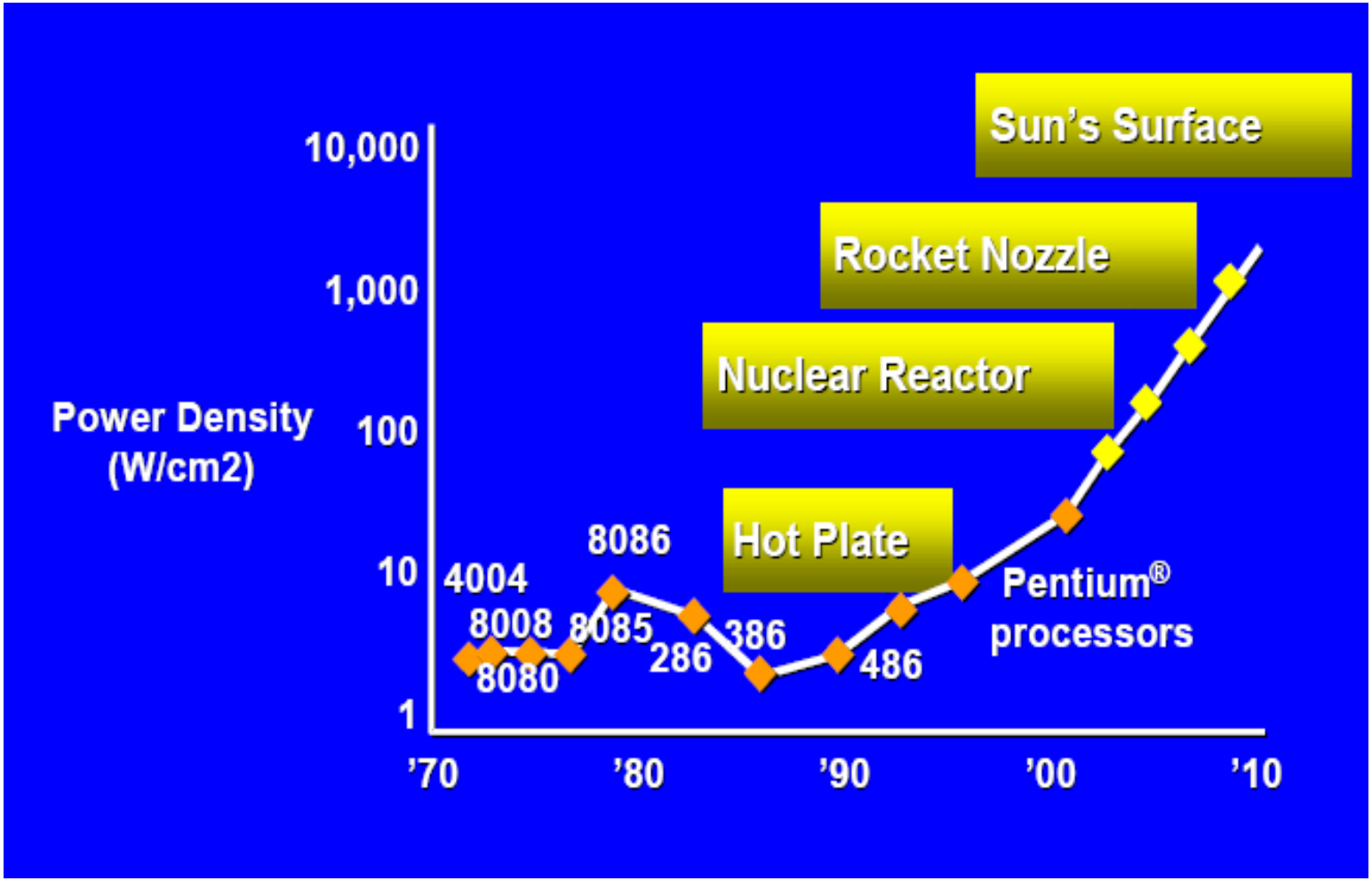


Cross-section of an Integrated Circuit

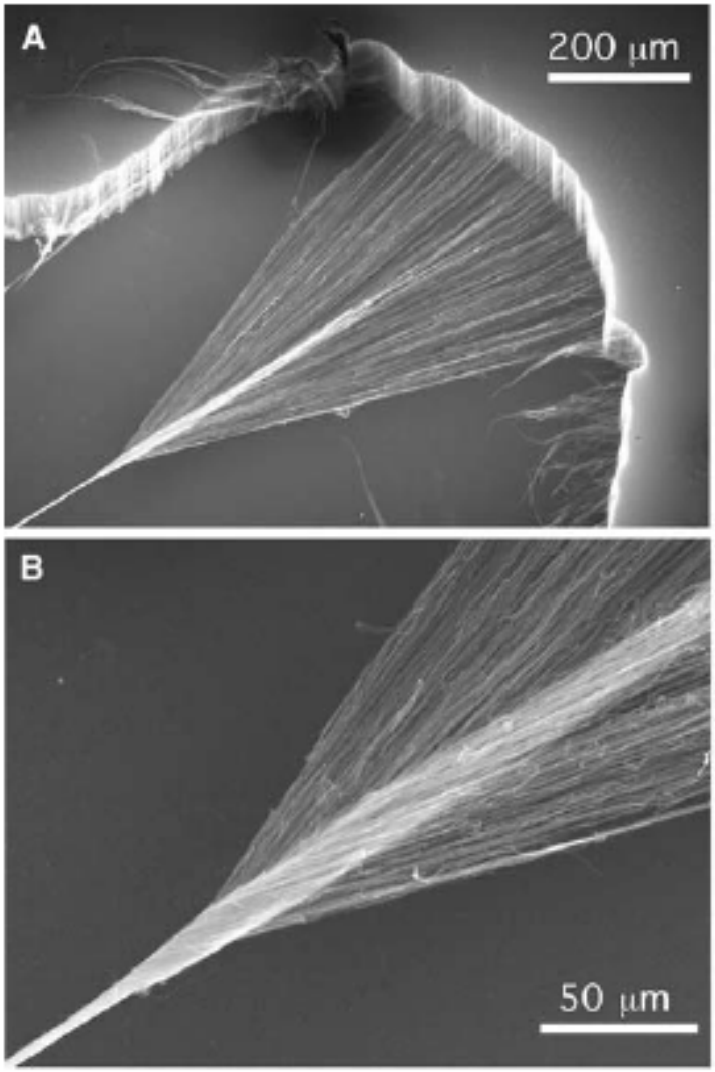
- Electromigration limits max current density in IC interconnects
- $J = 10^5$ A/cm^2 (Al), 10^6 A/cm^2 (Cu)
- CNTs have strong covalent bonds – less electromigration

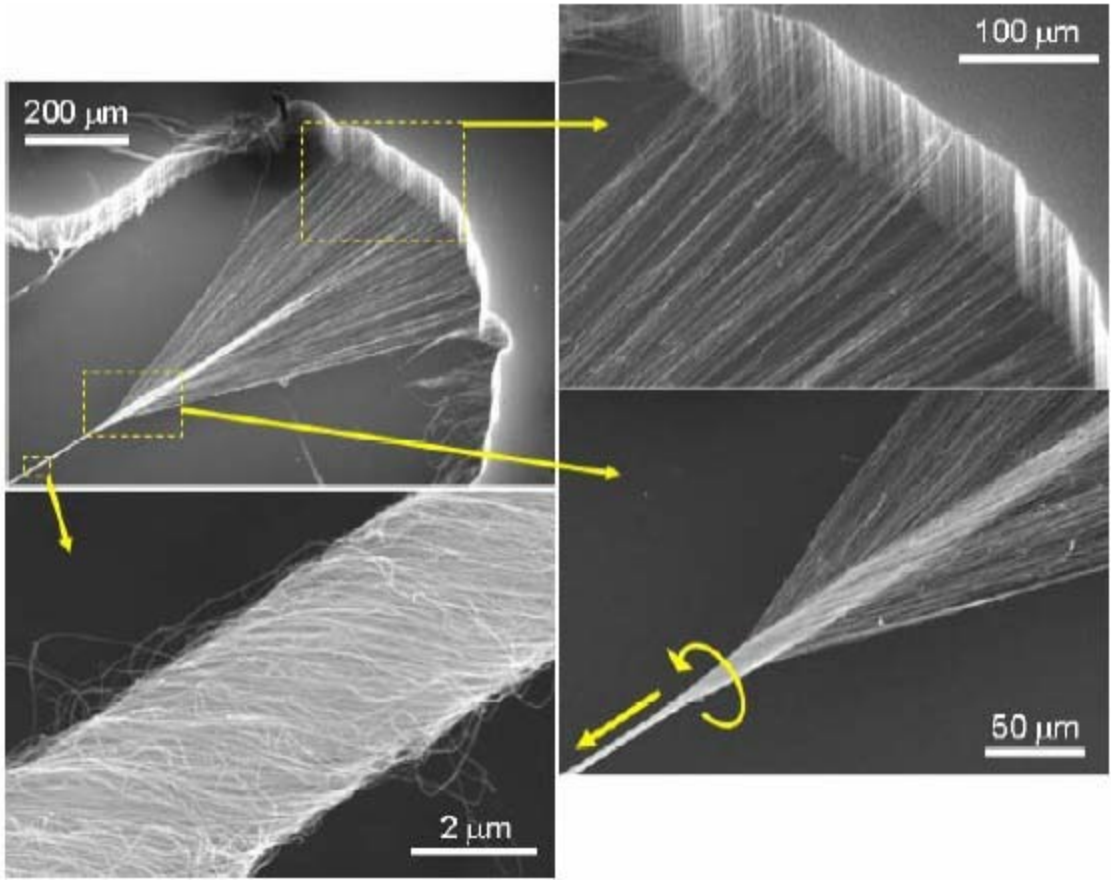
$$J_{max} = 10^9 \text{ A/cm}^2$$

Power limits scaling



Fibres spun from Mats





Spin fiber from side of CNT mat
Zhang, Baughman, Science 306 1356 (2004)

Fibre properties

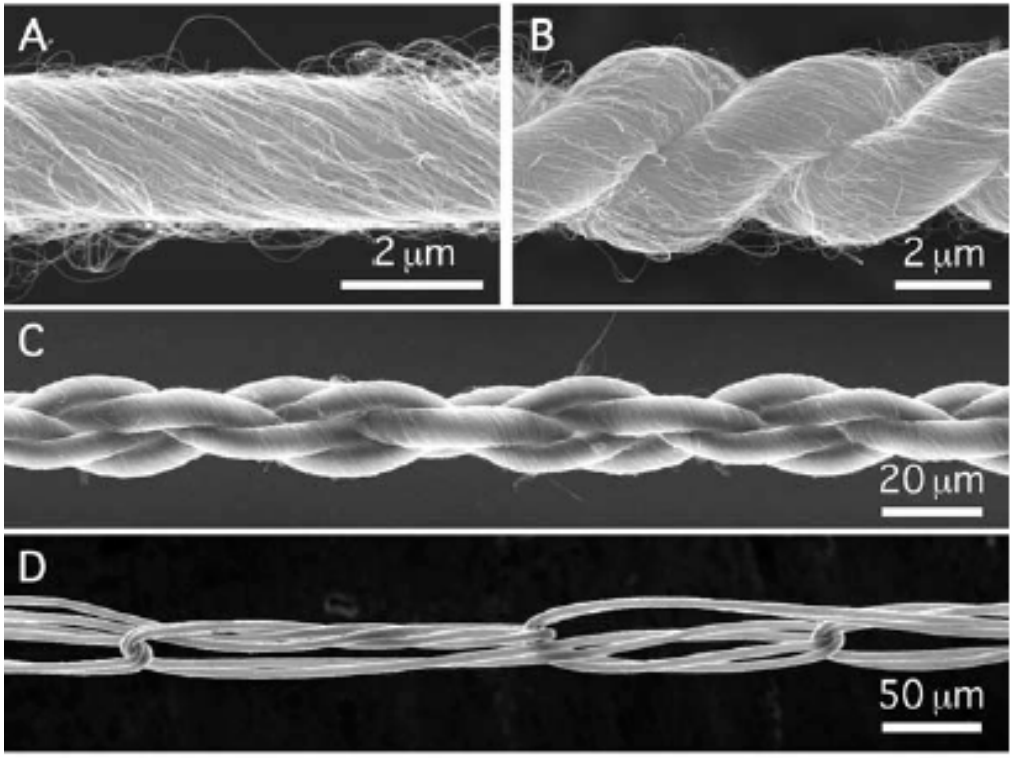
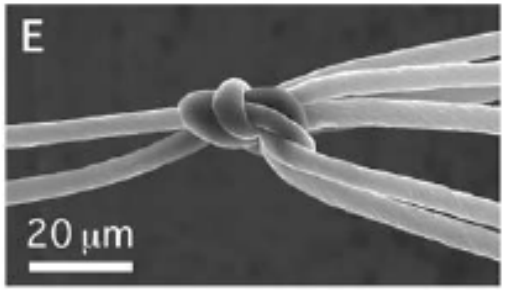
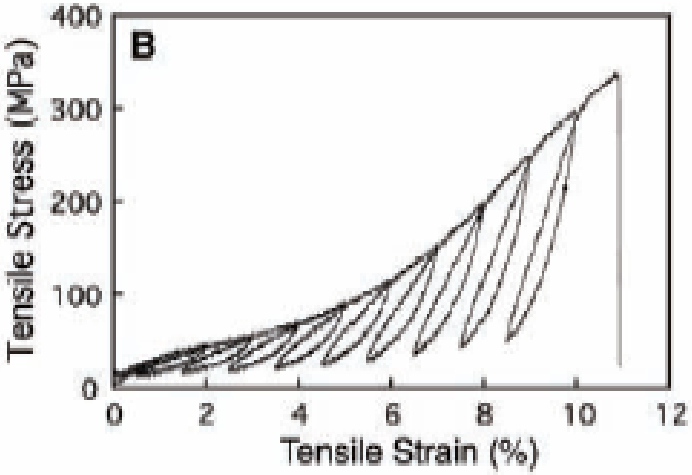


Fig. 2. SEM images of (A) singles, (B) two-ply, and (C) four-ply MWNT yarns, as well as (D) knitted and (E) knotted MWNT yarns.



Knot-able



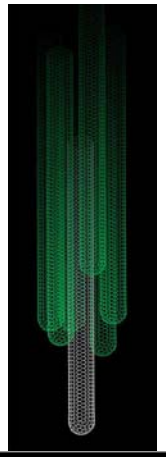
relaxation

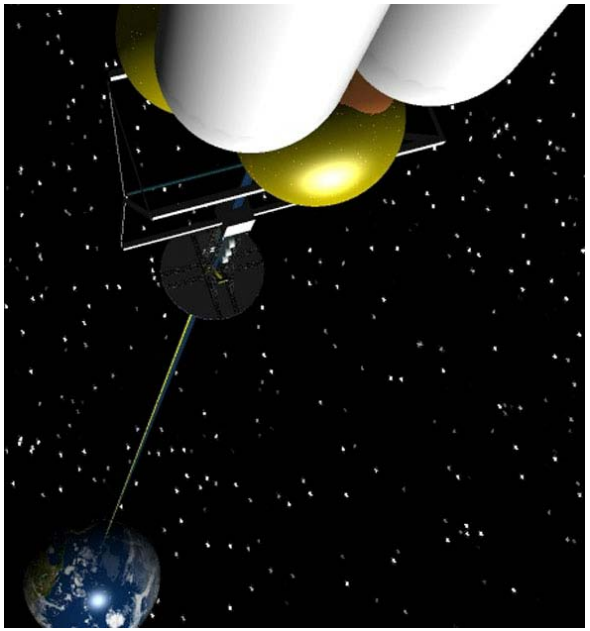
Space- elevator

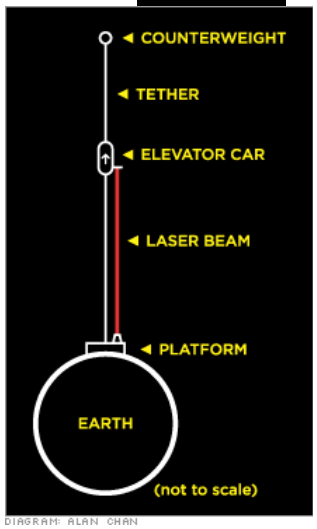
22 tons of cable

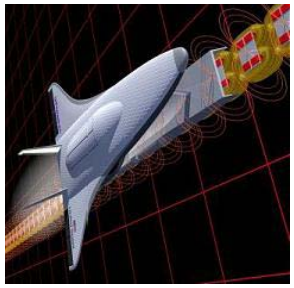
Geosynchrous altitude – 35 000 km

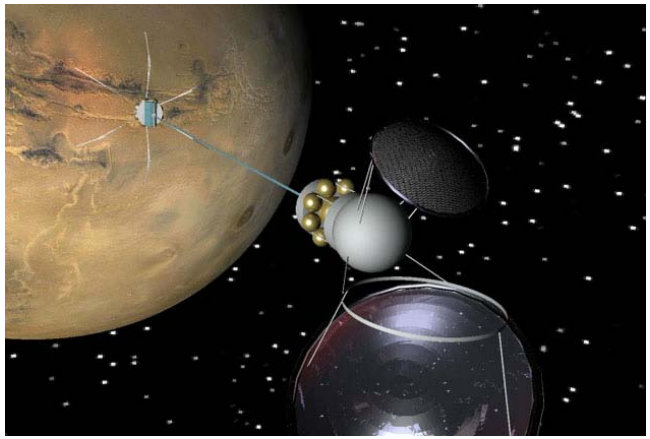
10 billion US$ (cf. Gibraltar bridge: 20 billion)



