Základy materiálů a nanostruktur

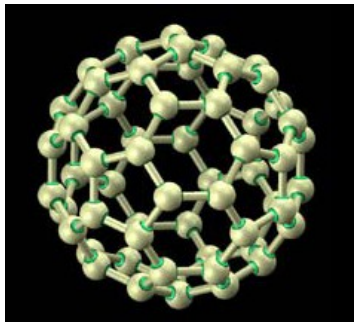
KFY/7ZMAN

Nanostruktury

Miroslav Kolos

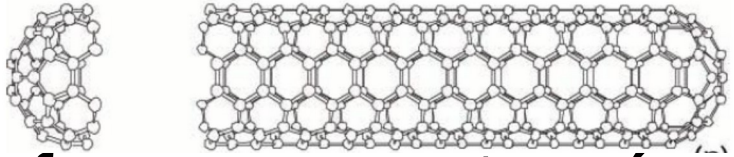
Nano historie

- 1959 – R. Feynmen, APS meeting, Pasadena: vize nanotechnologického věku, předpověď paměťového čipu, metod nanomanipulace
- 1981 – skenovací tunelová mikroskopie (STM): možnost 3D zobrazení s atomárním rozlišením, Nobelova cena – Binning, Rohrer (1986)
- 1985 objev fulerenu C_{60}, *Nature* 318 (1985) 162-163, Nobelova cena - Kroto, Smalley, Curl (1996)

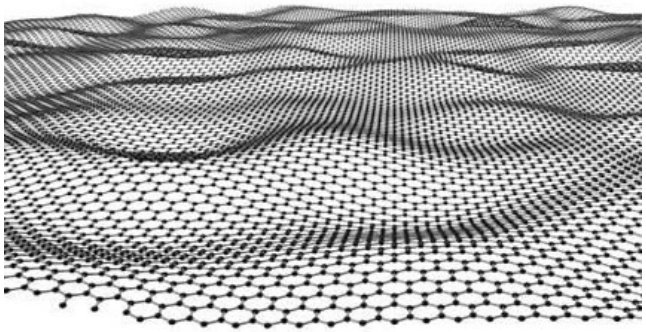


Nano historie

- 1991 – objev vícestěnných uhlíkových nanotrubiček, S. Iijima, *Nature* 354 (1991) 56-58
- 1993 – objev jednostěnných uhlíkových nanotrubiček, S. Iijima, T. Ichihashi: *Nature* 363 (1993) 603-605

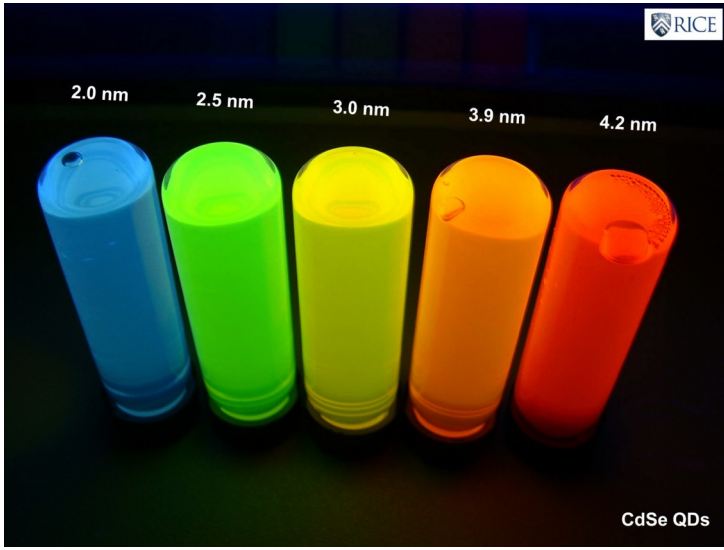


- 2004 – objev grafenu -monoatomární grafitová vrstva, první stabilní 2D struktura *Science* 306 (2004) 666-669. Nobelova cena – K. Novoselov, A. Geim (2010)



Nobelova cena za chemii 2023 – Kvantové tečky

- 👨‍🔬 Laureáti:
- Alexej Jekimov – objev kvantové velikostní závislosti (skleněné matrice, 1980s)
- Louis Brus – kvantové tečky v koloidních roztocích (1983)
- Moungi Bawendi – vysoce kvalitní syntéza koloidních kvantových teček (1993)
- ✨ Význam:
- Ukázali, že optické vlastnosti (barva absorbce/emise) závisí na velikosti částic.
- Otevřeli cestu k precizní kontrole nanostruktur na úrovni několika atomů.
- Aplikace: displeje (QLED TV), bioimaging, fotovoltaika, senzory.



Nanostruktury

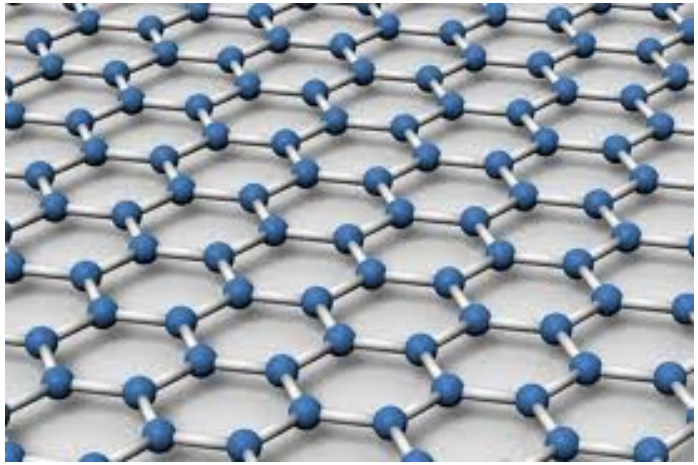
- objekty hmoty, u nichž alespoň jeden z rozměrů menší než 100 nm
- fyz.-chem. vlastnosti výrazně odlišné ve srovnání s „objemovými“ částicemi
- povrchové jevy, jevy na fázovém rozhraní, kvantové jevy
- nové materiály a strukturní formy hmoty (nanofilmy, nanokompozity, nanoprášky, trubičky, grafeny, nanovlákna…)
- nové vlastnosti hmoty (kvantové tečky, superparamagnetismus,…)

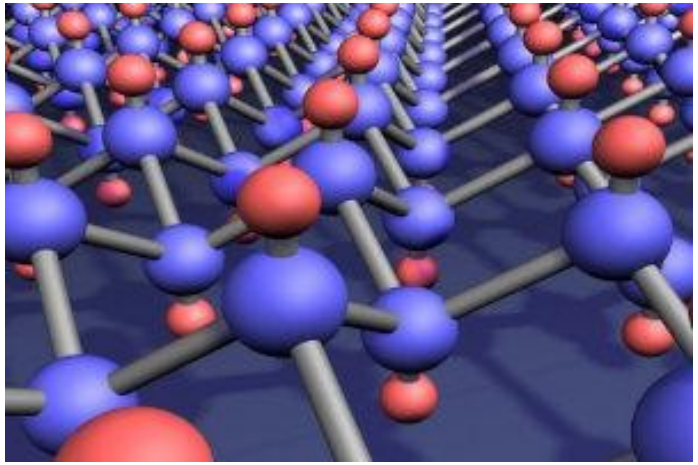
Klasifikace nanostruktur

- 3D – objemové, s nano- motivy
  - Nanokrystalické materiály, nanokompozity
- 2D
  - 2D materiály (grafen, …)
- 1D
  - Nanodráty, nanovlákna
  - Nanotrubičky
- 0D – nanočástice
  - Fullereny
  - Kovové nanočástice (nebo ze sloučenin kovů)