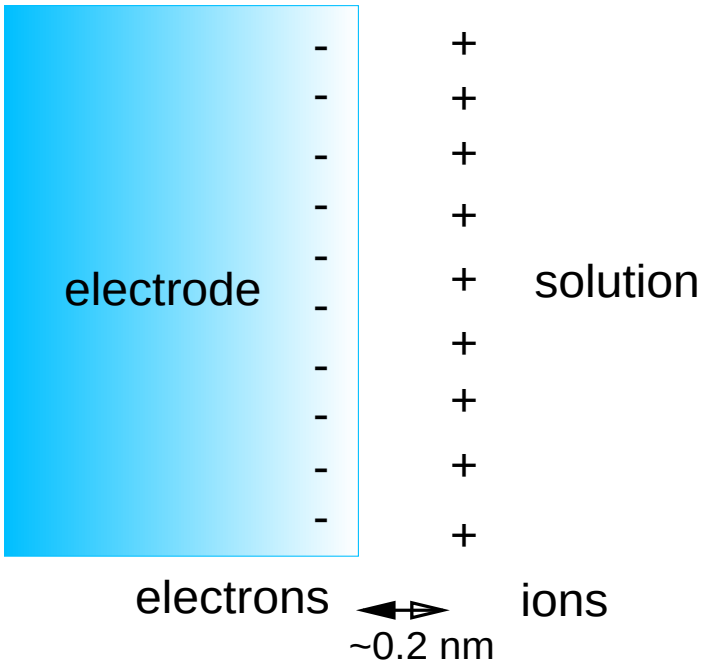








Electrochemistry - supercaps



Carbon is a stable, conductive electrode

Nanotubes have

- High surface area, 1500m^2/g
- Large Open porosity

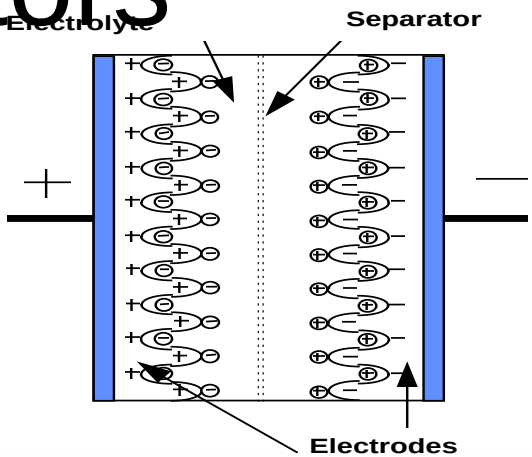
Electrochemical double layer (EDCL)

- EDCL is capacitor if $|V| < V_d$

$$C = \frac{\varepsilon A}{d}$$

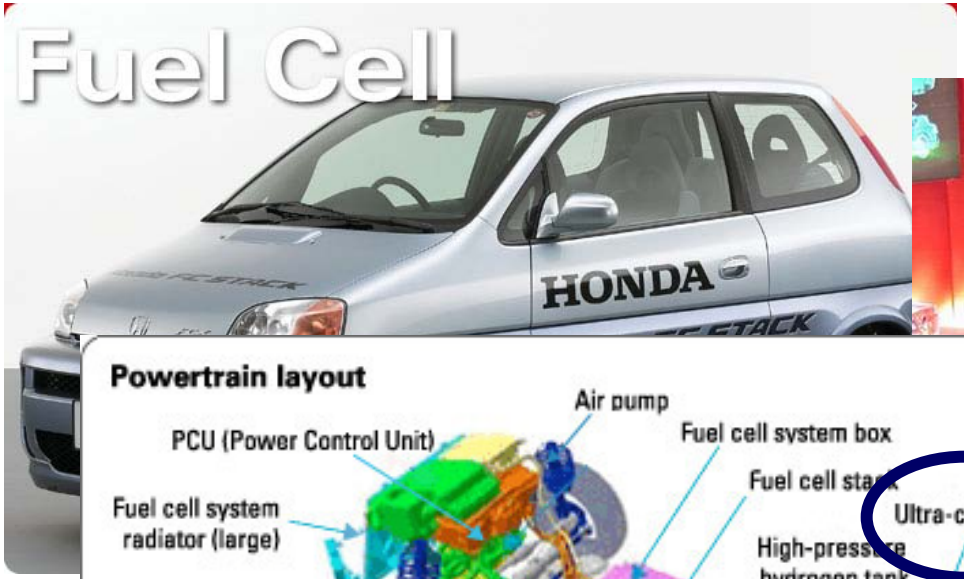
- 0.1 F/m^2 for d = 0.5 nm
- Non-aqueous electrolyte $V_d > 1.23$ V

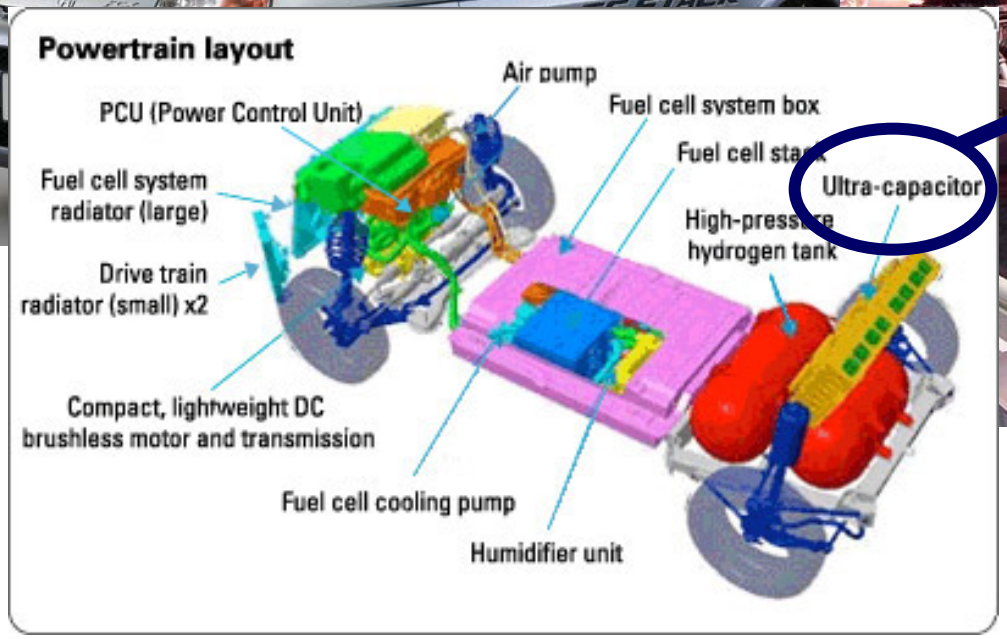
Supercapacitors



- Montena sA (CH)

- Polycarbonate electrolyte
- Ion permeable membrane separator
- Nanotubes would have largest possible surface area, 1500 m^2/g
- 1500 m^2/g = 10 F/g = 20 Wh/kg
- Allows *1000 F* caps at 2.5V in 2” diameter capacitor

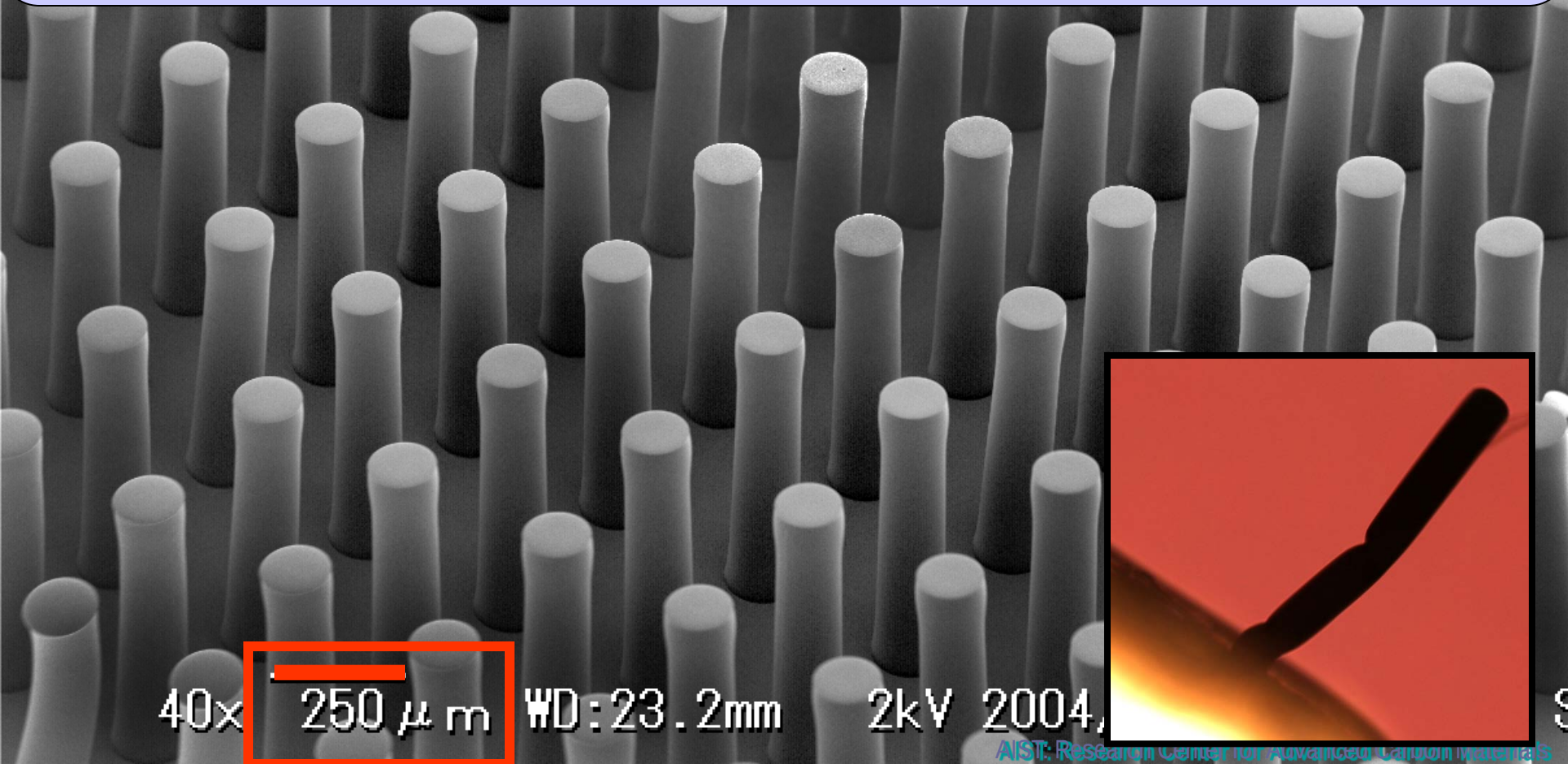




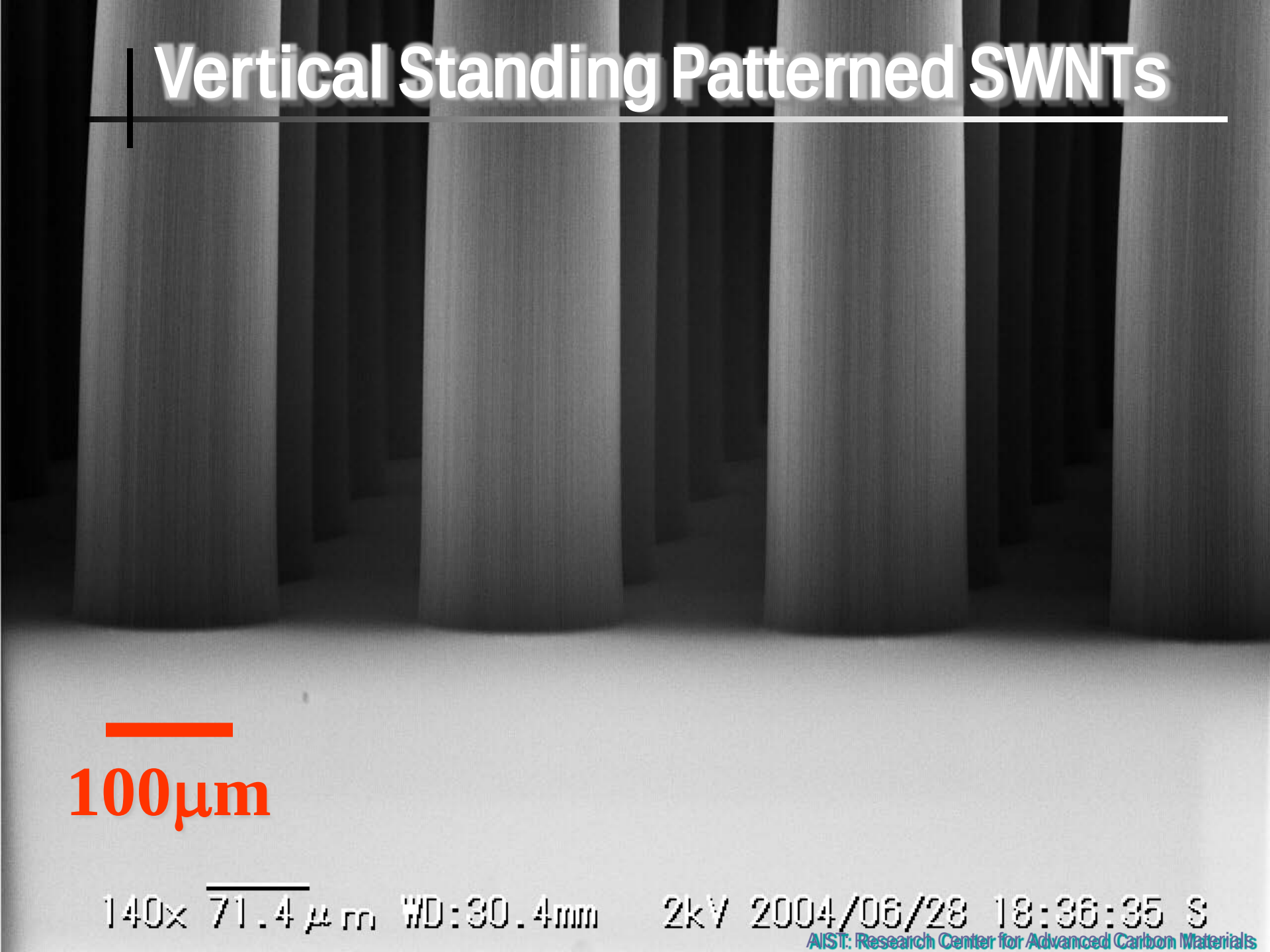
ultra-capacitor

Vertical Standing and Patterned

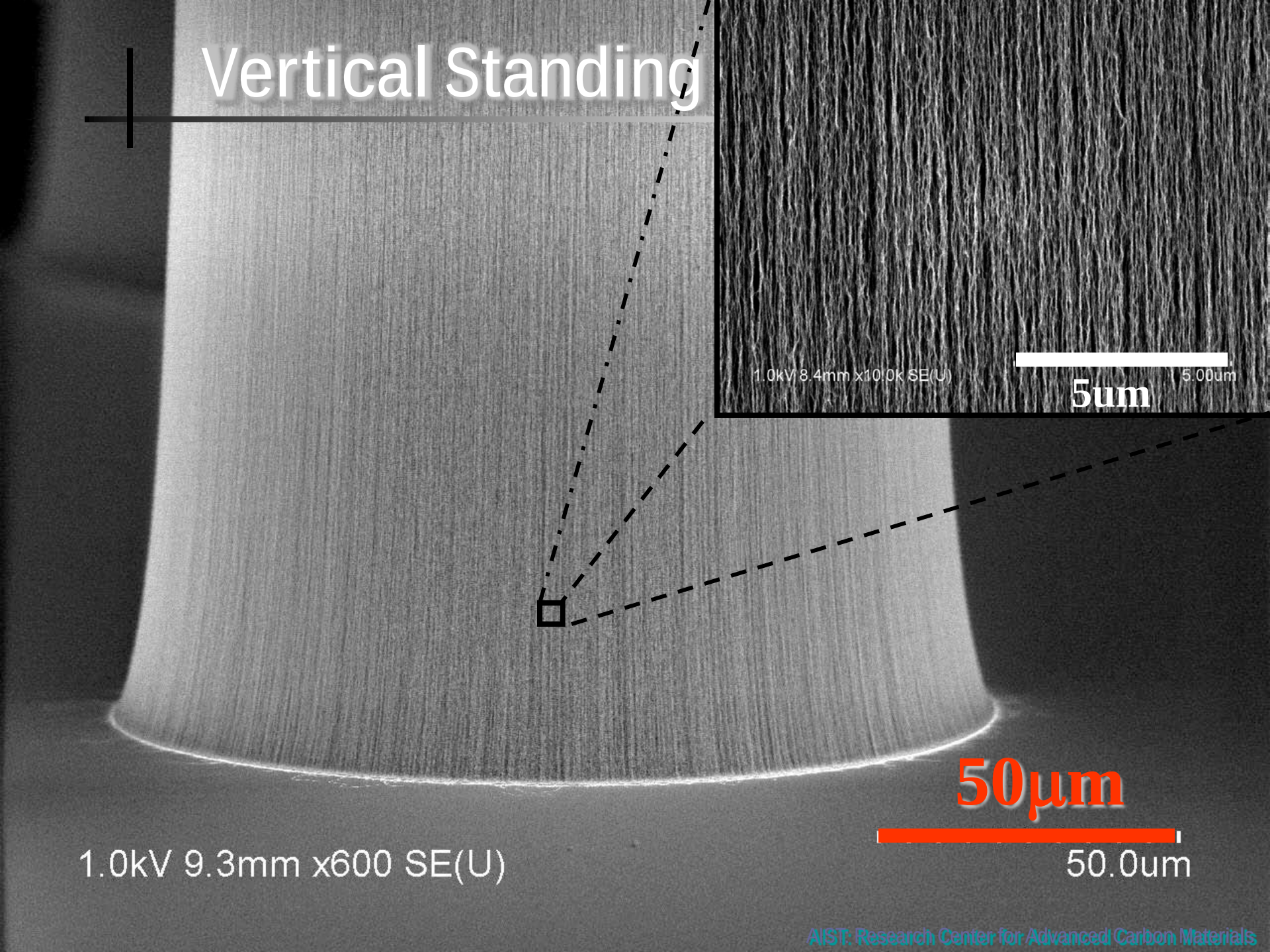
Build In Macroscopic Organized Structure just By Patterning Catalysts