Nejznámější dvojrozměrné materiály

Grafen

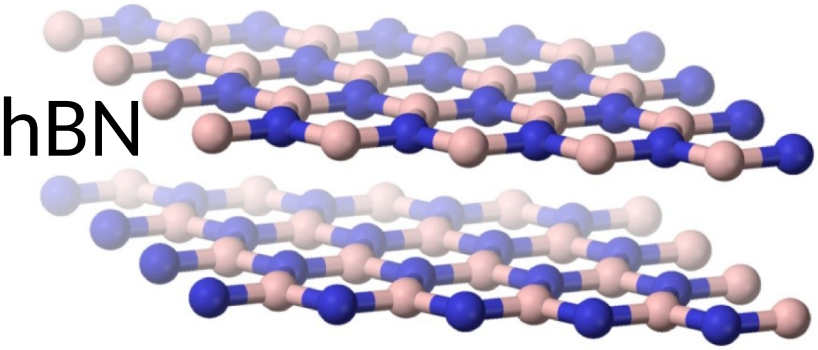


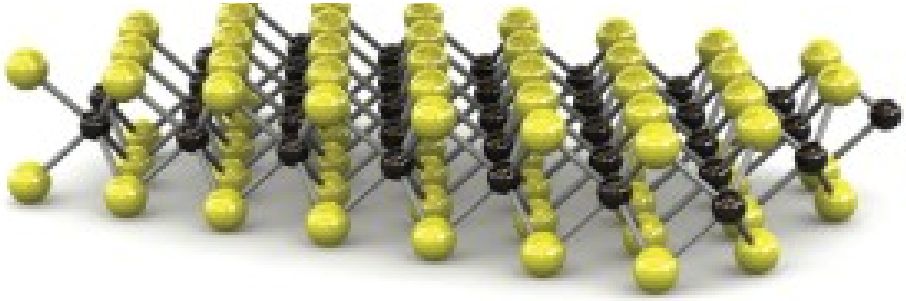


Fluorografen

Hexagonální nitrid boritý

hBN

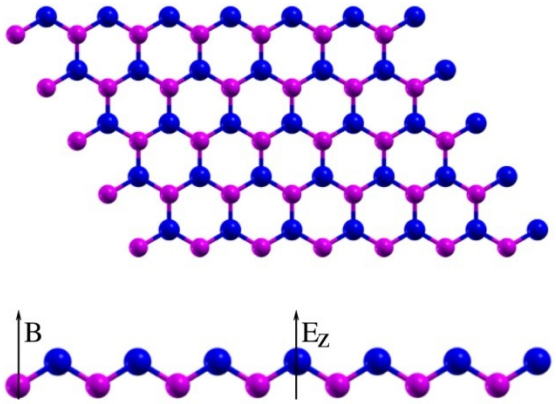




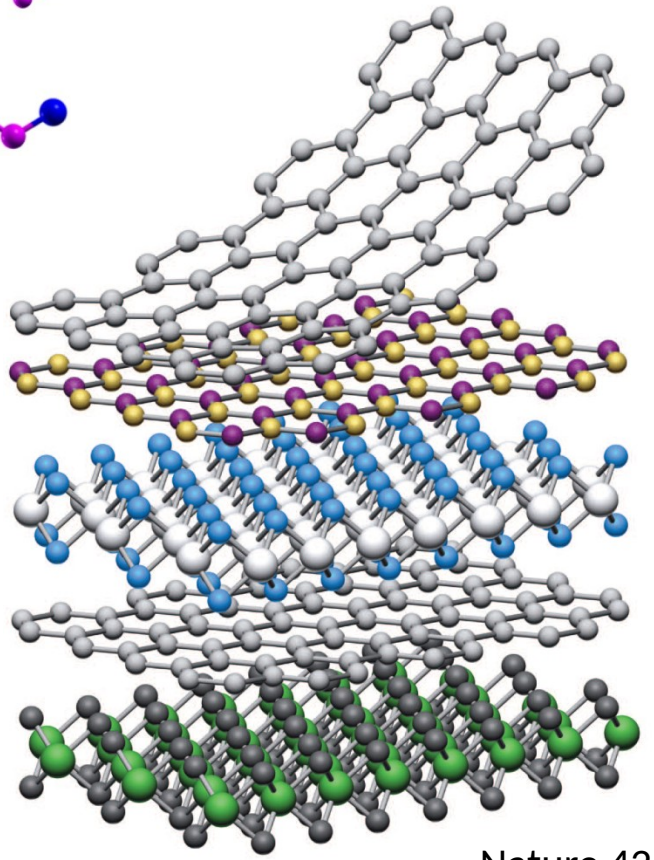
Dichalkogenity kovů MX_2

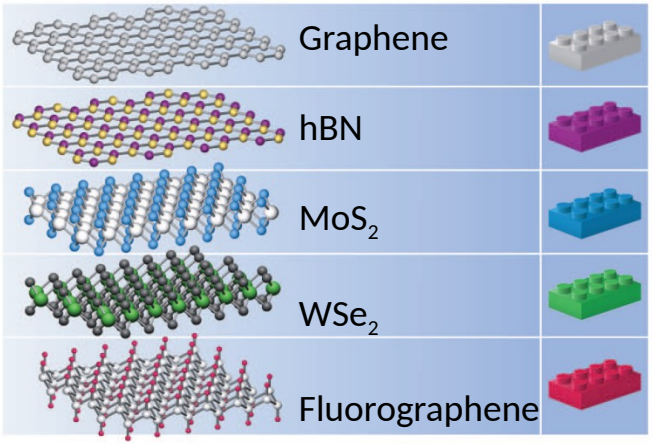
např. M = Mo, W, Ta, Nb, Ni,

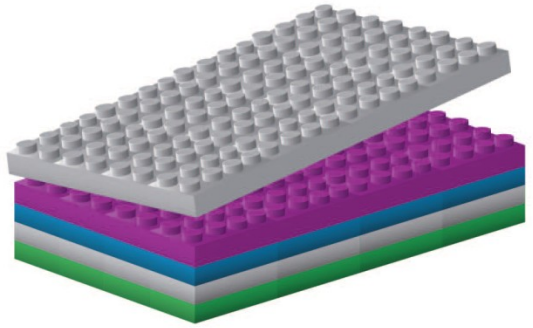
Hypotetické 2D materiály a heterostruktury



Silicen, germanen



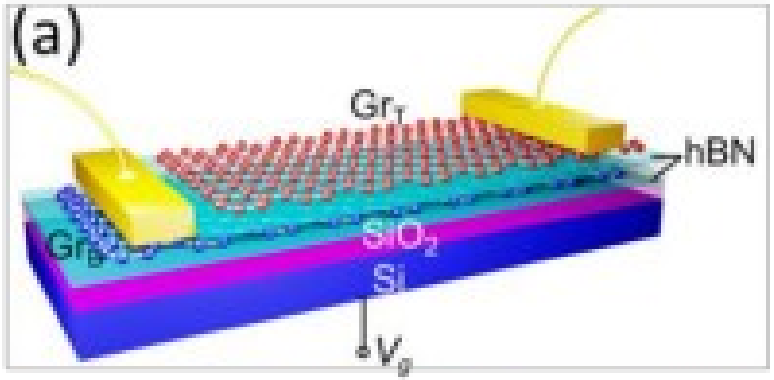


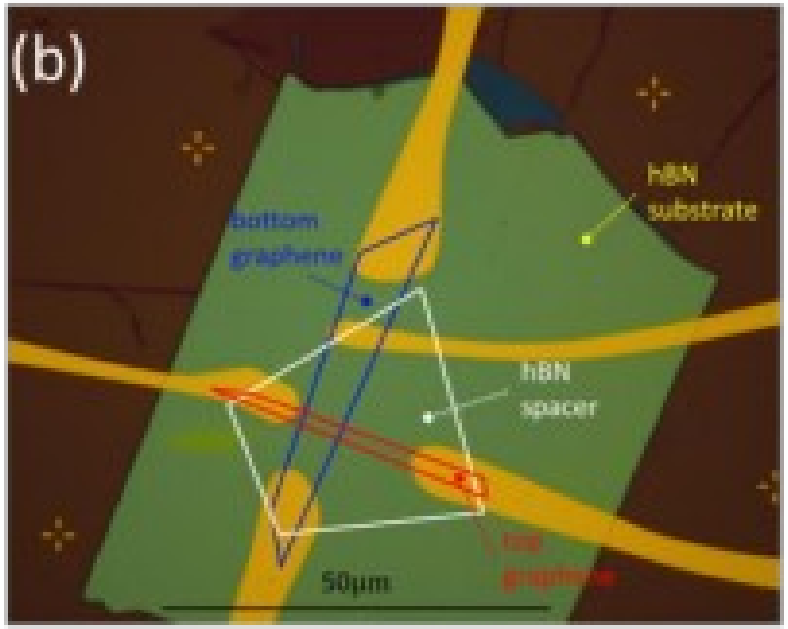


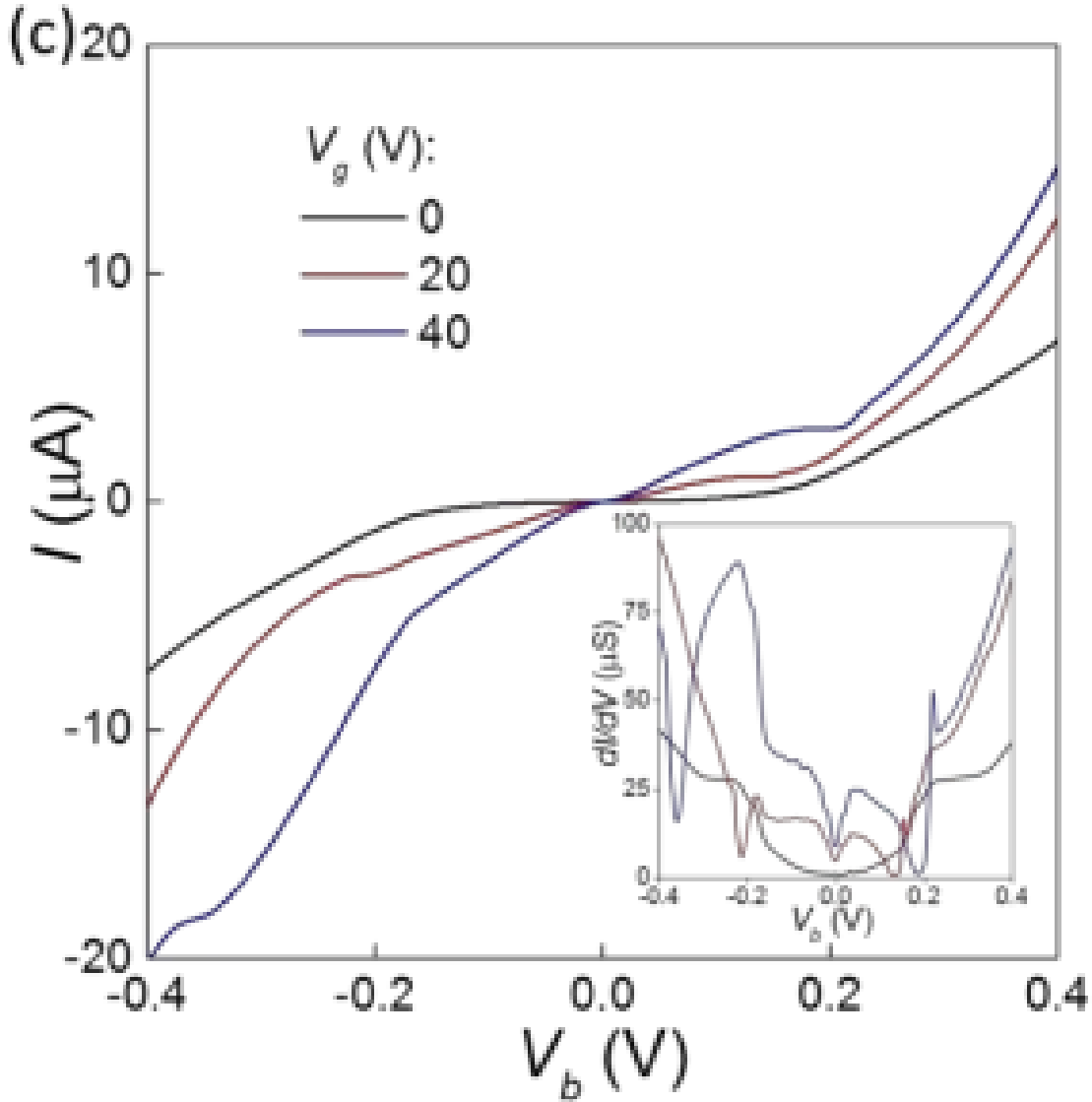
Nature 421 (2013) 499

Je to reálné?

Realizace tranzistoru na bázi grafen-hBN-grafen



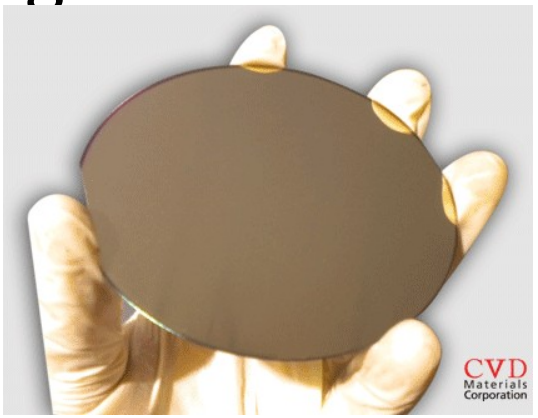




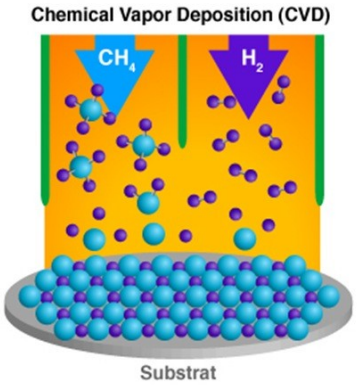
Zhu, Novoselov et al, 2D Mater. 2017, 4,

Grafen

- Grafen = monoatomární vrstva grafitu
- Příprava
  - Mechanické odlupování grafitu
  - Chemická exfoliace
  - Napařování (CVD) na substrát



CVDGraphene™ on a 4" Silicon Wafer on Ni film http://www.firstnano.com



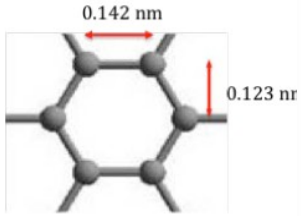
Způsoby přípravy

STM snímek grafenu

Vlastnosti grafenu

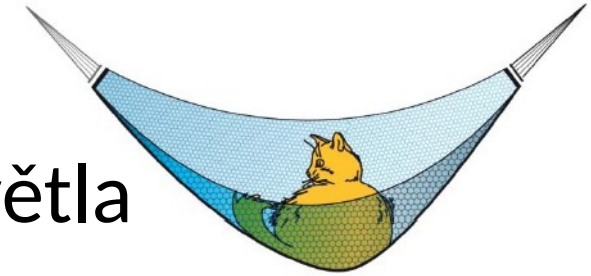
- Plocha elementární buňky 0,052 nm^2, obsahuje 2 atomy, 1m^2 z grafenu

  proto váží 0,77 mg

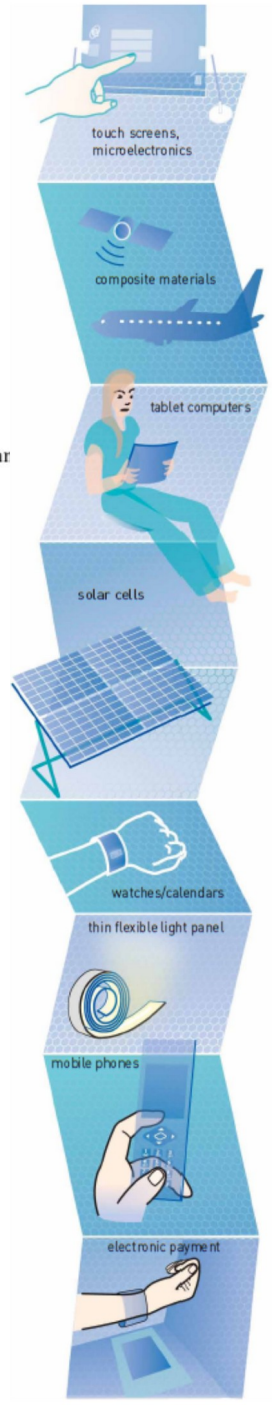


- Více než 100 krát pevnější než ocel (stejné tloušťky), 1m^2 by měl unést až 4kg
- Téměř transparentní,

  absorbuje jen 2,3% světla



- Teplo vede 10 krát lépe než měď
- Mírně větší elektrická vodivost než měď



Royal Swedish Academy of Sciences: *Scientific Background on the Nobel Prize in Physics 2010, www.nobelprize.org*

Stabilita

- Stabilita 2D vrstev a membrán po léta diskutována teoreticky
- Podle tzv. Merminova–Wagnerova teorému: dlouhovlnné fluktuace vedou ke zničení dlouhodosahovému uspořádání 2D krystalu
- U grafenu vysvětleno zvlněním o vlnové délce 50-100 A

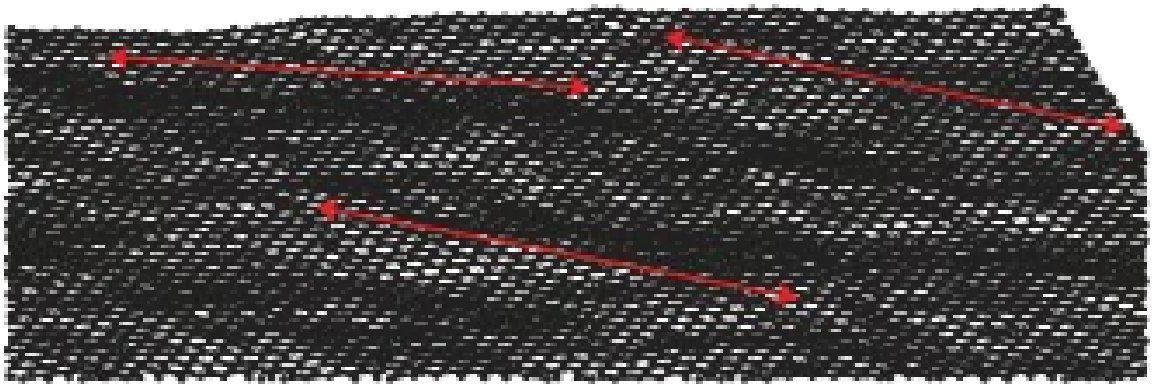
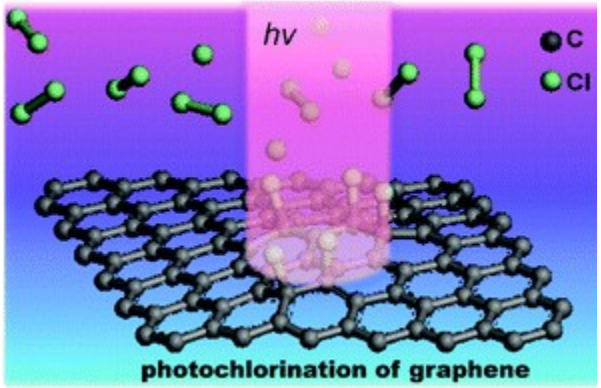


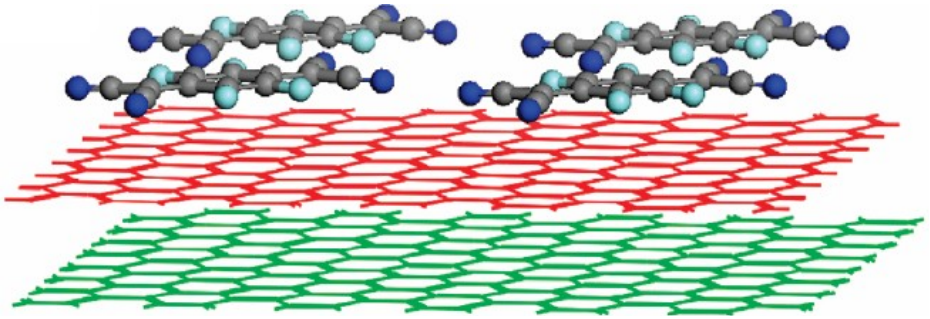
Figure 1 A representative configuration of the $N = 8{,}640$ sample at $T = 300$ K. The red arrows are ~80 Å long.

Nature Mater. 6 (2007) 858

Elektronické vlastnosti grafenu

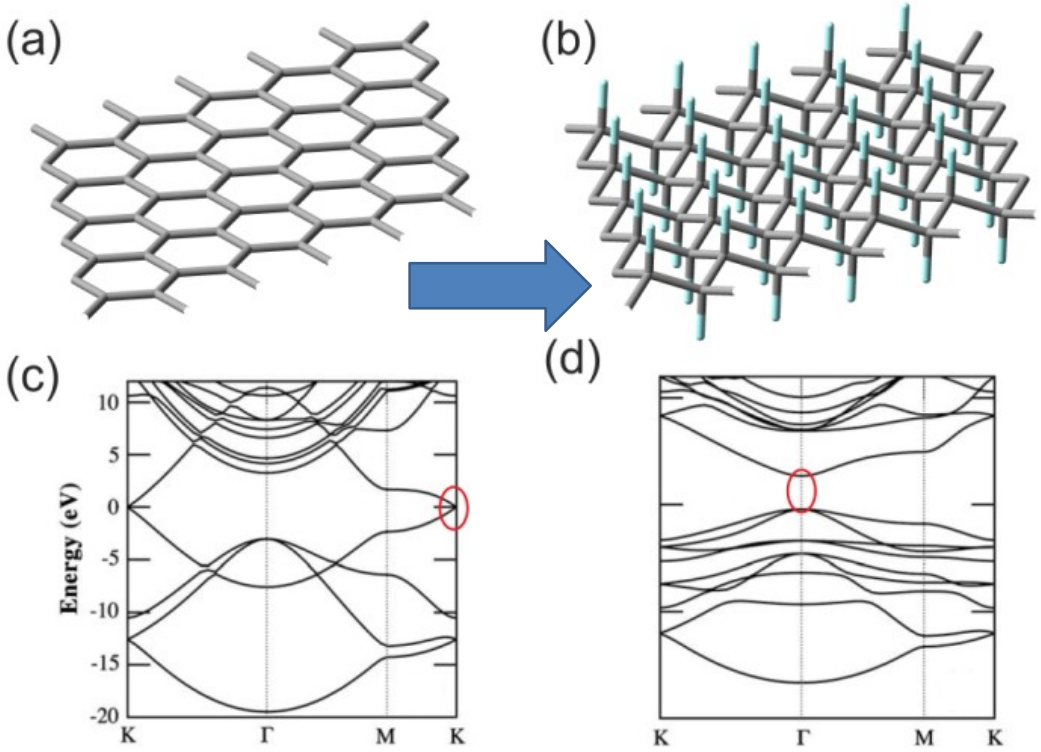
- Grafen je polokov – nulový zakázaný pás
- Pro elektroniku jsou výhodné materiály se zakázaným pásem (polovodiče E_g ~ 1 eV)
- Nejlépe, pokud lze zakázaný pás měnit
- Různé cesty k „otevření“ zakázaného pásu
- Chemická modifikace, chemisorpce, fyzisorpce, vliv vnějšího pole, mechanická deformace, …





Kovalentní modifikace grafenu

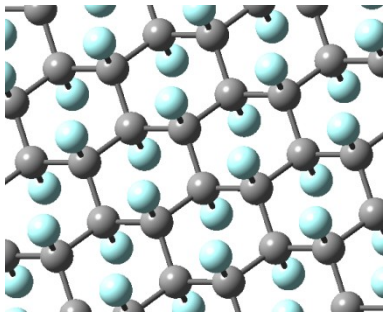
- Atomy nebo molekuly jsou kovalentně navázány na některé (nebo všechny) atomy uhlíku

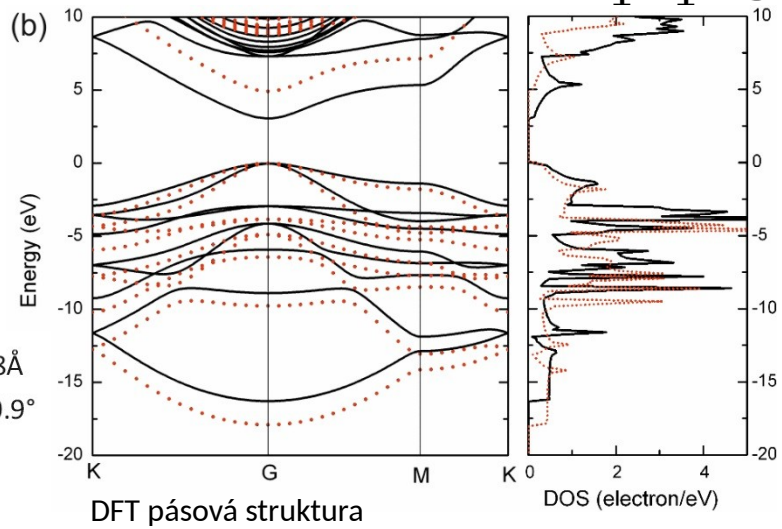


- sp^2 hybridizace se mění sp^3
- v Γ bodě (nebo jinde) se objevuje zakázaný pás

Fluorografen

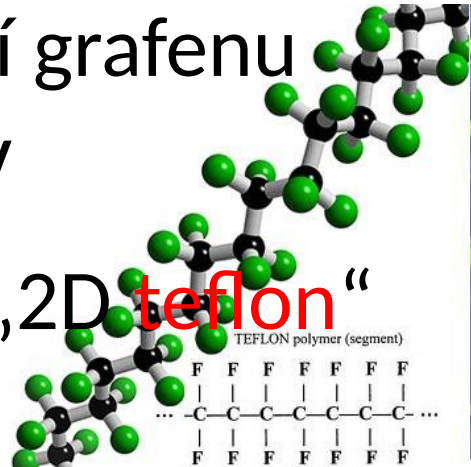
- Grafen plně pokrytý fluorem, C_1F_1, grafen fluorid



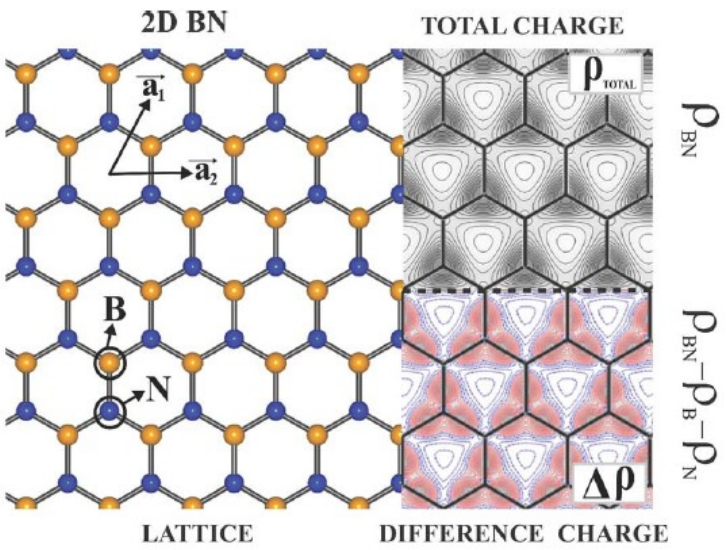


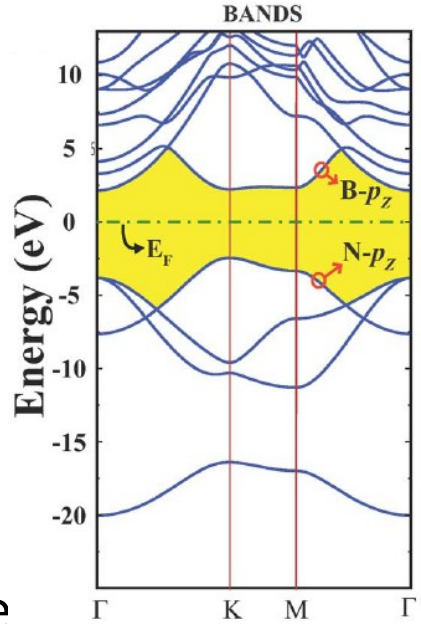
DFT pásová struktura (PBE, HSE)