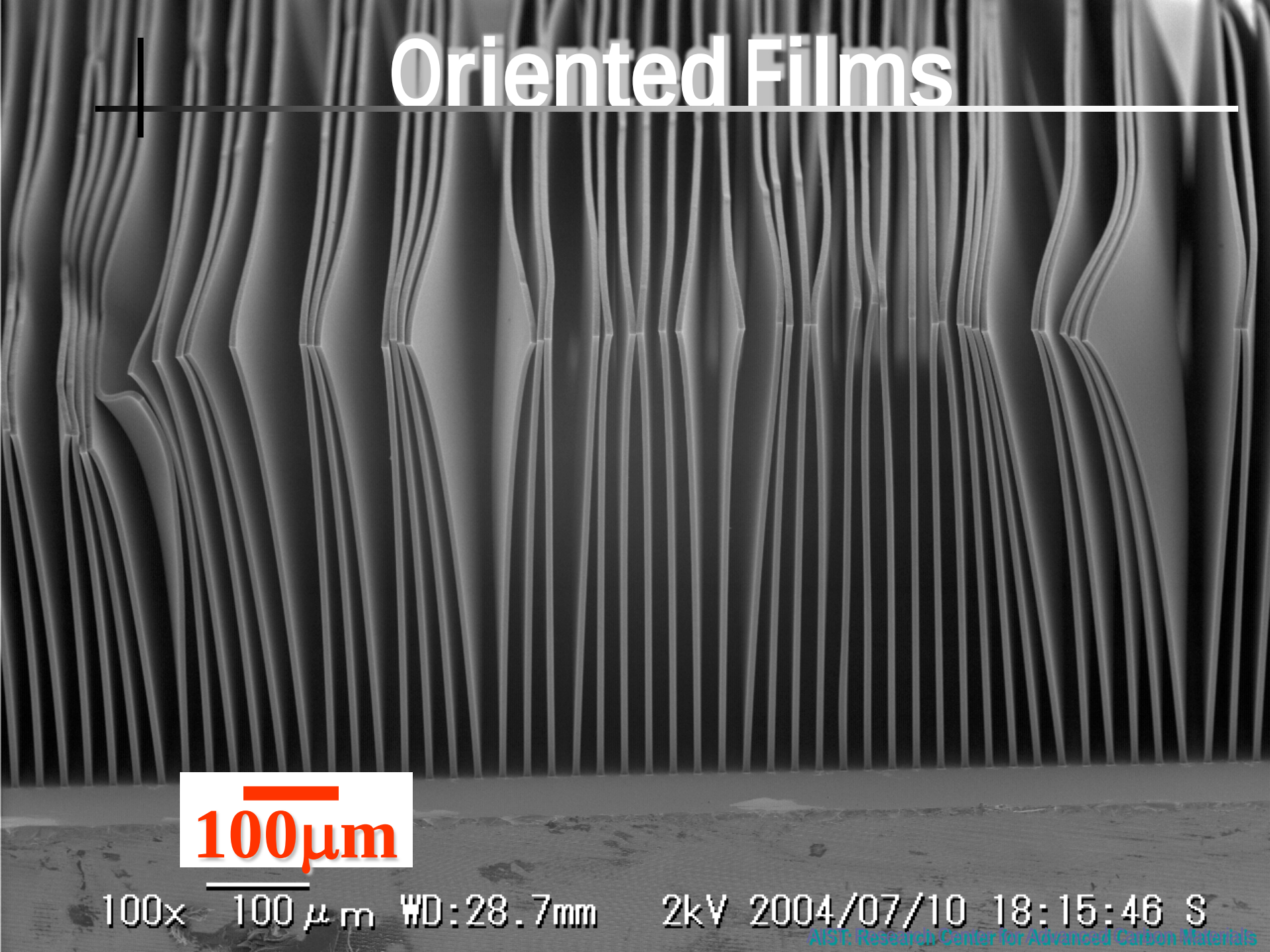
Vertical Standing Patterned SWNTs



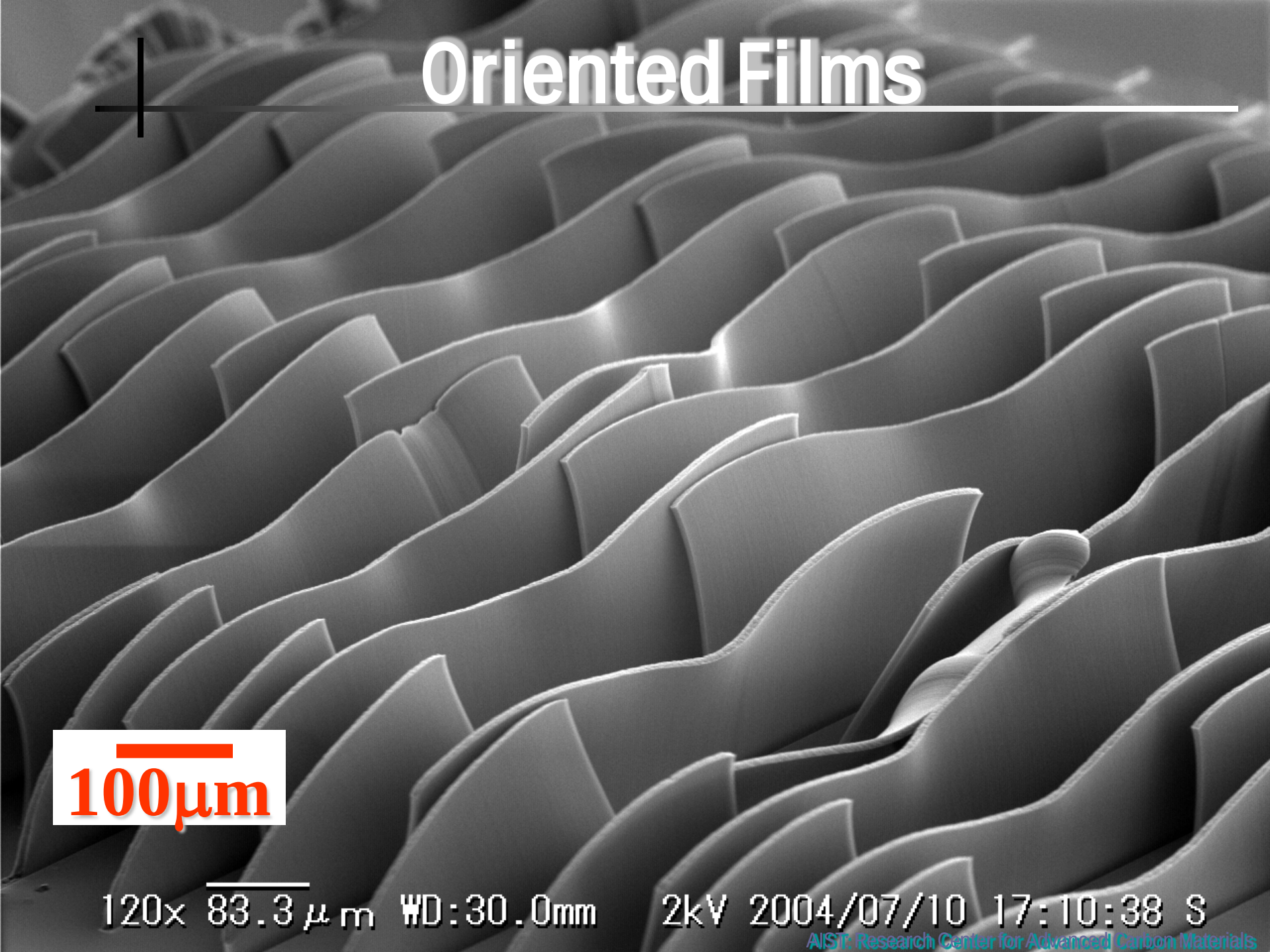
AIST: Research Center for Advanced Carbon Materials


Vertical Standing
1.0kV 8.4mm x10.0k SE(U)
5.00um
5um
50μm
1.0kV 9.3mm x600 SE(U)
50.0um
AIST: Research Center for Advanced Carbon Materials

Oriented Films

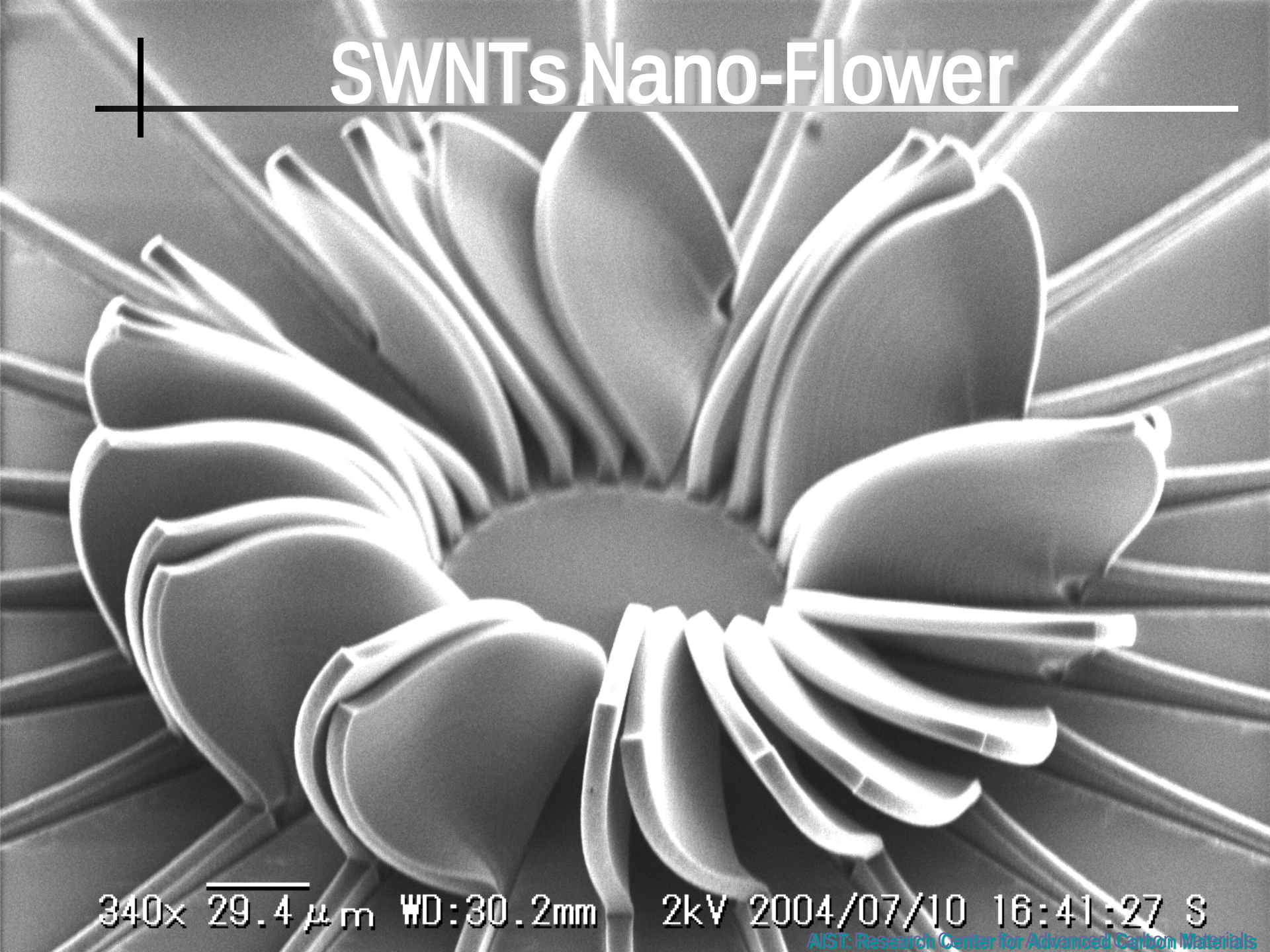


Oriented Films



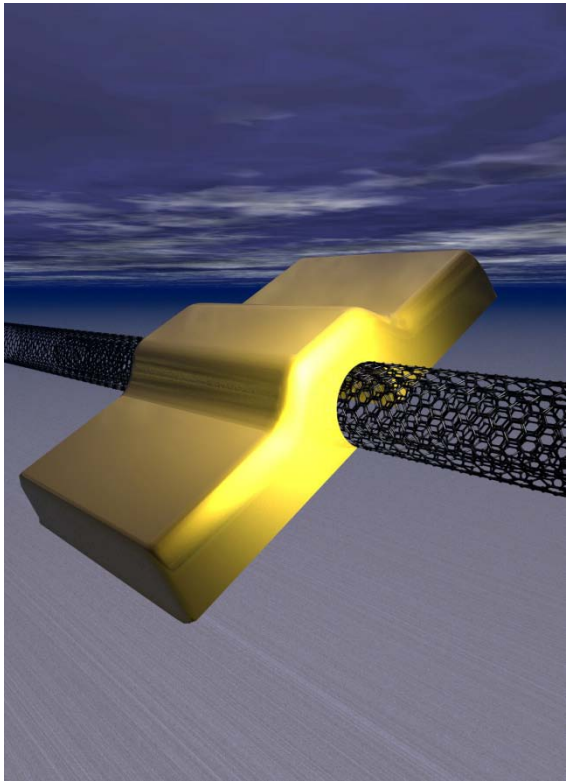
AIST: Research Center for Advanced Carbon Materials