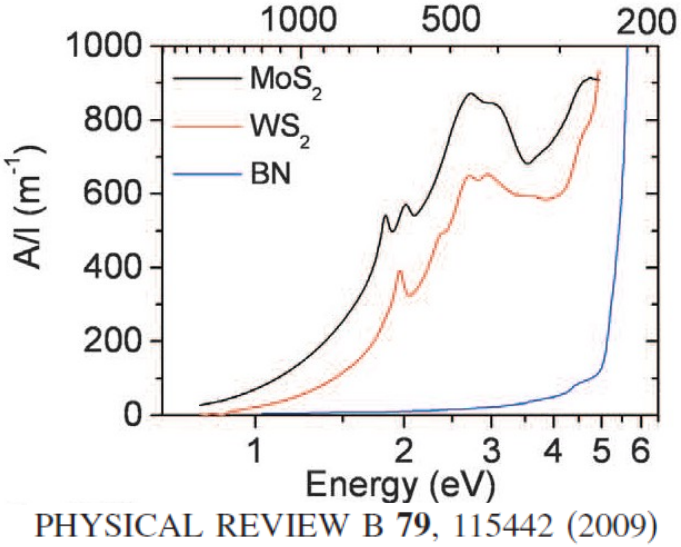
- Připraven 2010, mechanickou či chemickou exfoliací grafit fluoridu nebo fluorinací grafenu
- „Nejtenčí izolant na světě“, E_g ~ 7-8 eV
- Mechanicky a tepelně velmi odolný - „2D teflon“



Hexagonální nitrid boritý







PHYSICAL REVIEW B **79**, 115442 (2009)

Absorpce až v ultrafialové oblasti

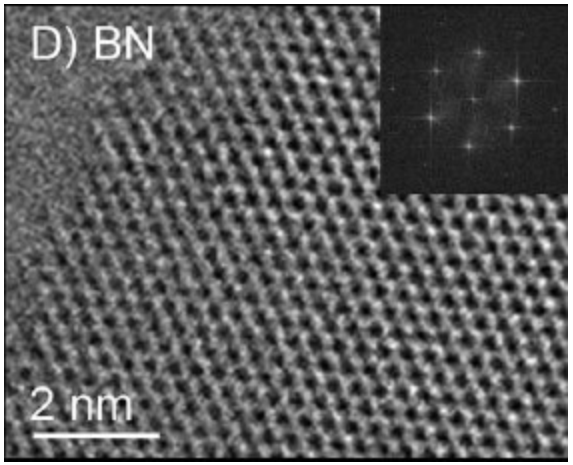
- Struktura podobná grafe
- Iontový charakter vazby B-N
- Nepřímý materiál, izolant (E_g ~ 4,6 eV, DFT), 2 atomy v buňce, 4 obsazené pásy

B: [He]$2s^2 2p^1$

N: [He]$2s^2 2p^3$

	E_{gap}^{indir}	$E_{gap}^{M/K}$	E_{gap}^{opt}	E_b^{exc}
calc. AA′	6.08	6.53	5.71	0.82
calc. AB	6.17	6.39	5.61	0.78
exp. [1,2]	6.08	6.42	5.69	0.73

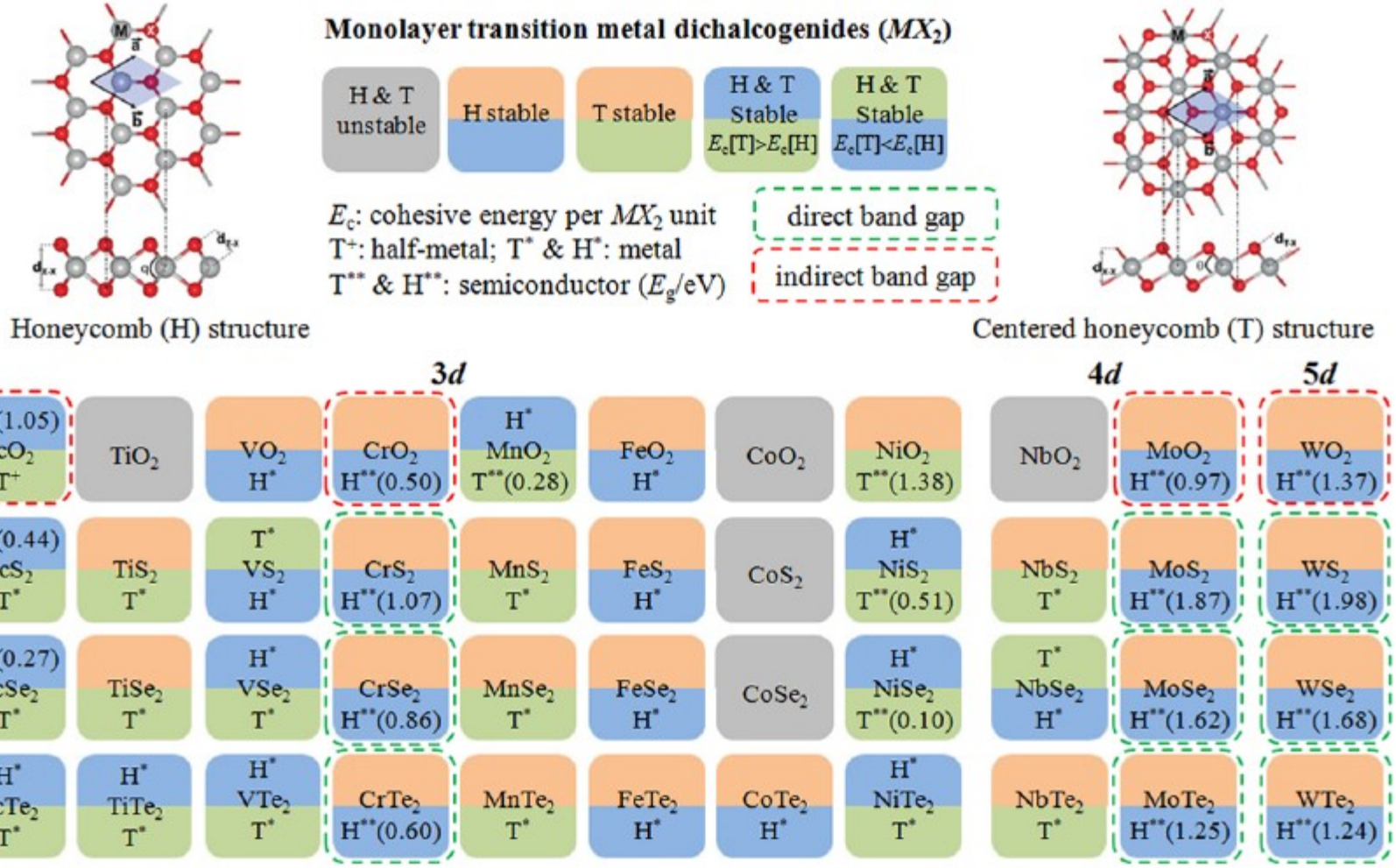
Kolos, Karlický, Phys. Chem. Chem. Phys. 21(7), 3999–4005, 2019



High-resolution TEM

Science **331**, 568

Dichalkogenity přechodných kovů



Stabilita a elektronické vlastnosti 2D dichalkogenitů. Výsledné struktury (T or H) mohou být polokovy (+), kovy (*) nebo polovodiče (**) s přímým nebo nepřímým zakázaným pásem.

Chem. Rev. 113 (2013)

Considered Materials - MXenes

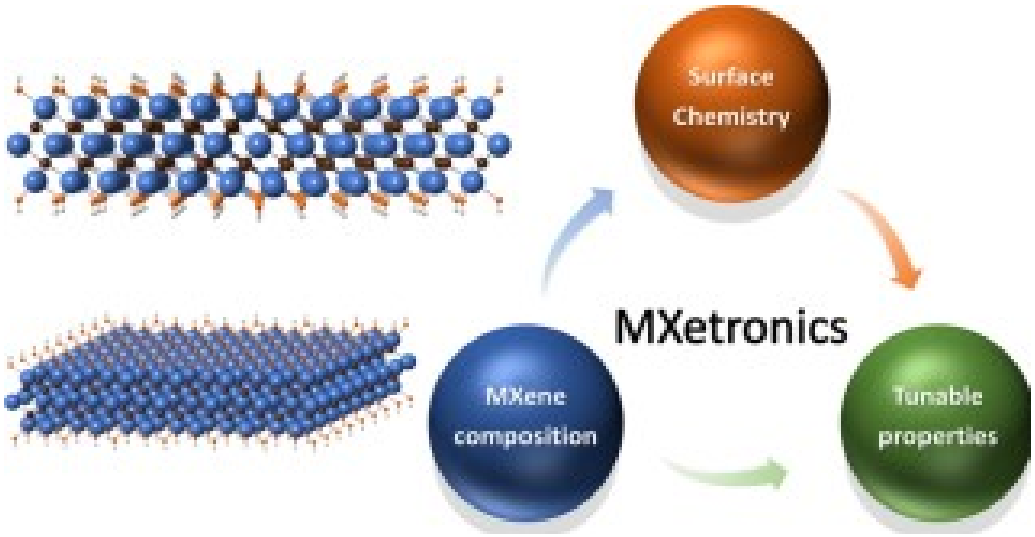
2D materials

$M_{n+1}X_nT_x$

M = transition metal,

X = nitrogen/carbon

T = functional group (-F, -O or -OH)



ACS Materials Lett. 2 (2020) 55

Our search – carbides, light metals (3d), semiconducting, n=1

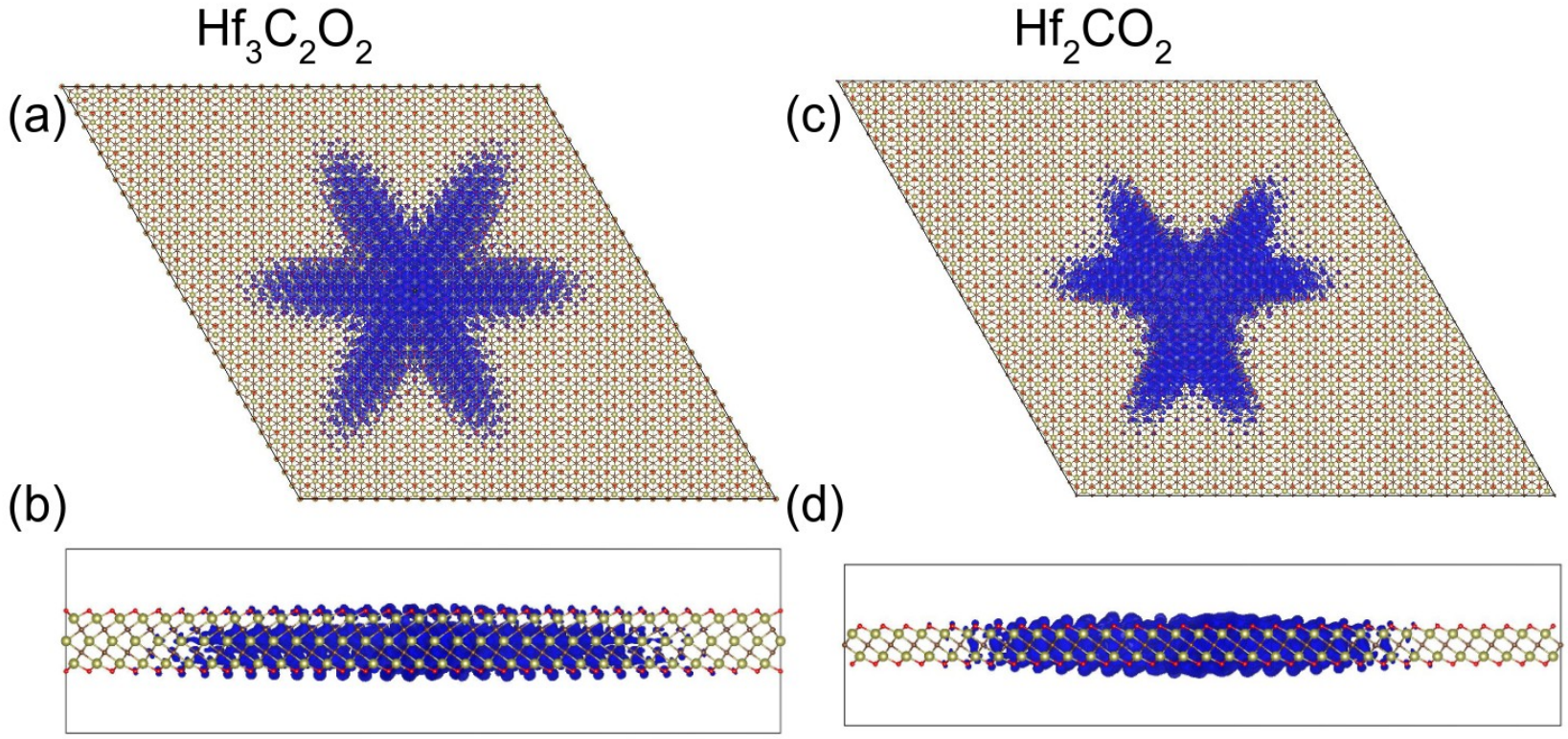
Sc_2CF_2, $Sc_2C(OH)_2$, Ti_2C, Ti_2CO_2, Cr_2CF_2, $Cr_2C(OH)_2$, and Mn_2CO_2

Fundamental properties for applications: gap, absorbance, excitons

Ketolainen, Karlický, *J. Mater. Chem. C* 10 (2022) 3919–3928

UNIVERSITY OF OSTRAVA
FACULTY OF SCIENCE

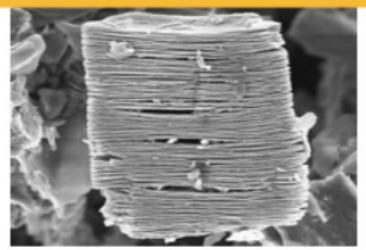
Excitons in Hf MXenes

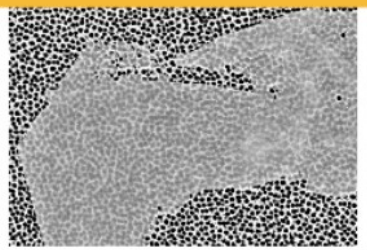


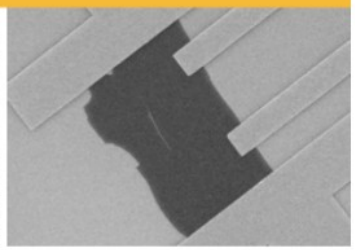
Kumar, Kolos, Bhattacharya, Karlický: J. Chem. Phys. 160(12), 124707, 2024

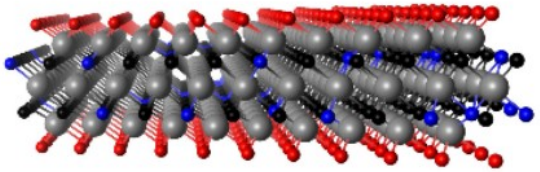
ABOUT MXenes

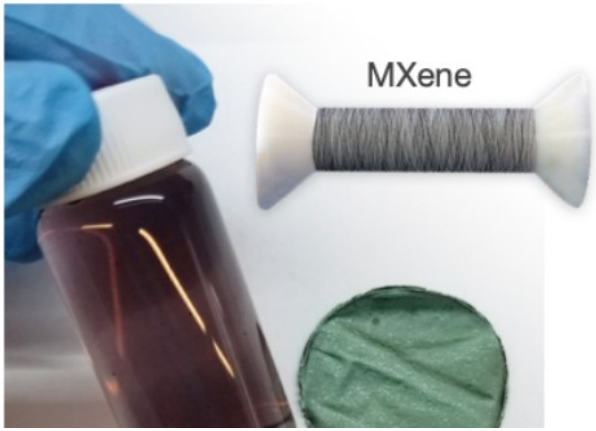
MXenes conduct electricity like metals, but they are nanometer (one billionth of a meter) thin flakes like graphene. They can also be dispersed in water like clay.







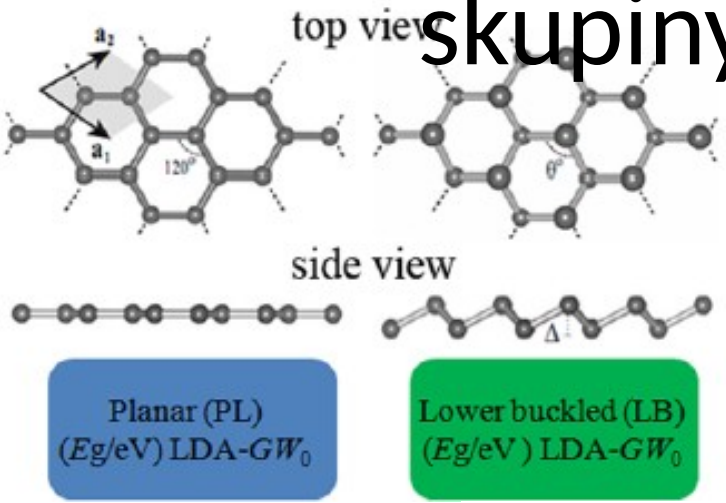




CAPABILITIES:

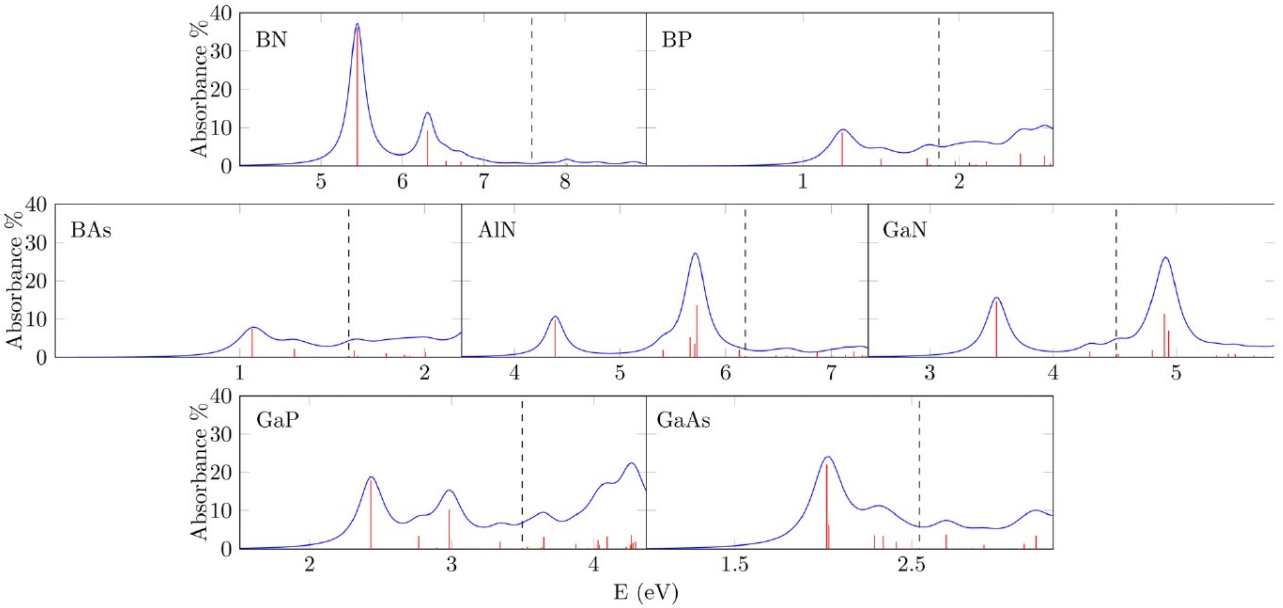
- Store energy much faster than carbon and other materials used in current batteries and supercapacitors
- Protect our electronics (cell phones, etc.) from electromagnetic noise and also protect our credit card information from being stolen
- Purify water and produce drinking water from salt water
- Sense dangerous species in air
- Remove toxic heavy and radioactive elements from water
- Treat cancer
- Make wearable kidney a reality
- Increase strength of plastics, metals and ceramics
- Create energy storing windows that can change color when a small voltage is applied
- Generate printable antennas for 5G communication and Internet of Things
- Enable a new generation of flexible and printable electronic and optoelectronic devices

2D binární sloučeniny prvků IV. skupiny a skupiny III–V



Si (0)	SnGe (0.23-0.40)	AlN (3.08-5.57)	InAs (0.86-2.07)	BAs (0.71-1.24)
Ge (0)	SiGe (0.02-0.0)	GaN (2.27-5.0)	InSb (0.68-1.84)	GaP (1.92-3.80)
SiC (2.52 -4.19)	SnSi (0.23-0.68)	InN (0.62-5.76)	GaAs (1.29-2.96)	AlSb (1.49-2.16)
GeC (2.09-3.83	SnC (1.18-6.18)	InP (1.18-2.88)	BP (0.81-1.81)	BSb (0.39-0.23)

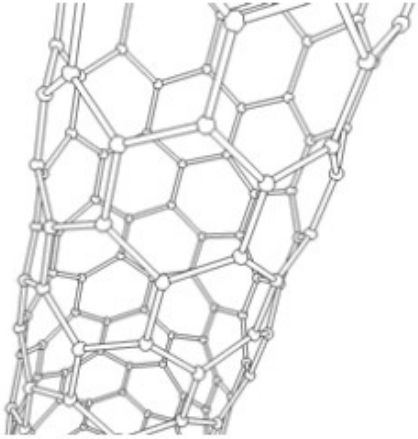
Absorptanční spektrum sedmi III-V 2d materiálů

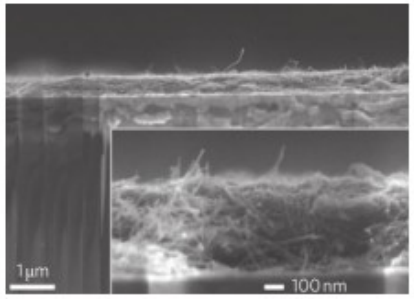


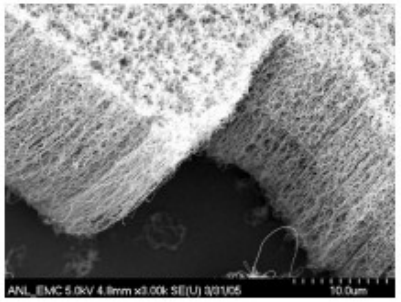
Kolos, Karlický:Phys. Chem. Chem. Phys. 24(44), 27459–27466, 2022