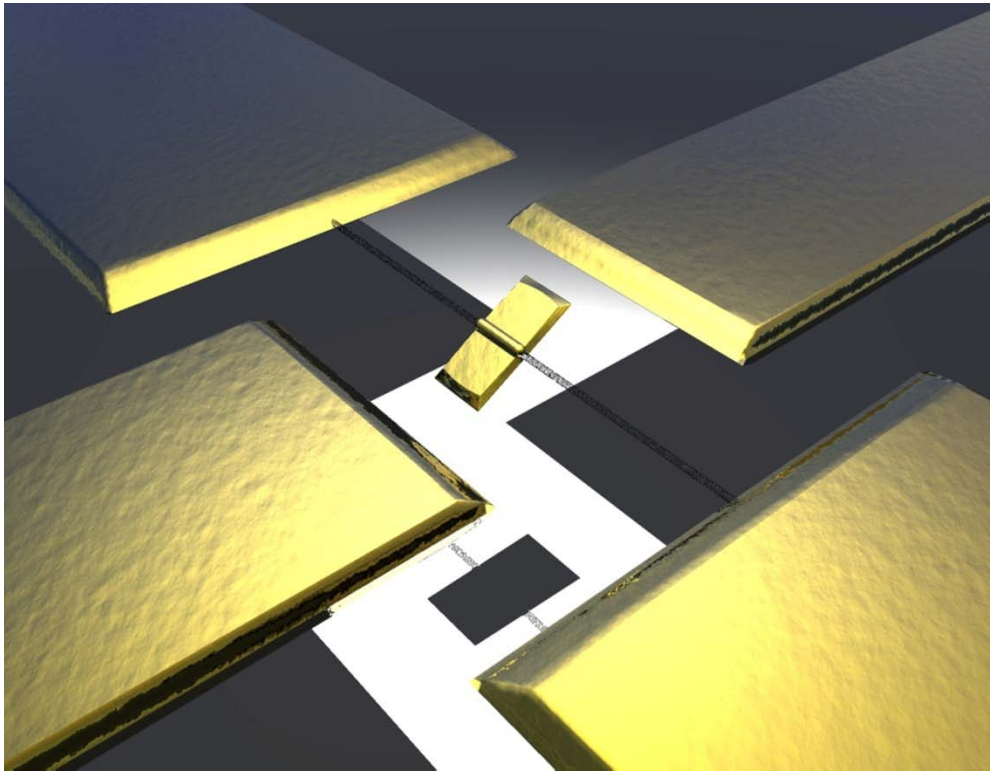
SWNTs Nano-Flower



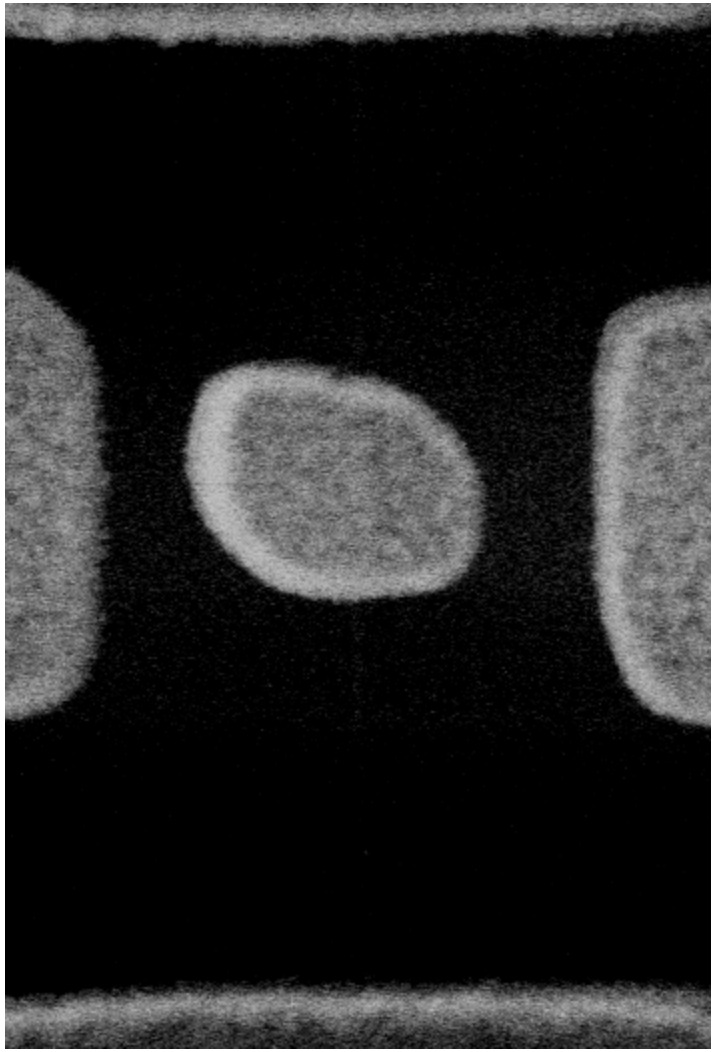
AIST: Research Center for Advanced Carbon Materials

Nano-machines: DWCNT + rotor

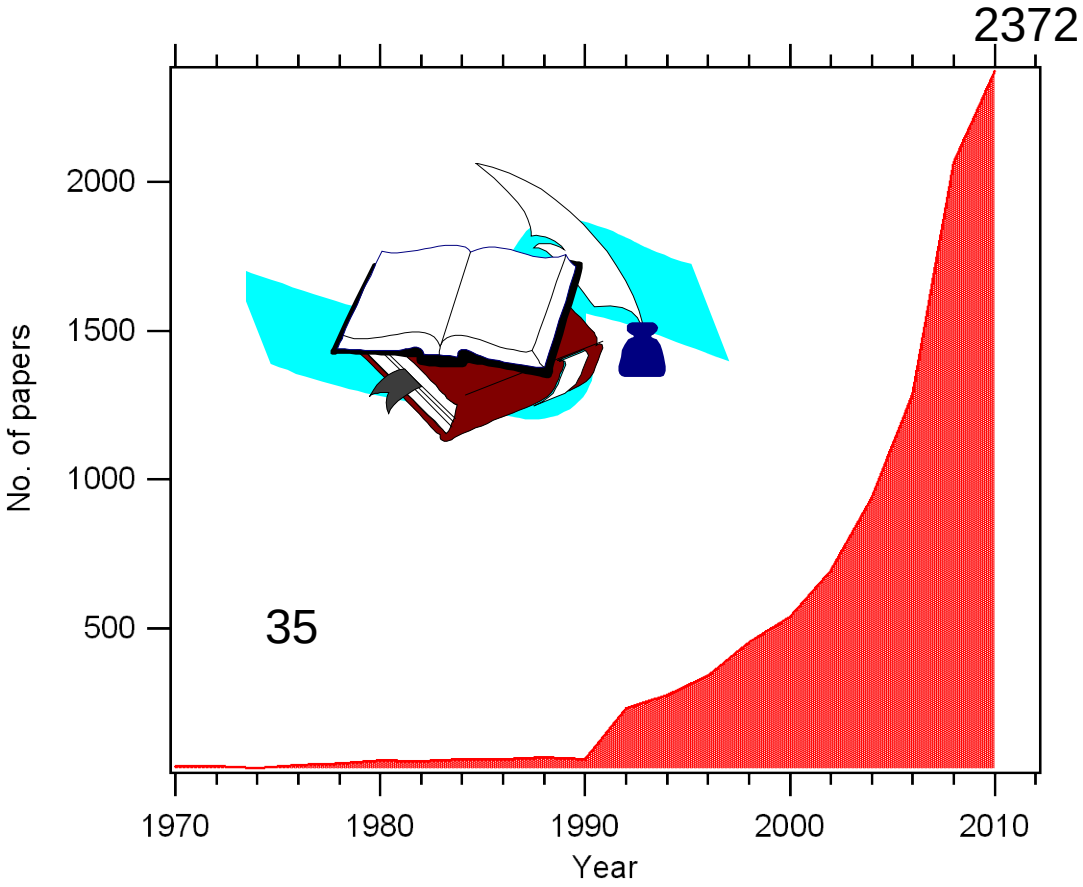




Nano-machines: DWCNT + rotor SEM image



Počet publikací o oxidu titaničitém (WoS)



TiO_2 MODIFICATIONS

Natural

- Rutile *$P4_2/mmm$*.... (5-12 kJ/mol vs. anatase)
- Anatase *$4_1/amd$* ..... (TMD stable if ∅ < 10 nm)
- Brookite *Pbca*

Synthetic

Columbite	*Pbcn*	TiO_2(II)	α-PbO_2	(≈20 Gpa)
Baddeleyite	*$P2_1c$*	TiO_2(III)	ZrO_2	(>30 Gpa)
Cotunnite *	*Pnma*	TiO_2(OII)	$PbCl_2$	(>60 Gpa, 1000 K)
Hollandite	*I4/m*	TiO_2(H)	KTi_4O_8	
Ramsdellite	*Pbnm*	TiO_2(R)	$LiTi_2O_4$	
Bronze	*C2/m*	TiO_2(B)	$K_2Ti_4O_9$	

*Hardest known oxide (2001)

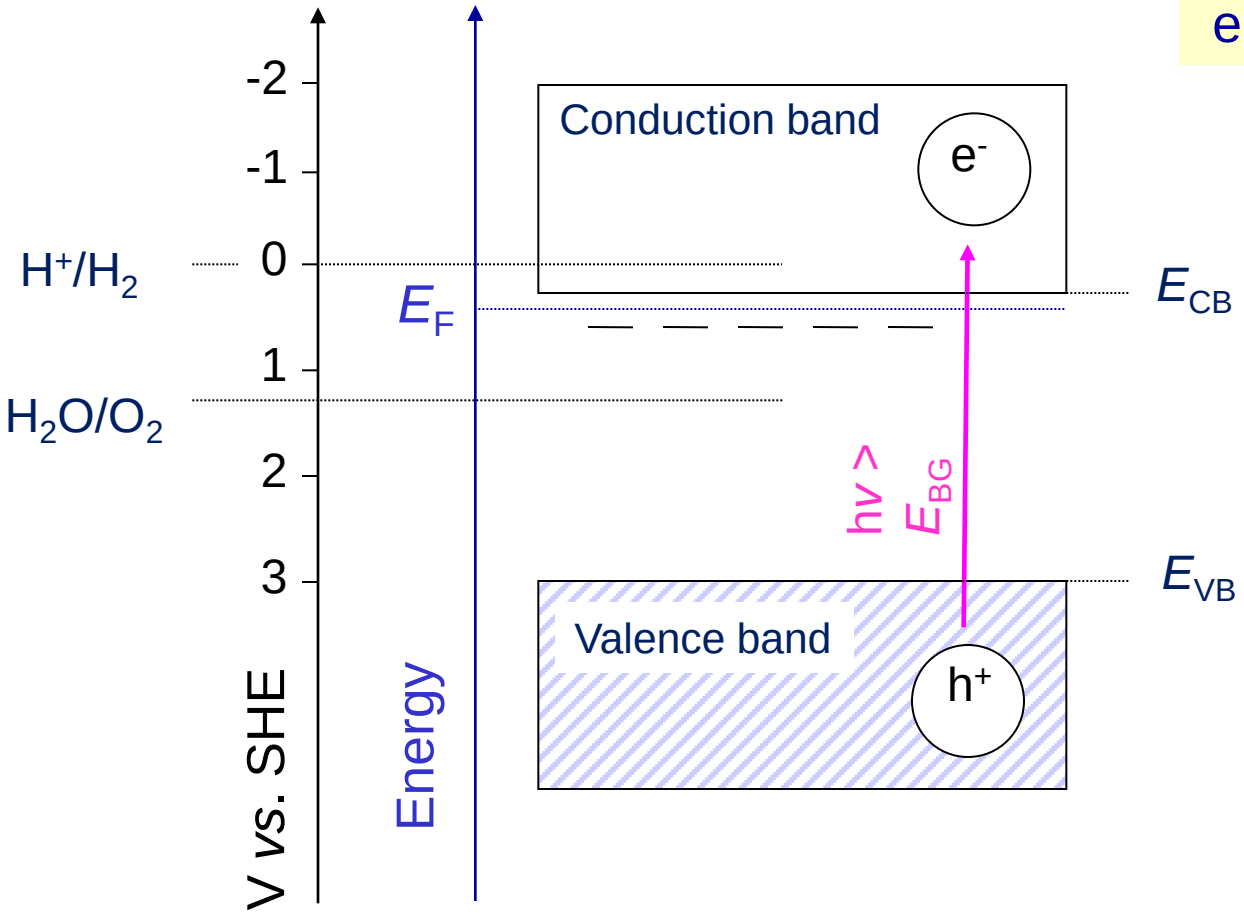
TiO_{2-x} , $x \approx 0.01 \Rightarrow$ n-doping: $Ti^{4+} \rightarrow Ti^{3+}$

Fujishima A., Honda K.

"Water can be decomposed (on TiO_2) by ~~visible~~ UV light into O_2 and H_2 with~~out~~ the application of ~~any~~ external voltage"

Nature **238**, 37 (1972)

Fundamentals of light energy conversion

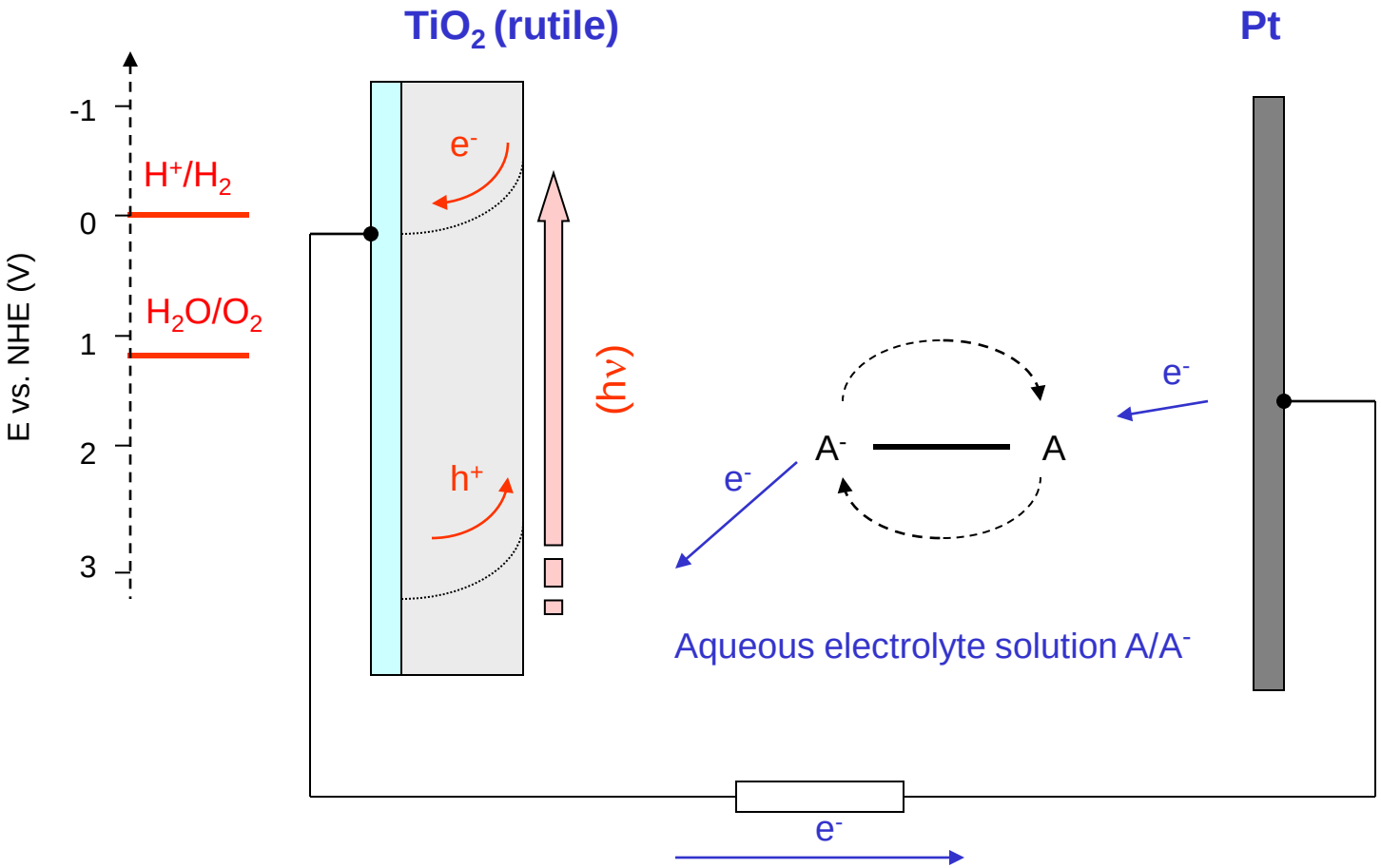


$E_{BG} = E_{CB} - E_{VB}$ = 3.2 eV (anatase) ≈ λ = 388 nm

= 3.0 eV (rutile) ≈ λ = 414 nm

$E_{photon} = h\nu = hc/\lambda$

Fujishima & Honda (1972): photoelectrochemical cell

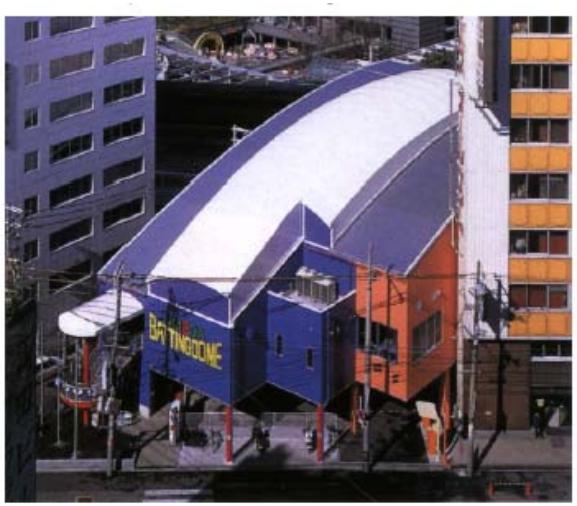


$E_{FB} = E_0$ - 0.06pH [V]; $E_0 \cong 0.02$ V (rutile); $E_0 = -0.2$ V (anatase)
[Kavan et al., *JACS* **118**, 6716 (1996)]