Uhlíkové nanotrubičky

- sp^2, válec
- dělí se dle počtu stěn
  (SWNT, DWNT, MWNT)
- velká pevnost v tahu
- nejvyšší tepelná vodivost
- cca 1nm x 1nm x 10μm
  velká orientační závislost



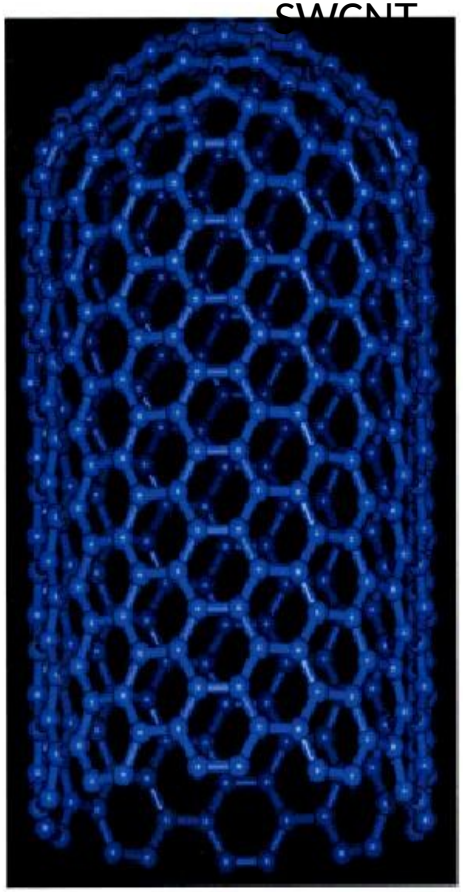


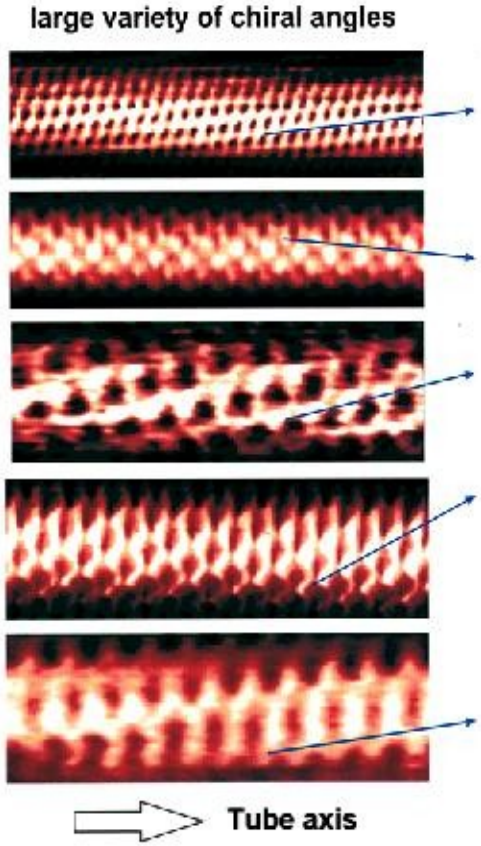


M. M. J. Treacy, T. W. Ebbesen and J. M. Gibson, Nature, 1996, 381, 678
S. T. Huxtable et al. Nat. Mat., 2003, 2, 731
J. A. Misewich et al. Science, 2003, 300, 783

Uhlíkové nanotrubičky

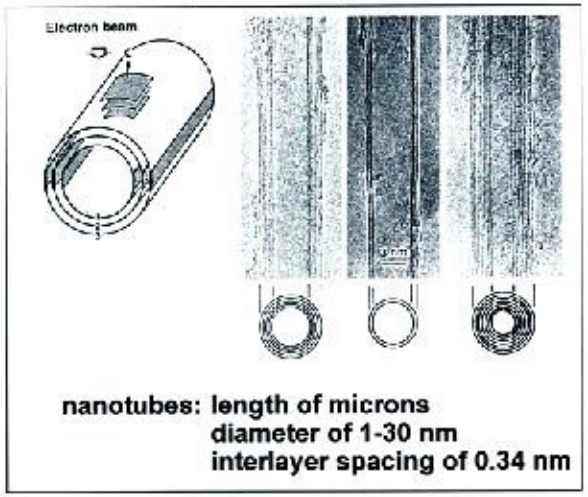
Carbon nanotubes = CNT, single wall (jednostěnné) = SWCNT





brief history of nanotubes

- 1991: multi-wall nanotubes
  lijima



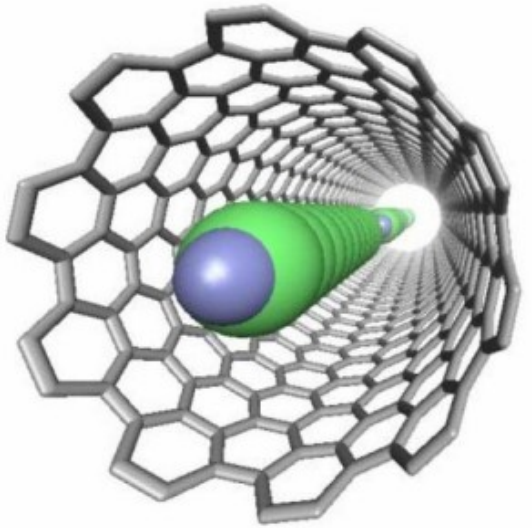
- 1993: single-wall nanotubes
  lijima; Bethune et al
- 1995: laser vaporisation of tubes
  Smalley et al

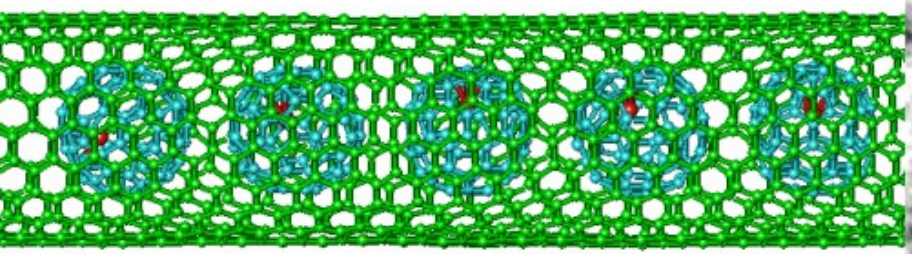
- Mechanics: Tubes as ultimate fibers.
- Electronics: Tubes as quantum wires.
- Capillary: Tubes as nanocontainers.

Widoer, Venema, Rinzler, Smalley, Dekker, Nature **391**, 59 (1998).

Uhlíkové hrášky (peapods)

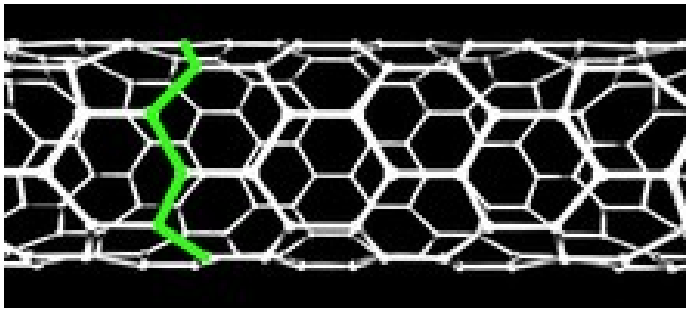
- CNT s uzavřenými molekulami
  - plyny, kovy, fullereny…
- možnost uzavřít i velmi nestabilní molekuly – třeba polyyny



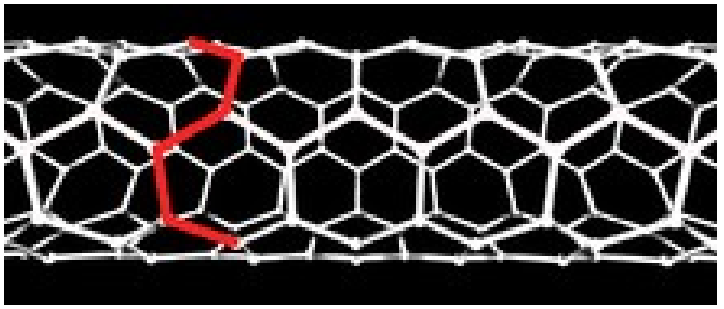


Smith, 1998
N. Shinogara, 2006, Nagano

Uhlíkové nanotrubičky - popis

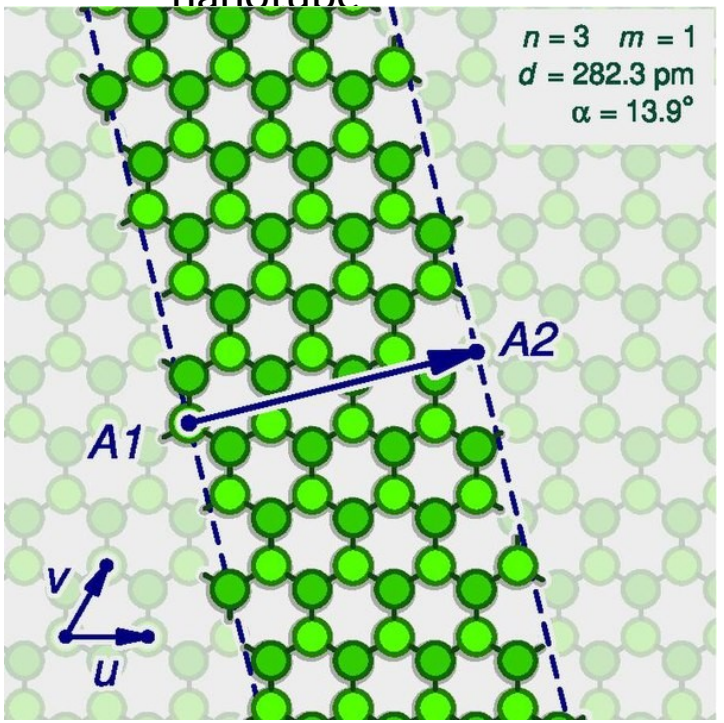


Zigzag nanotube

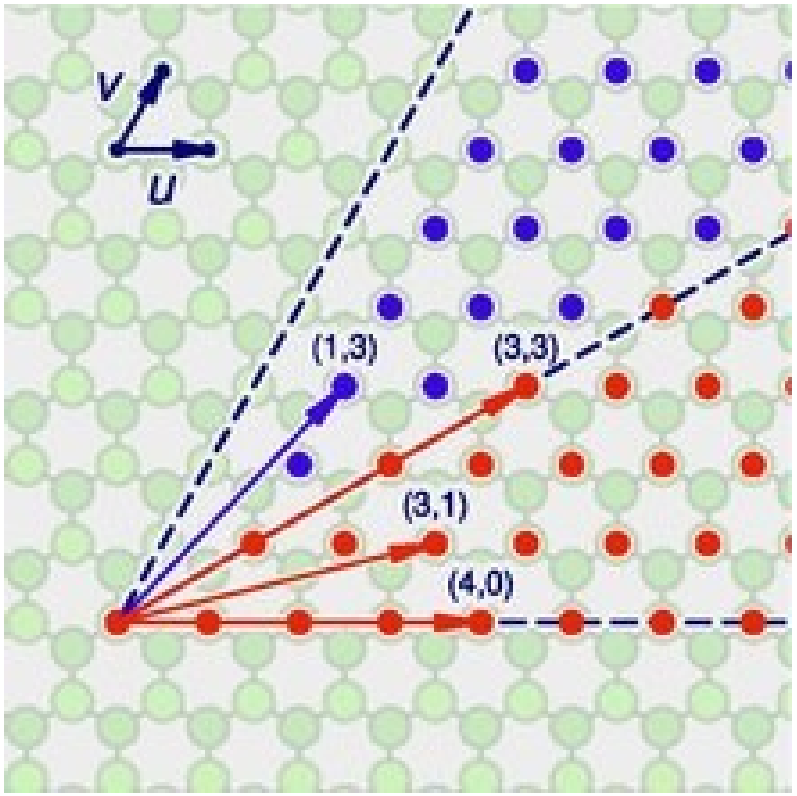


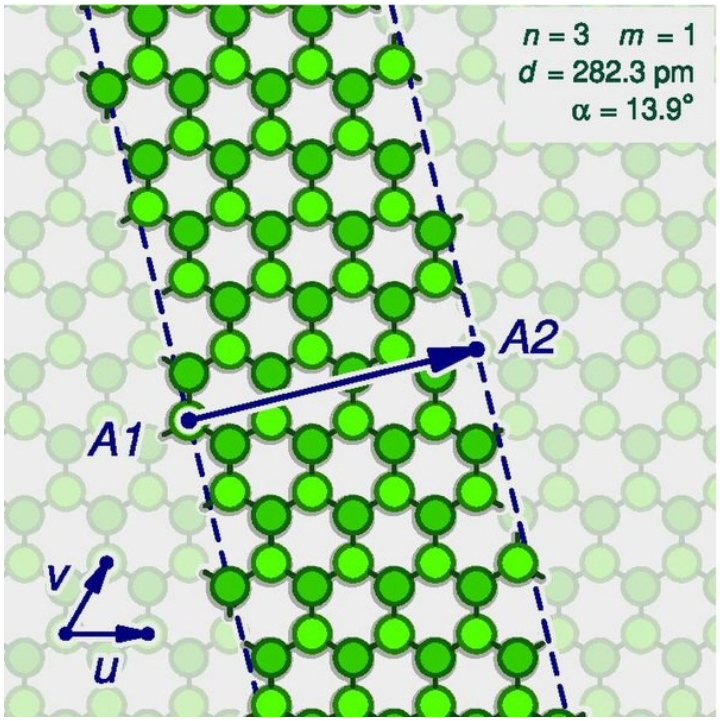
Armchair nanotube

- Obecný popis: notace (n,m)
- Vzhledem ke struktuře grafenu – jeho translačních vektorů
- Využije se vektor kolmý na „směr“ nanotrubičky



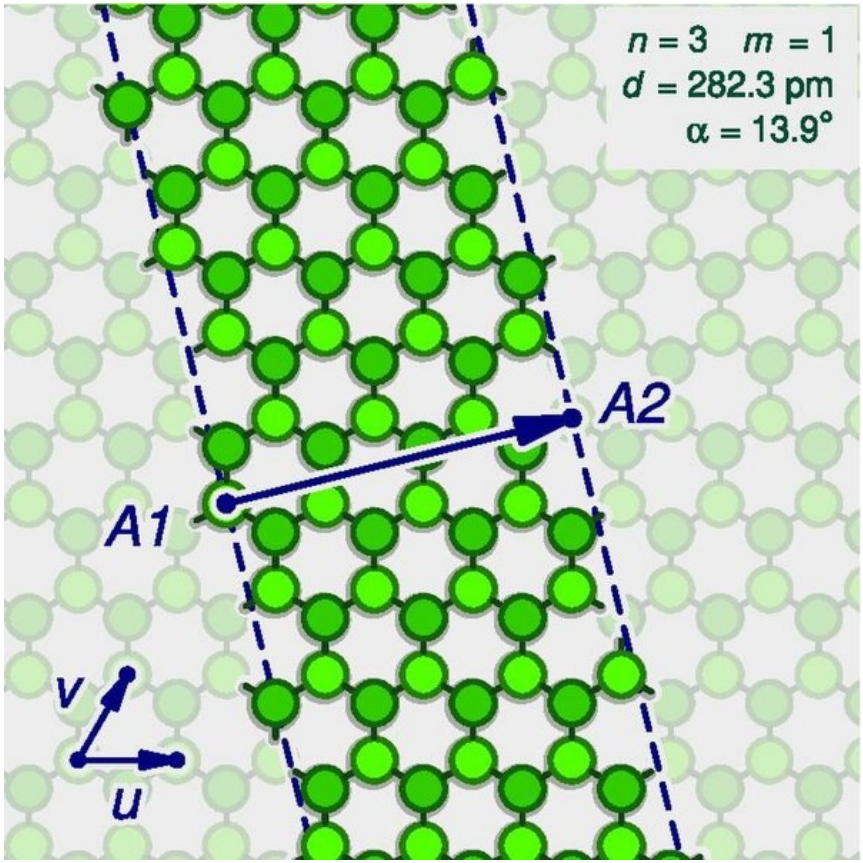
Uhlíkové nanotrubičky - popis



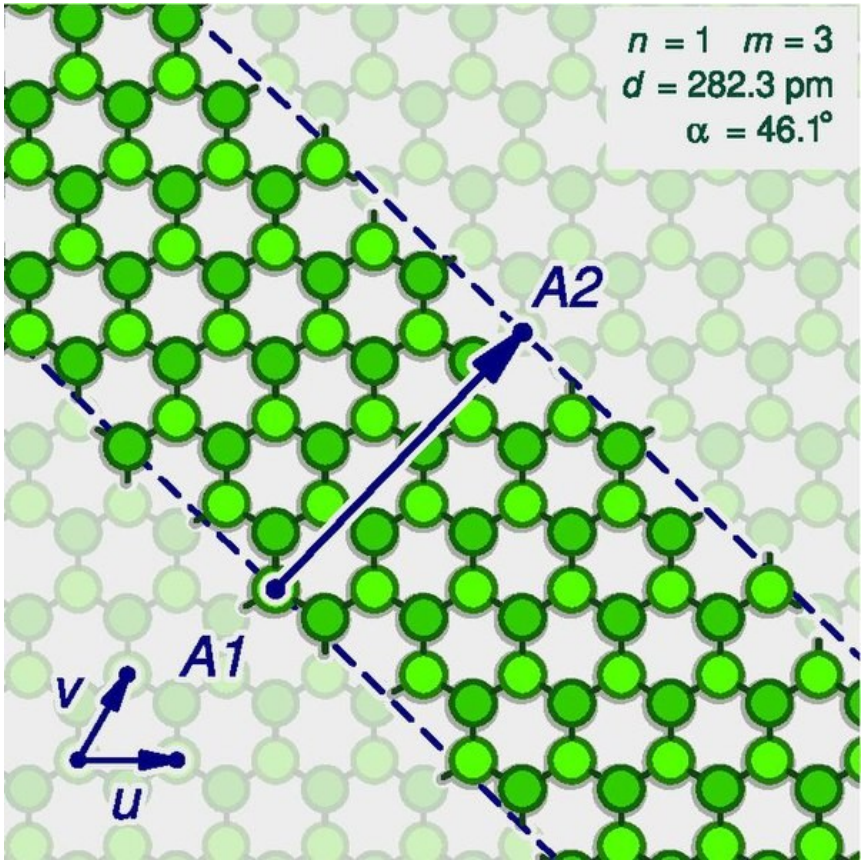


- Obecný popis: notace (n,m)
- Vzhledem ke struktuře grafenu
- Využije se vektor kolmý na „směr“ nanotrubičky

Uhlíkové nanotrubičky - typy

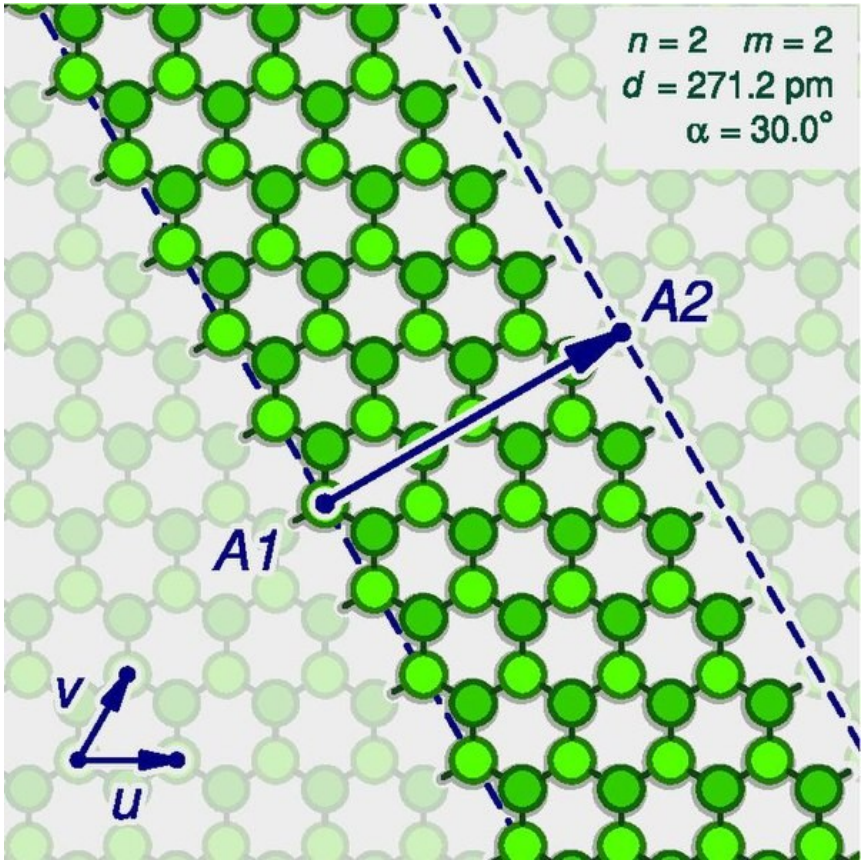


Chirální nanotrubička typu (3,1),
tj. 3***u***+1***v***

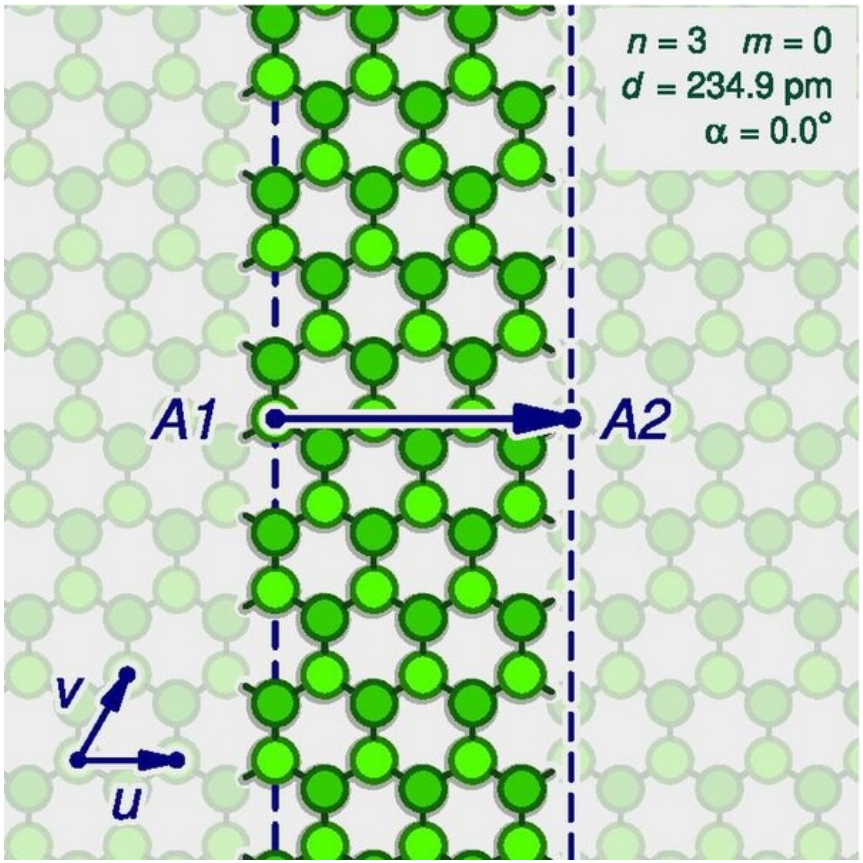


Chirální nanotrubička typu (1,3)