Oxidations by holes in anatase: $h^+ \approx 3$ V

$H_2 + 2\,h^+ \rightarrow 2\,H^+$	$E^0 = 0.00$ V
$2\,H_2O + 2\,H^+ + 2\,h^+ \rightarrow 2\,H_2O_2$	$E^0 = 1.78$ V
$OH^- + h^+ \rightarrow OH^{\cdot}$	$E^0 = 2.02$ V
$H_2O + O_2 + 2\,h^+ \rightarrow 2\,H^+ + O_3$	$E^0 = 2.08$ V
$(2\,F^- + 2\,h^+ \rightarrow F_2$	$E^0 = 2.87$ V)

Self-cleaning TiO_2 layer on a roof or facade



Self-cleaning layer on a car

Uncovered
(blank)

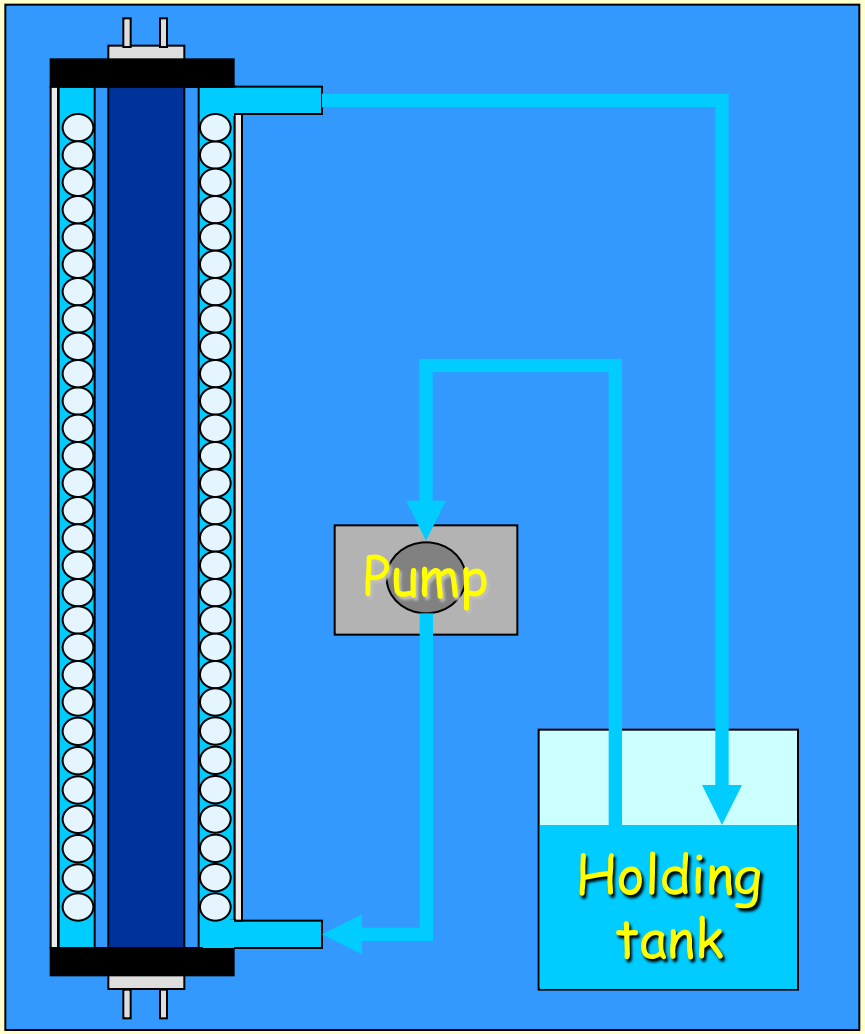
covered
by TiO_2

Antifogging mirrors with TiO_2 layer

Car side-view mirror (uncovered)

Covered by TiO_2

Model photoreactor for water purification



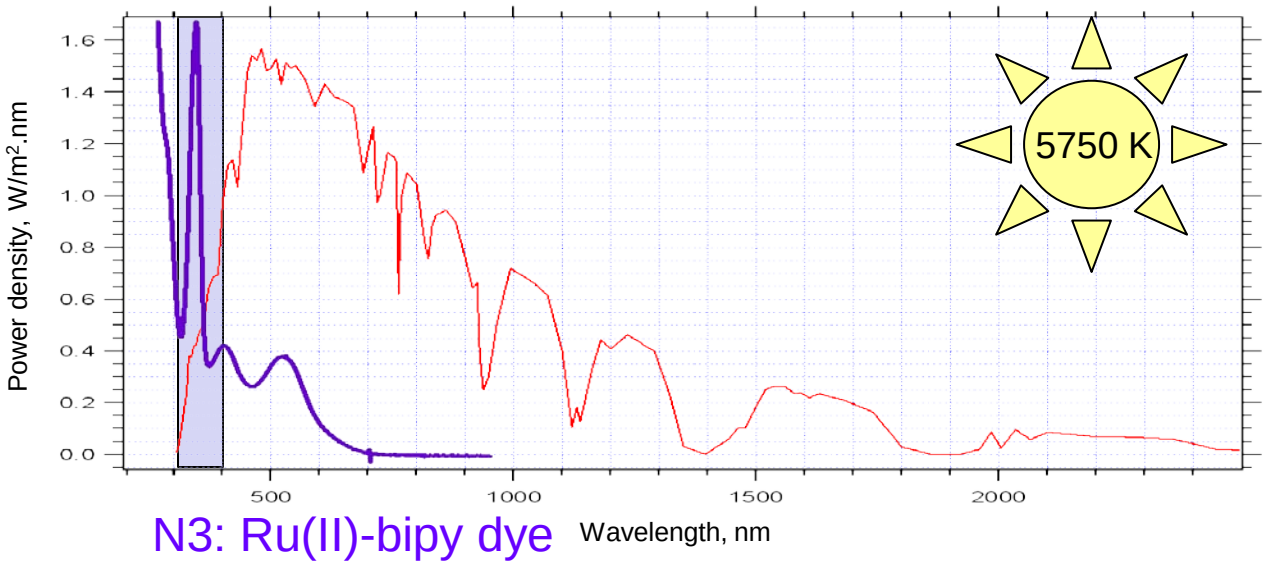
- **Body**
  - Two coaxial quartz tubes with input and output olives
- **Photocatalyst bed**
  - Column of glass spheres with TiO_2 coating
- **Irradiation source**
  - Black light fluorescent lamp (8 W, 30 cm)
- **Cover**
  - Aluminum foil
- **Reservoir for purified water**
  - Brown glass bottle (1 L)
  - Magnetic stirrer
- **Circulation**
  - Peristaltic pump (mL/min to L/min)

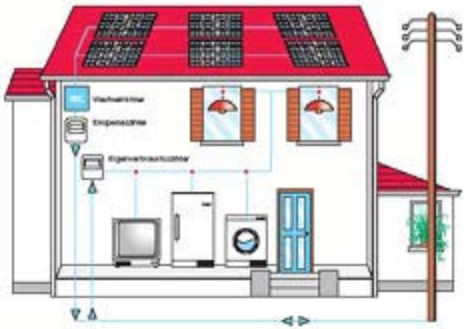
Pilot photoreactors for spa water purification (1)

Pilot photoreactors for spa water purification (2)

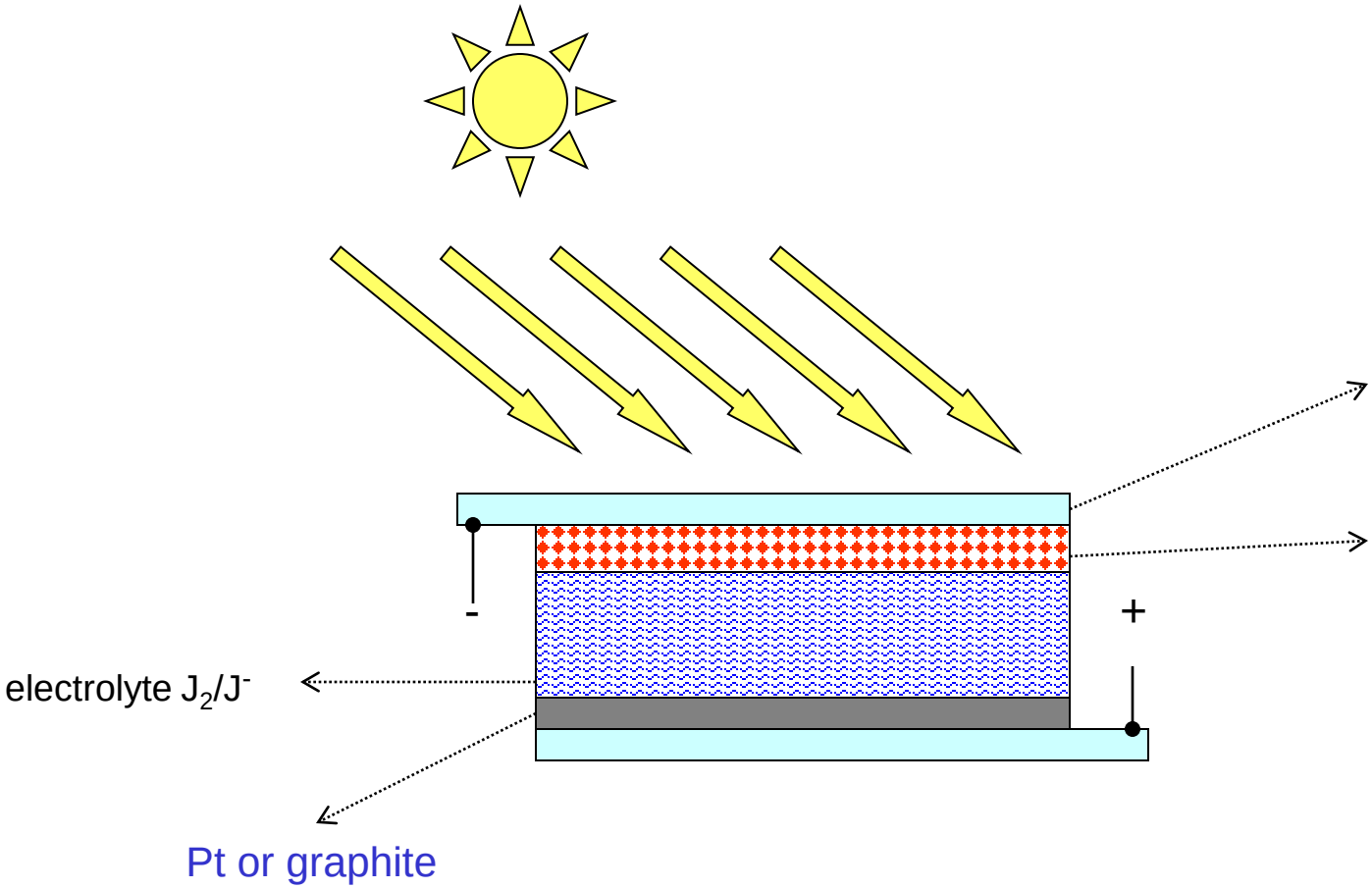
Konverze solární energie na TiO_2

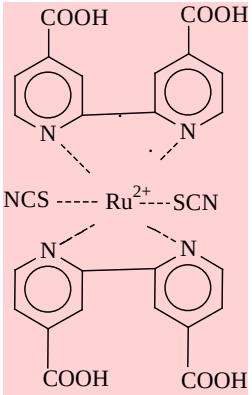
P ≈ 1 kW/m^2 (Evropa, červen, jasno, poledne) špičkový výkon AM 1.5





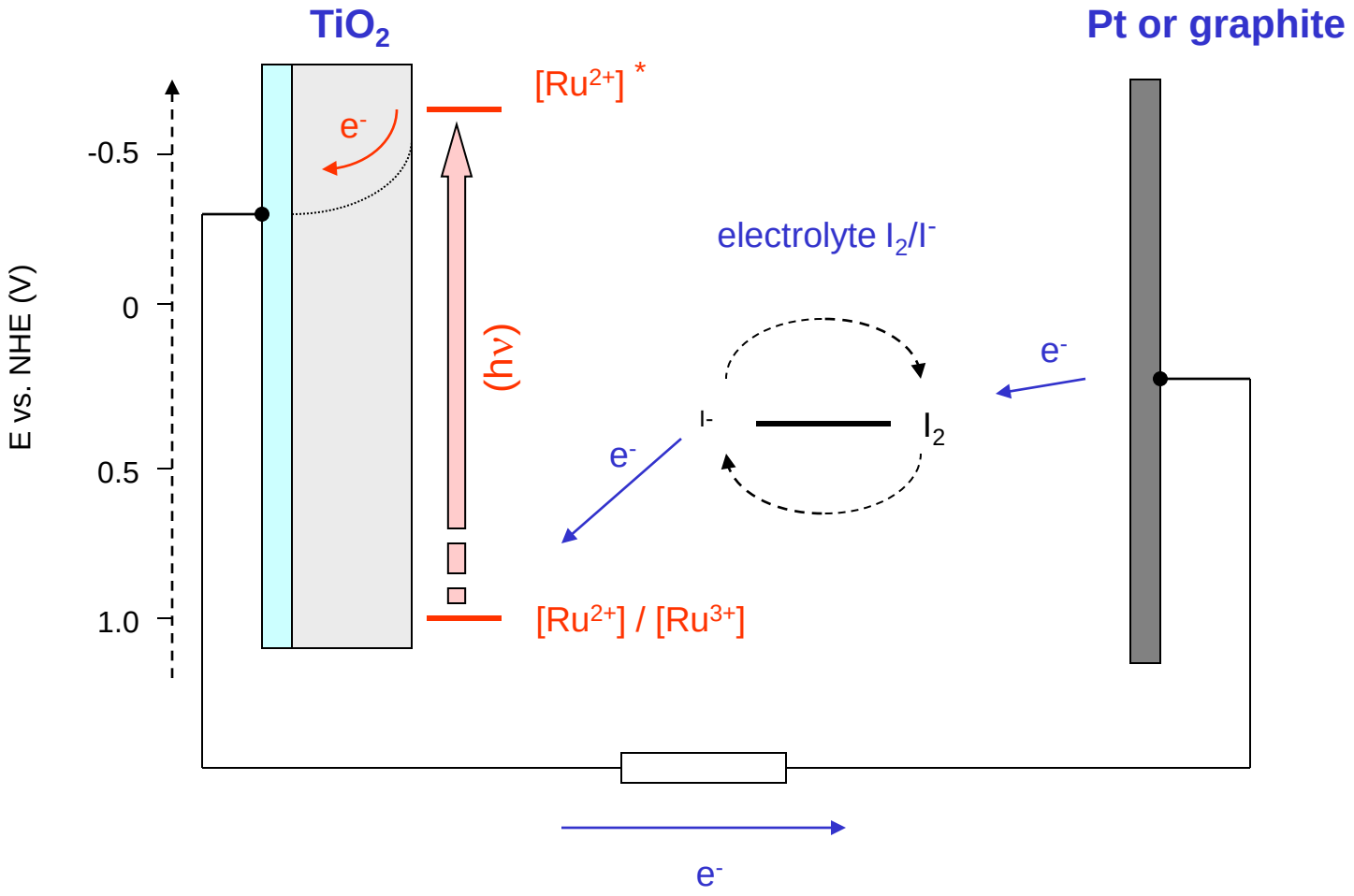
- *Solární energie globálně*.....3•10^{24} J/yr
- Fotosyntéza.....10^{21} J/yr (0.03 %)
- *Svět . spotřeba elektřiny*.....3•10^{20} J/yr (0.01 %)



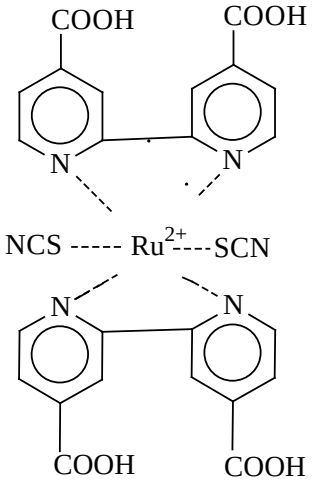


M. Graetzel et al., *Nature* 353, 737 (1991); 385, 593 (1998), 414, 338 (2001);
JACS 107, 2988 (1985); 123, 1613 (2001) …
M. Zukalová et al. *Nano Letters* 5, 1789 (2005)

Dye-sensitized Solar Cell: η = 10.4 %



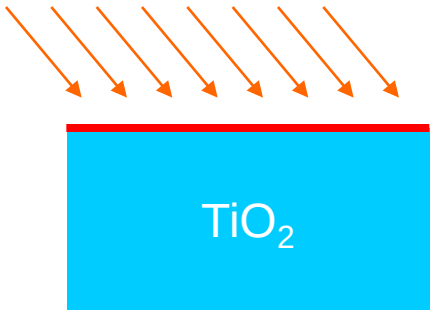
Sensitizer: [Ru(2,2'-bipy-4,4'di-COOH)$_2$(SCN)$_2$] (N3)

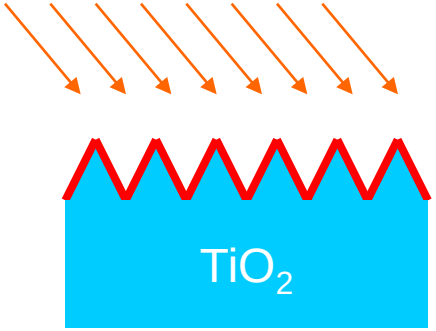


$$IPCE = \Phi_{LH} \cdot \Phi_{inj} = (1 - 10^{-\Gamma\varepsilon}) \cdot \Phi_{inj}$$

$$\varepsilon_{530} = 1.27 \cdot 10^{7}\, cm^{2} / mol$$

$$\Gamma \approx 0.55\, molecules / nm^{2}$$

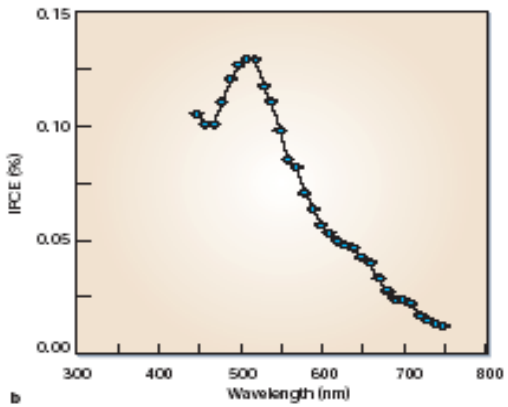




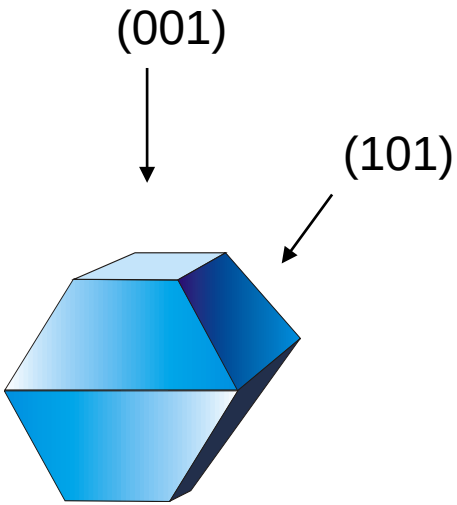
r.f. = 1 → IPCE = 0.27%

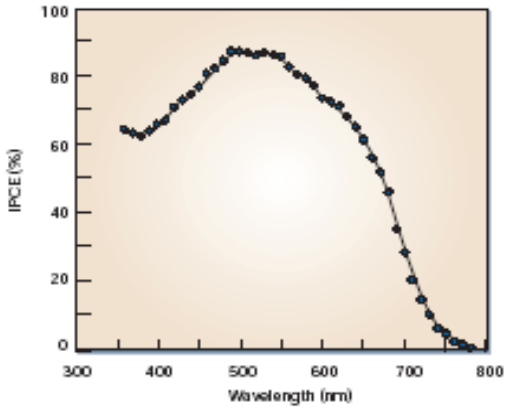
r.f. = 1000 → IPCE = 93.2%

N3 sensitized anatase



Single crystal (101)



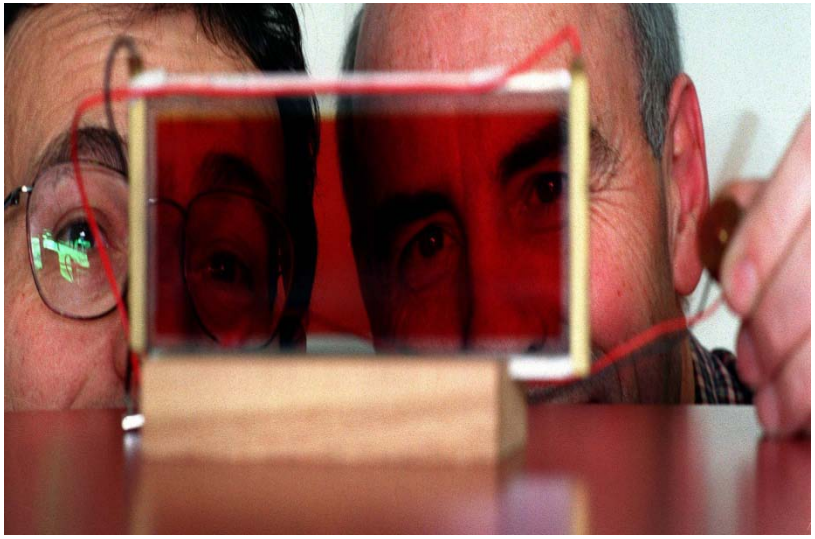


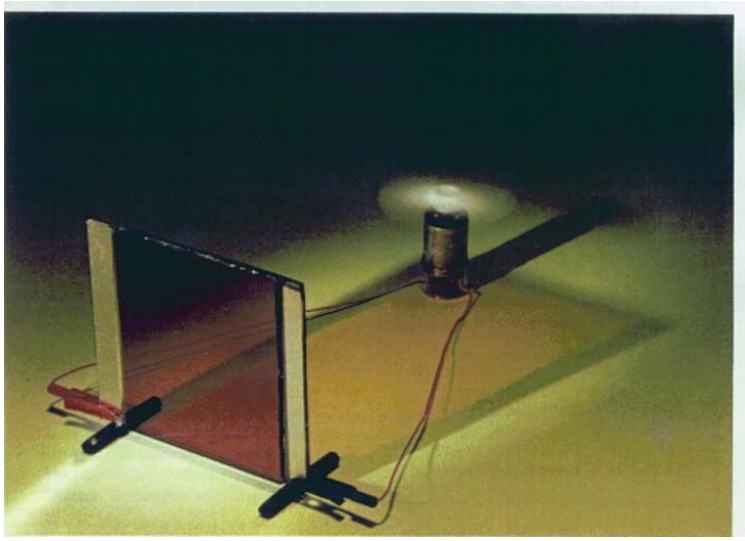
Nanocrystalline

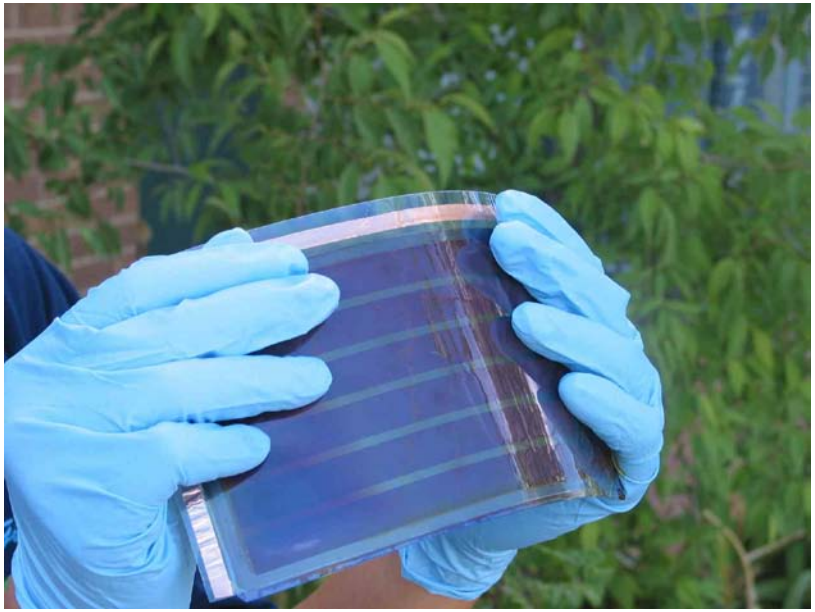
Dye Sensitised Solar Cells

Laboratory modules:

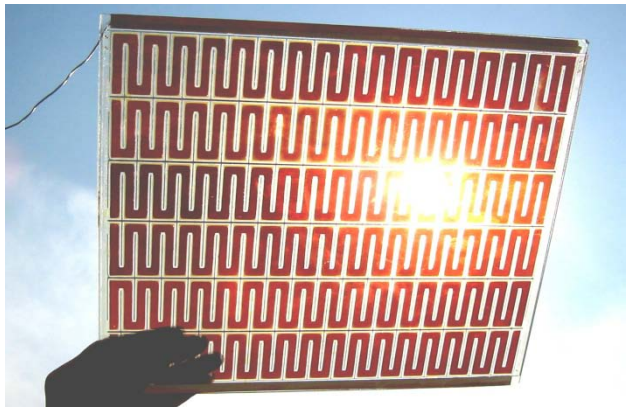
Glass-supported
Flexible (PET-supported)

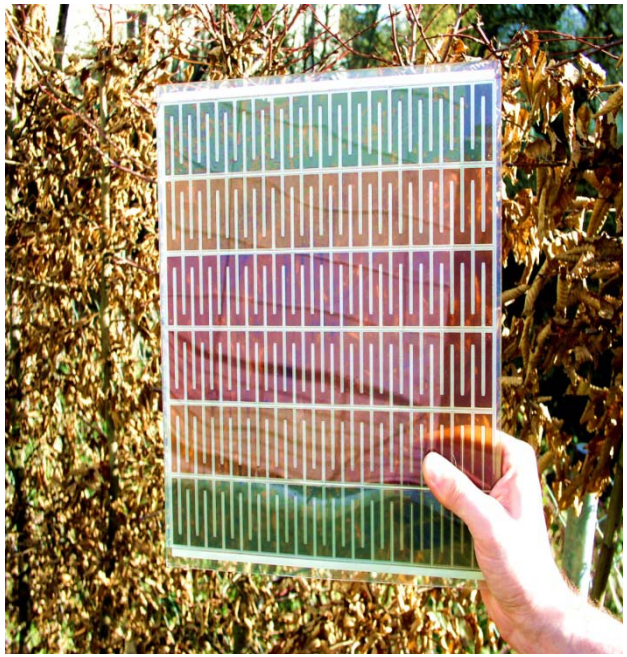






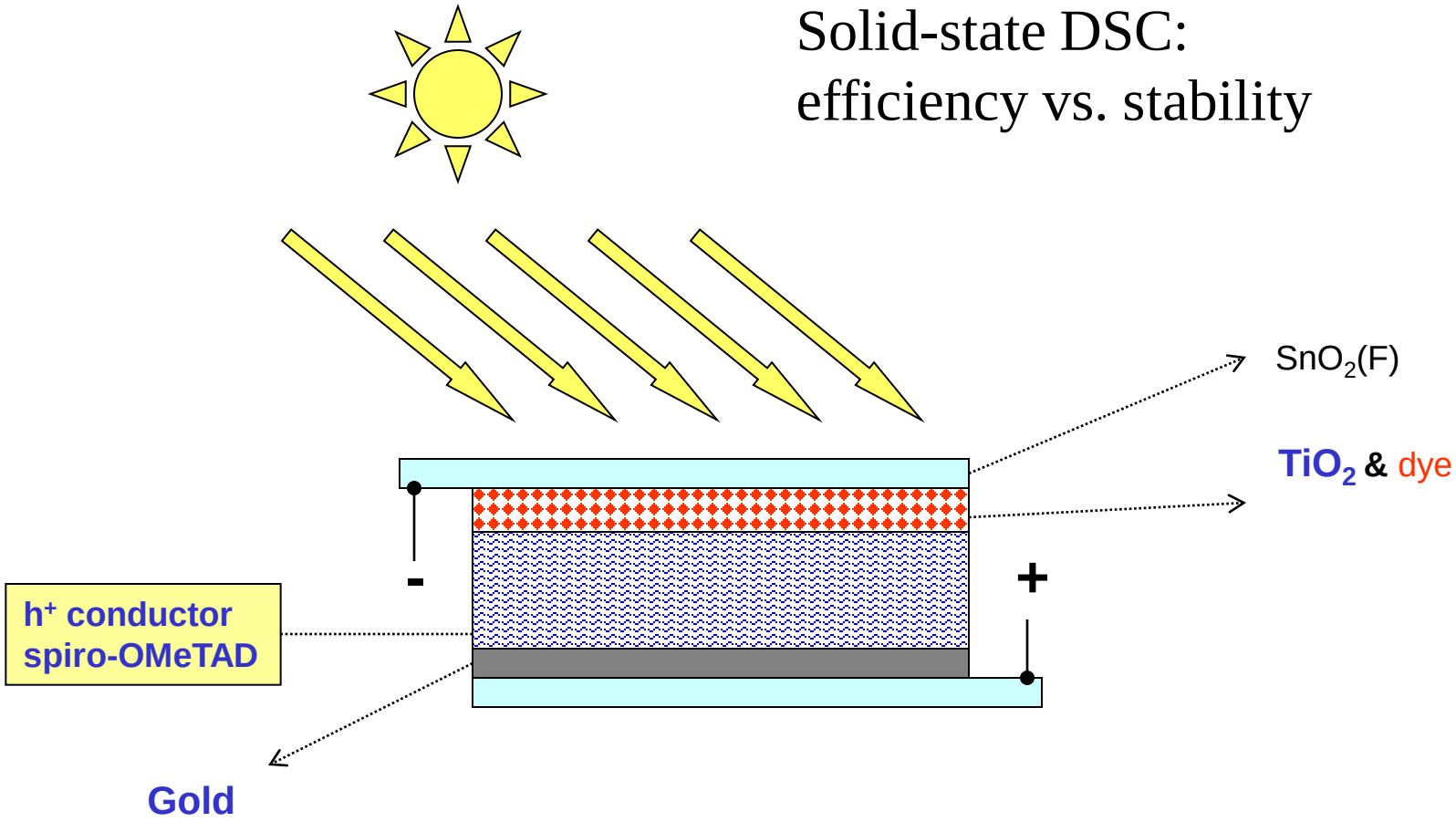
Barevná variabilita senisbilizovaných článků





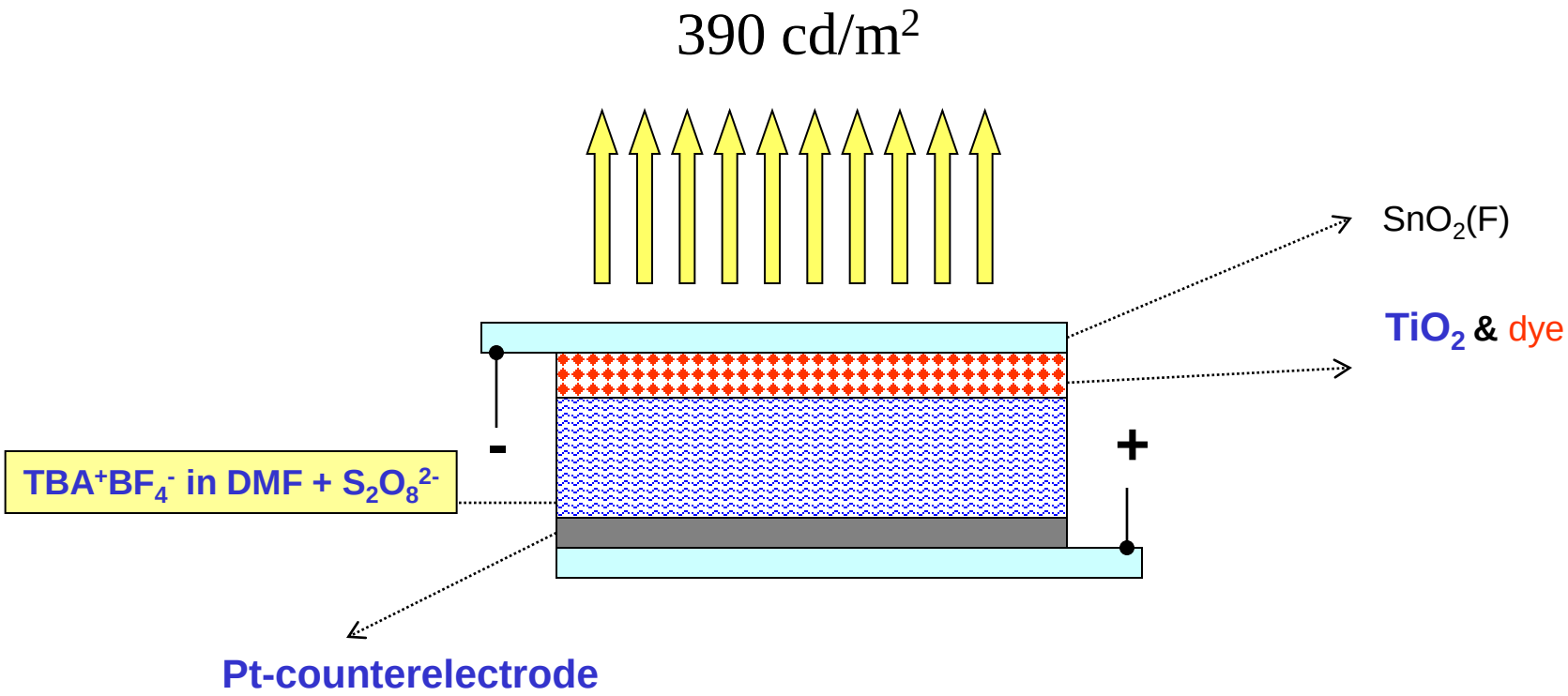
Solární články v oknech a střešních panelech

Solid-state DSC: efficiency vs. stability



M. Graetzel et al., *Nature* **395**, 550 (1998);
Adv. Mater. **17**, 813 (2005) …. **4%**

Light - emitting device: electroluminescence

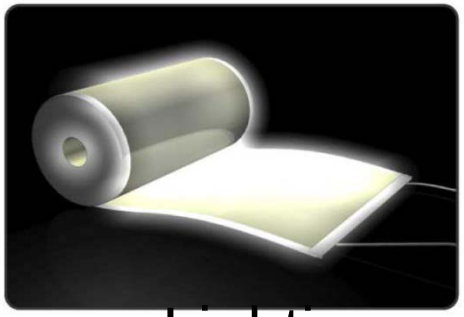


Dye = RuL_2L'
L = 2,2'-bipy-4,4'-diphosphonic acid
L' = 4,7-diphenyl-1,10-phenanotroline

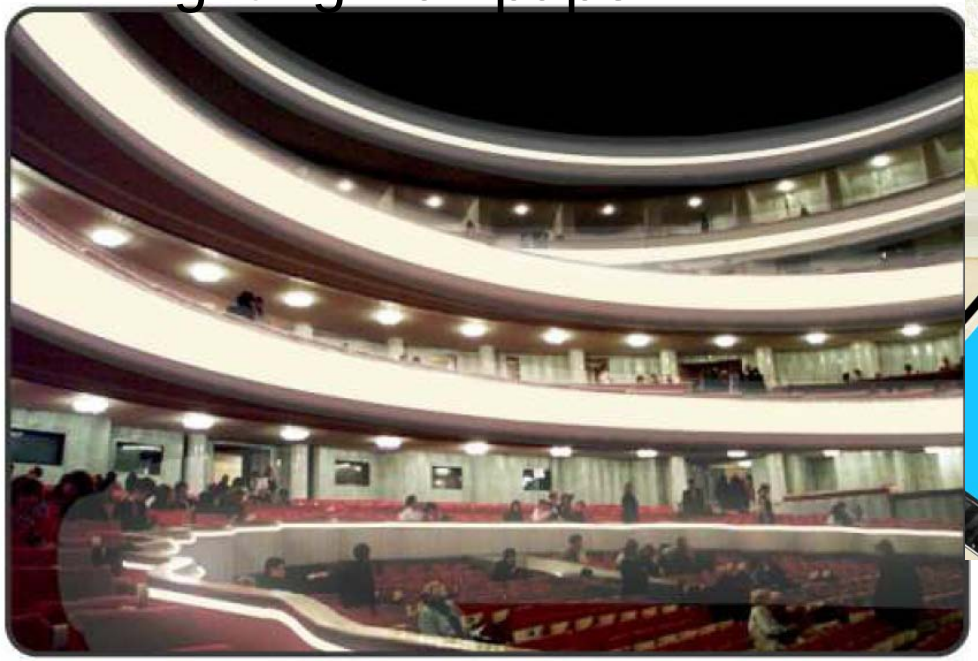
Graetzel et al. JPCB **101**, 2558 (1997)

TiO_2-based LED for Displays

Motivation ⇒ New lighting designs

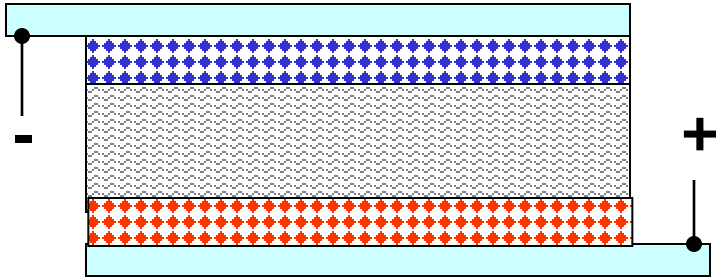


Lighting wall paper



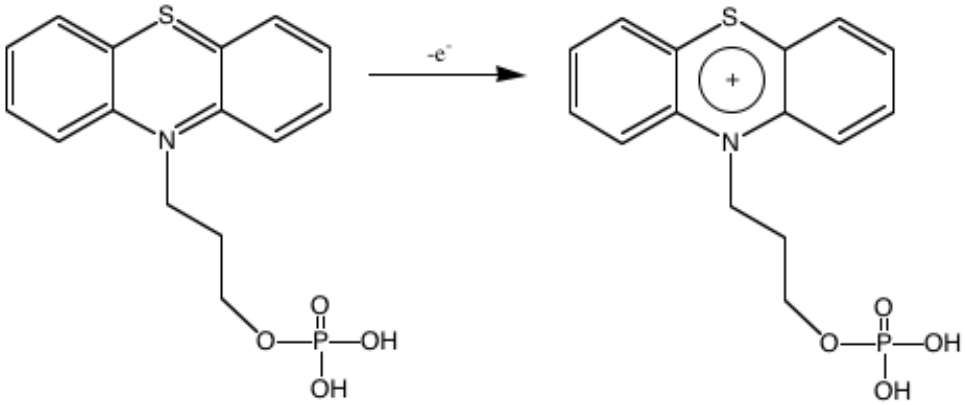
Transparent Lighting

OSRAM

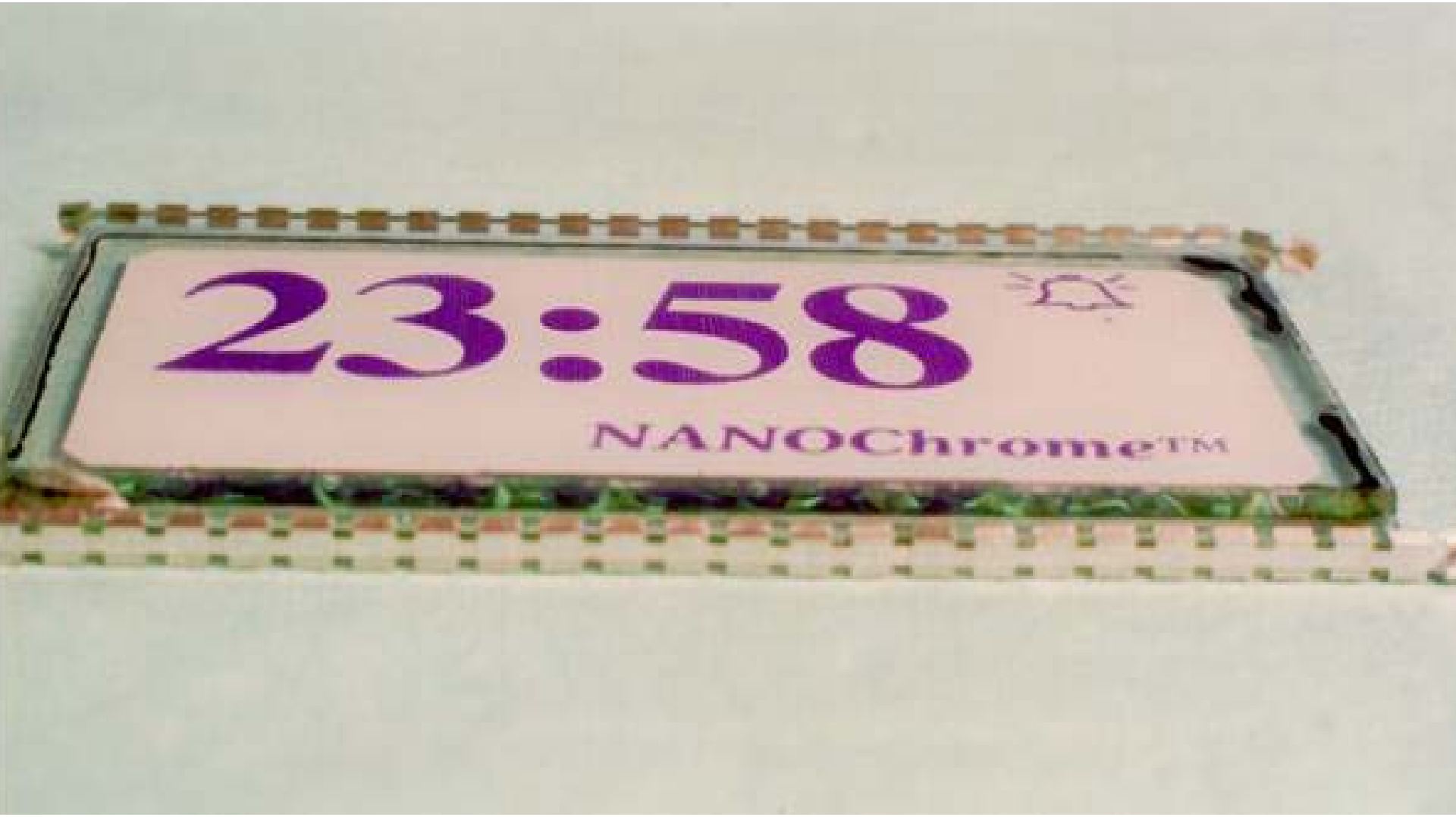


Cathode: $MV^{2+} + e^- \rightarrow MV^+$

Anode:

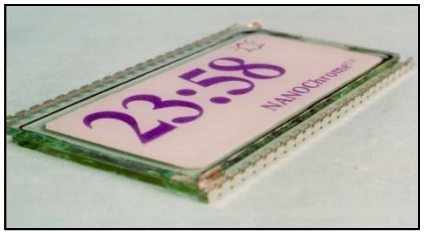


TiO_2 – based electrochromic display



Electrochromics – Paper Quality Displays

High contrast
High reflectivity



Angular independence

Fundamentally it looks like ink on paper

Applications of nanomaterials in (electrochemical) energy storage:
supercapacitors, batteries, fuel cells

Gaston Planté (1834-1889)

Inventor of lead acid battery (1859)

Gastornis: "Gaston's bird“
(flightless bird from paleoncene)

12V, 40 Ah car battery:

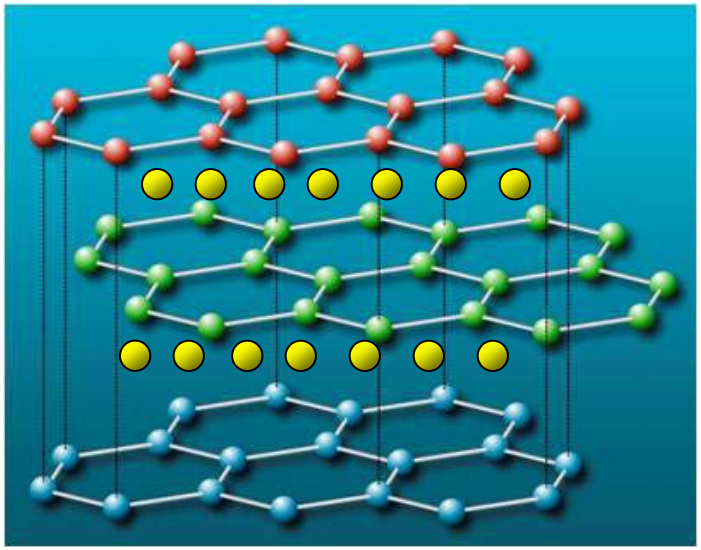
40 Ah @ C/24 discharge rate

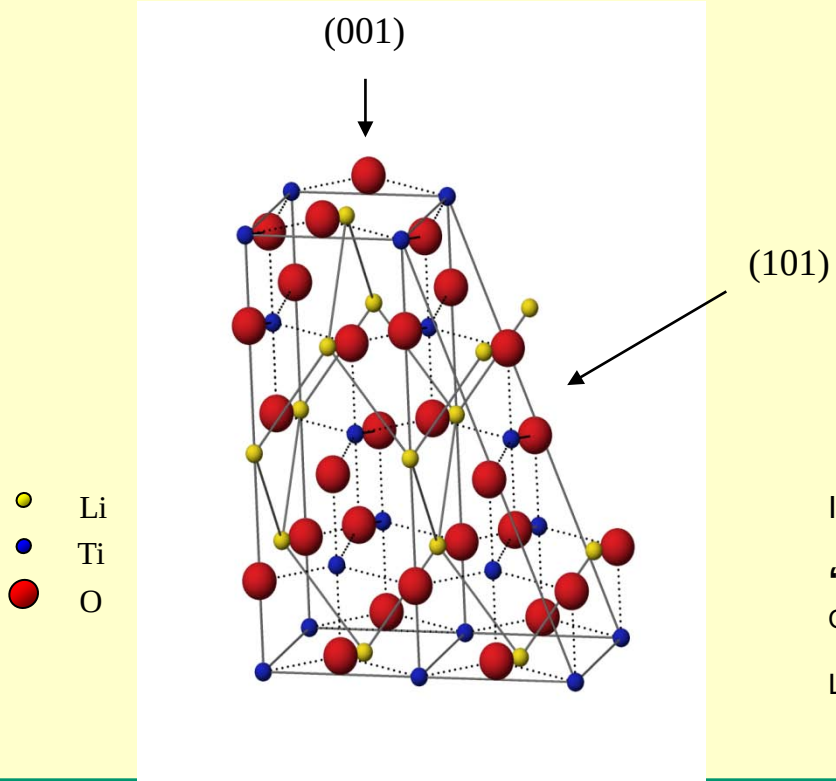
● Li^+

Graphite intercalation:

$C + 1/6\ (e^- + Li^+) \rightarrow 1/6\ LiC_6$

E_{form} ≈ 0.2 V vs. Li/Li^+
Q_{spec} = 1340 C/g = 372 mAh/g





TiO_2 (anatase) insertion:

$TiO_2 + 1/2\ (e^- + Li^+) \rightarrow Li_{0.5}TiO_2$

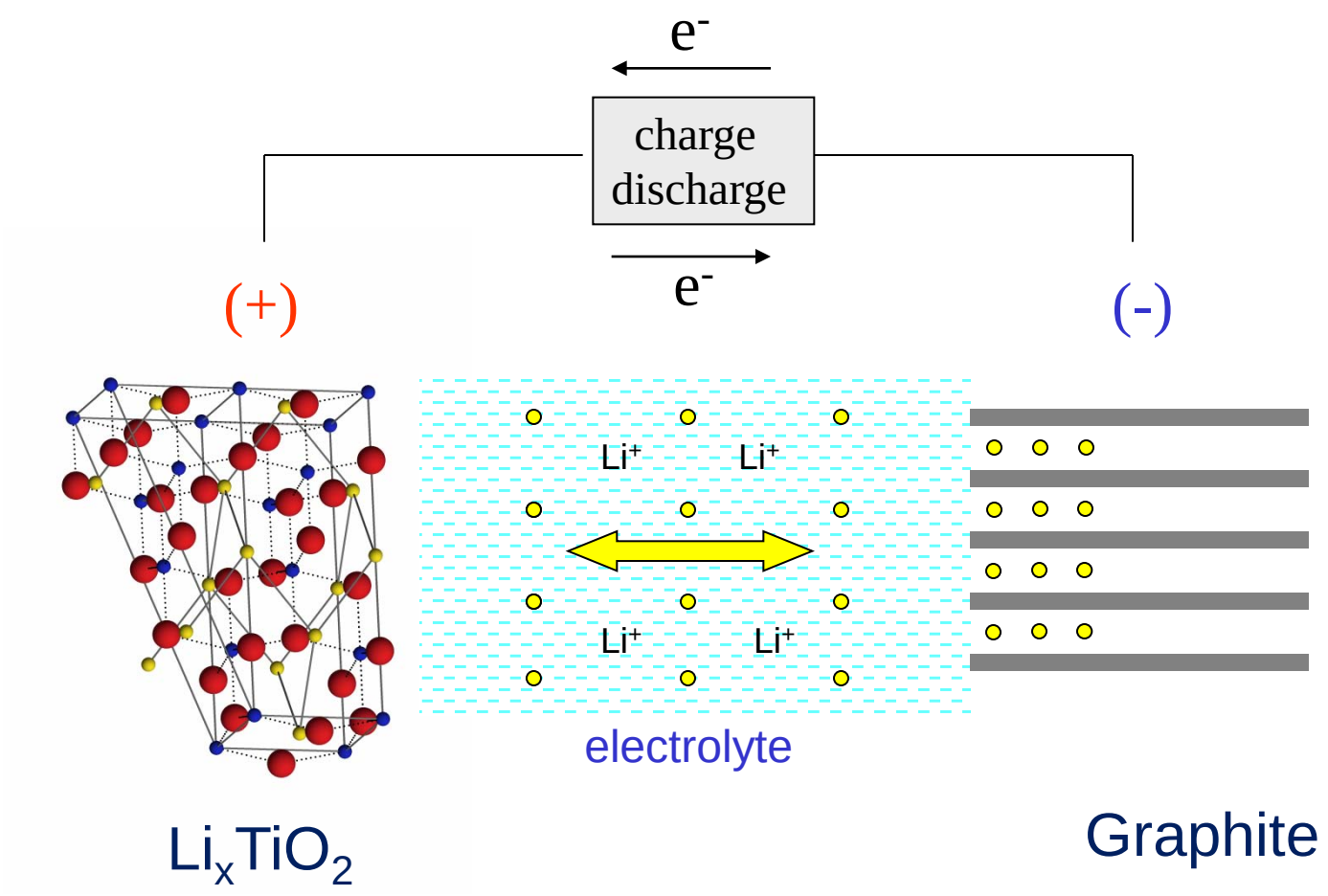
E_{form} ≈ 1.85 V vs. Li/Li^+
Q_{spec} = 168 mAh/g

IUPAC definition:

"Intercalation" = non covalent inclusion into laminar hosts
G. P. Moss, P. A. S. Smith, D. Tavernier, *Pure Appl. Chem.* **1995,** *67,* 1307-1375

Lat.: *mensis intercalarius* (Julian/Gregorian reform of the calendar, 46 BC)

Battery Li-ion



[$Li_4Ti_5O_{12}$, graphite...]

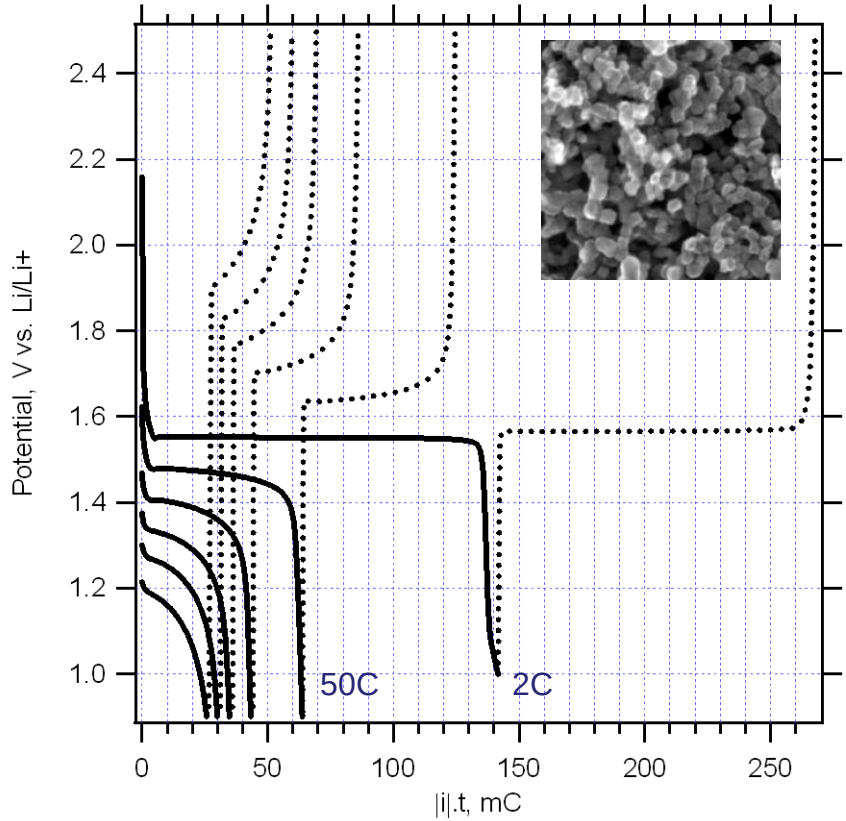
[$LiCoO_2$, $LiNiO_2$, $LiMn_2O_4$, $LiFePO_4$, ...]

$Li_4Ti_5O_{12}$ (spinel): galvanostatic charge/discharge

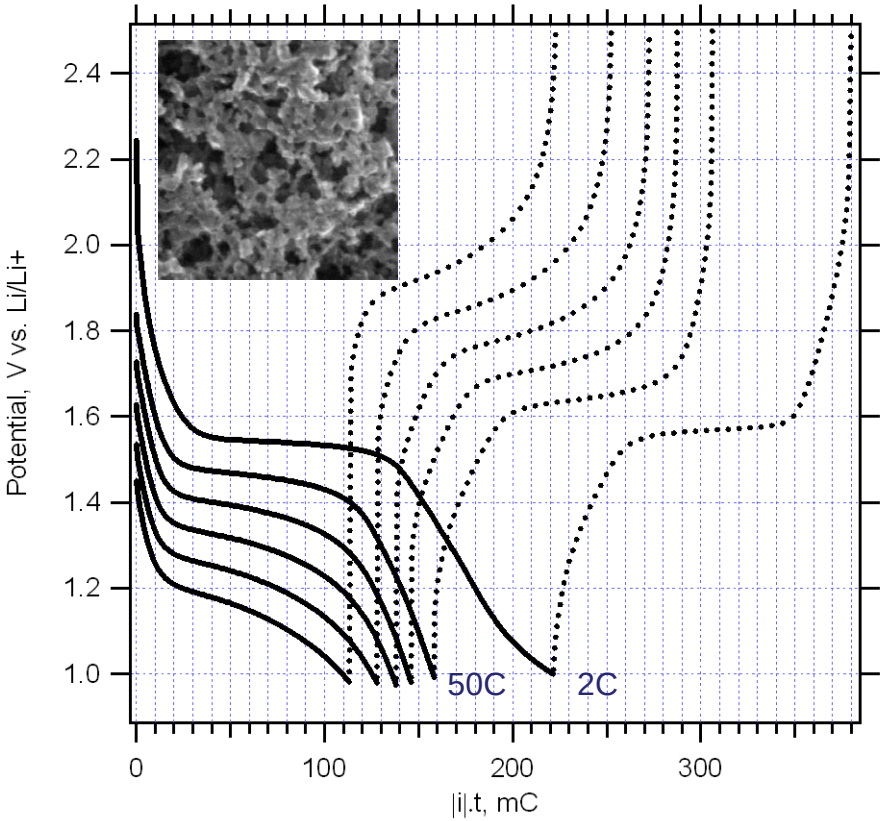
Charging rates:

2C, 50C, 100C, 150C, 200C, 250C

$Li_4Ti_5O_{12} + (3e^- + 3Li^+) \rightarrow Li_7Ti_5O_{12}$

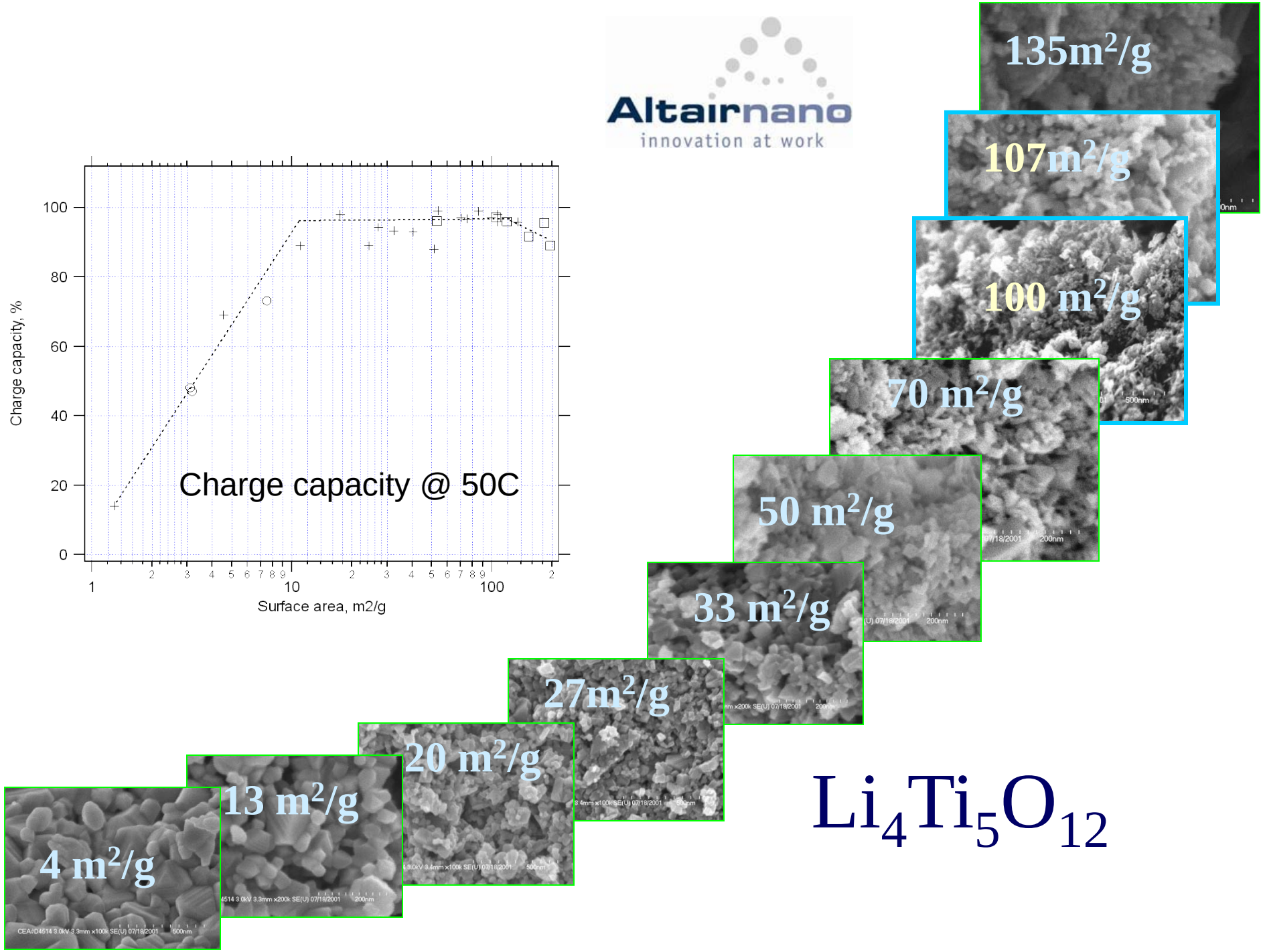


- commercial material (∅ ≈ 1 μm)



- mesoscopic material (∅ ≈ 10 nm)

Altairnano
innovation at work

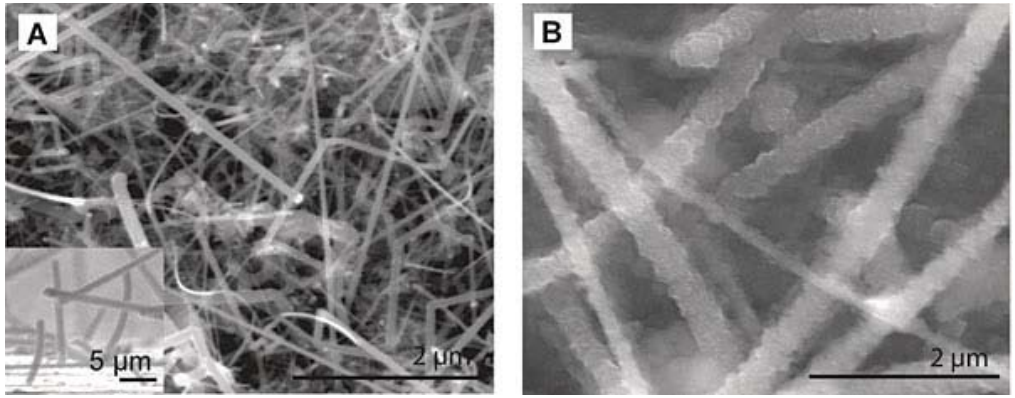


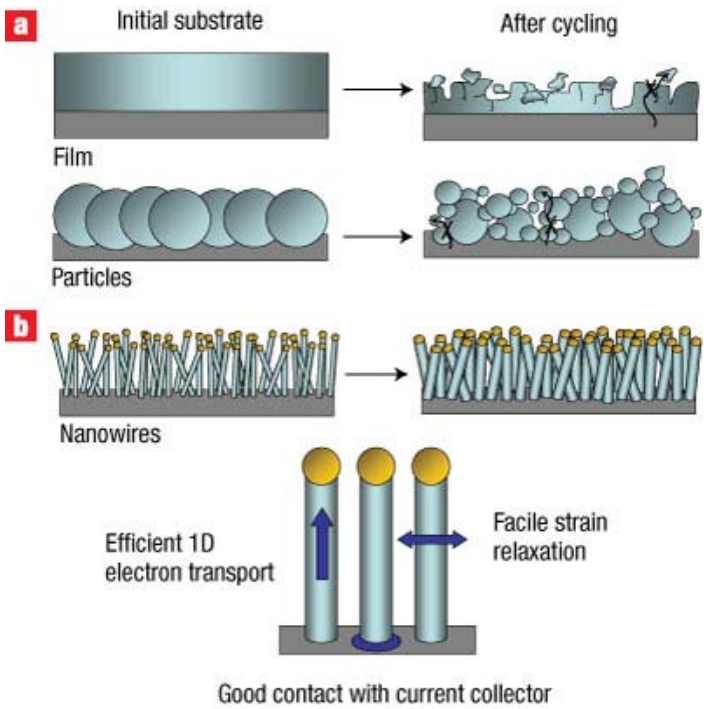
$Li_4Ti_5O_{12}$

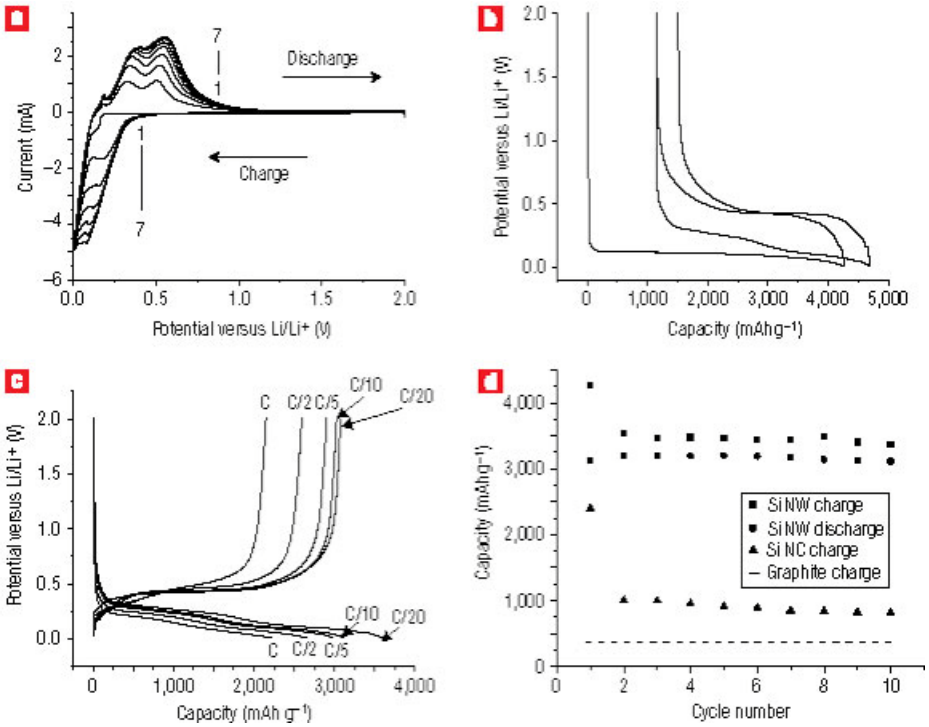
Si-nanowires: anode for Li-ion

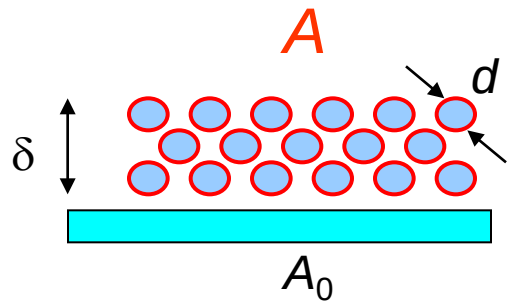
>3000 mAh/g (cf. graphite 372 mAh/g)

Nature Nanotechnology, 3, 31, 2008









Surface area (δ = 10 μm)

$$\frac{A}{A_0} = \frac{2 \cdot \delta \cdot 0.74}{d}$$

d = 100 nm ⇒ A/A_o=150
d = 10 nm ⇒ A/A_o=1500

photocatalysis
(self-cleaning)

Light harvesting (δ = 10 μm)

$$\Phi_{LH} = 1 - 10^{\varepsilon \Gamma A / A_0}$$

d = 100 nm ⇒ Φ_{LH} = 69%
d = 10 nm ⇒ Φ_{LH} = 99%

solar cells
(energy conversion)

Li^+ - diffusion (D = $4 \cdot 10^{-13}$ cm^2/s)

$$\frac{d}{2} = \sqrt{\pi D t}$$

d = 100 nm ⇒ *t* = 2000 s
d = 10 nm ⇒ *t* = 20 s

Li-batteries
(energy accumulation)