Uhlíkové nanotrubičky - typy



Nanotrubička typu (2,2), „nejtenčí“
nanutrubička „armchair“

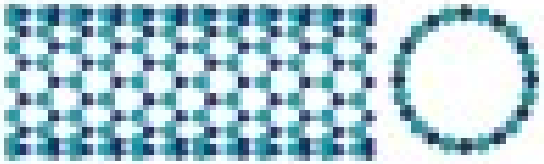


Nanotrubička typu (3,0), „nejtenčí“
nanutrubička „zigzag“

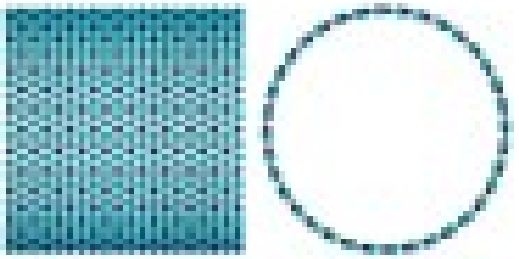
Další nanotrubičky

a) optimized single-wall (6,6) *ac*-BN NT (aside and across images), D_{NT} = 0.84 nm;

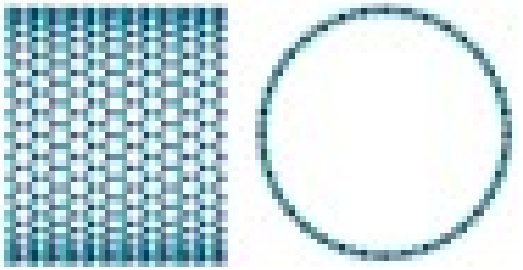
b) optimized single-wall (12,0) *zz*-BN NT (aside and across images), D_{NT} = 0.96 nm;



c) optimized single-wall (18,18) *ac*-BN NT (aside and across images), D_{NT} = 2.49 nm;

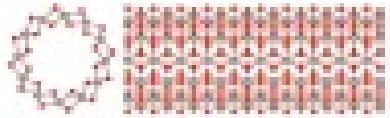


d) optimized single-wall (36,0) *zz*-BN NT (aside and across images), D_{NT} = 2.87 nm.



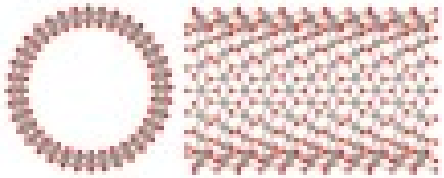
Další nanotrubičky

a) across and aside images of optimized 3-layer (6,6) TiO_2 NT with D_{NT} = 1.01 nm;

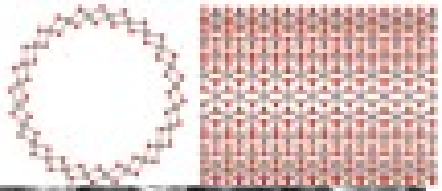


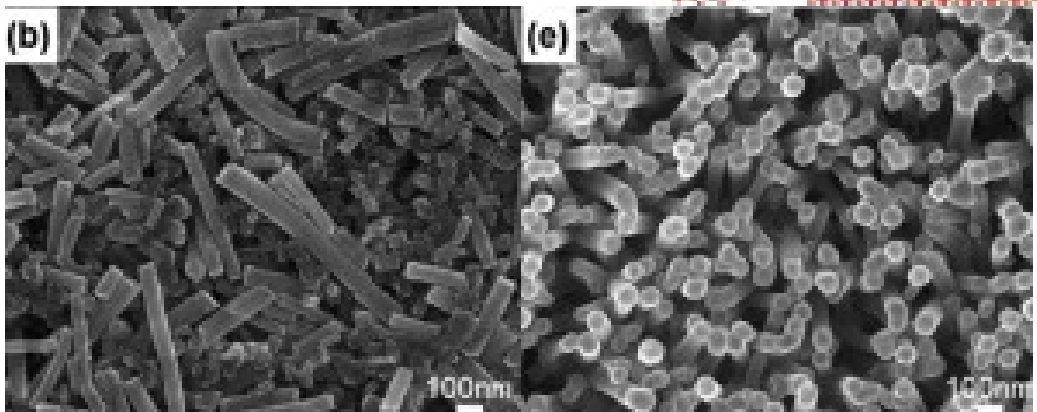
b) across and aside images of optimized 3-layer (12,0) TiO_2 NT with D_{NT} = 1.17 nm;

c) across and aside images of optimized 3-layer (18,0) TiO_2 NT with D_{NT} = 1.72 nm;



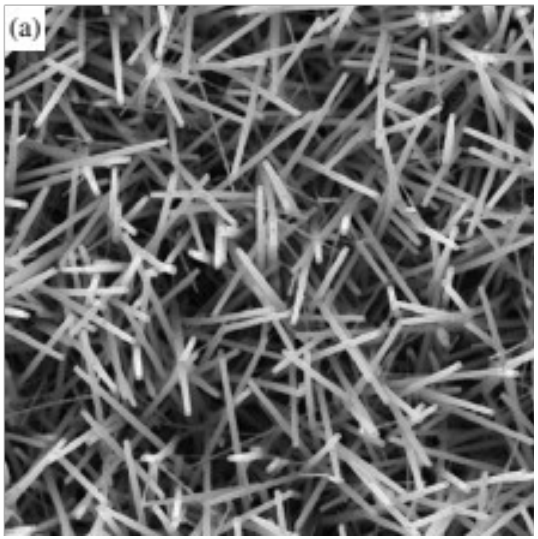
d) across and aside images of optimized 3-layer (12,12) TiO_2 NT with D_{NT} = 1.97 nm.





… a jiné útvary

5. Nanostructures and the growth processes
   - 5.1. Nanorods
   - 5.2. Nanobelts
   - 5.3. Ultranarrow nanobelts
   - 5.4. Hierarchical nanostructures
   - 5.5. Nanocombs and nanosaws
   - 5.6. Nanosprings and nanospirals
   - 5.7. Seamless nanorings



J. Phys.: Condens. Matter **16** (2004) R829–R858

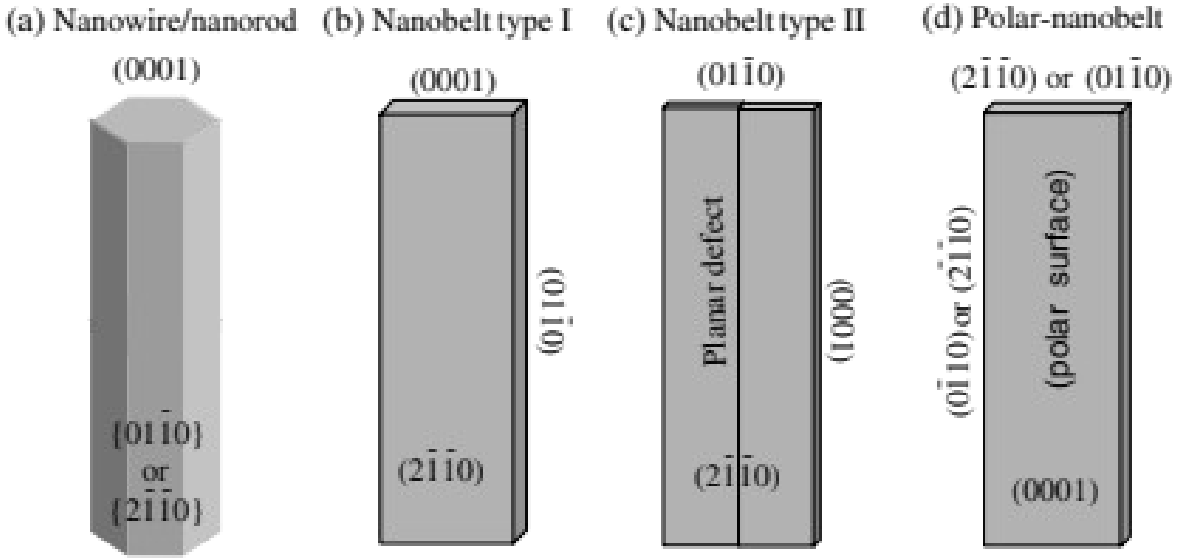


Figure 2. Typical growth morphologies of one-dimensional ZnO nanostructures and the corresponding facets.

Grafenové (nano)pásky

Graphene nanoribbons = GNR

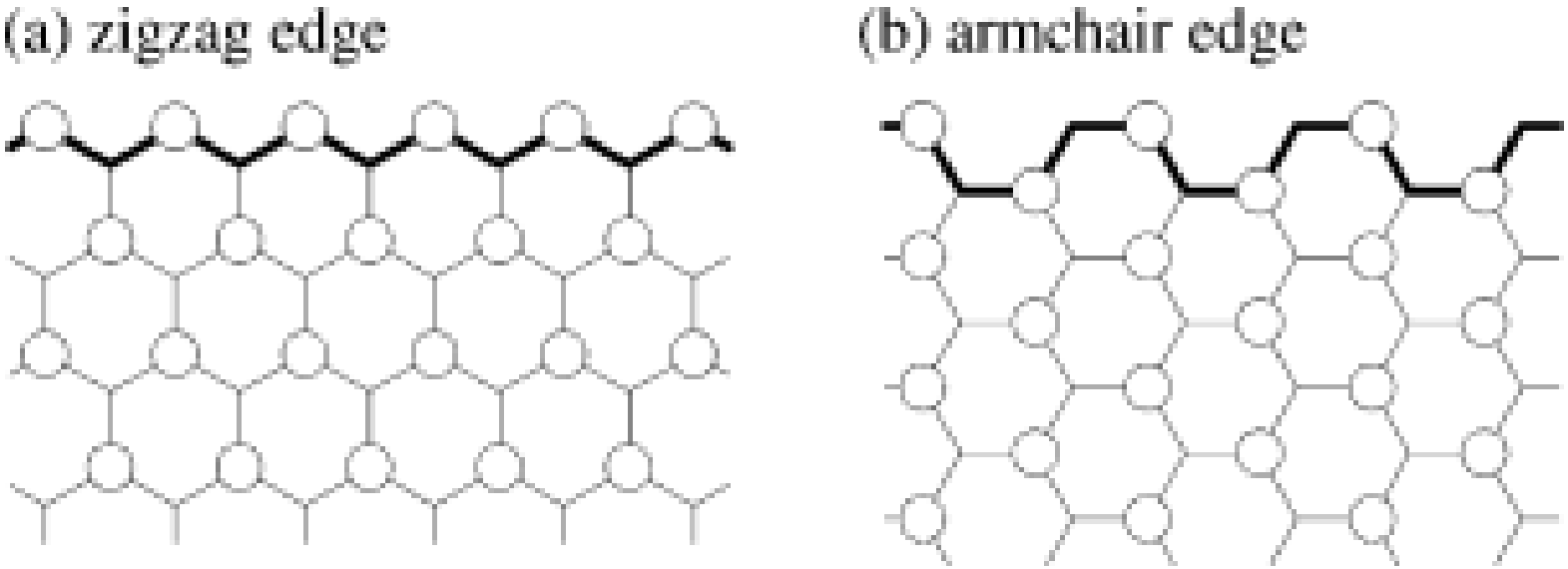
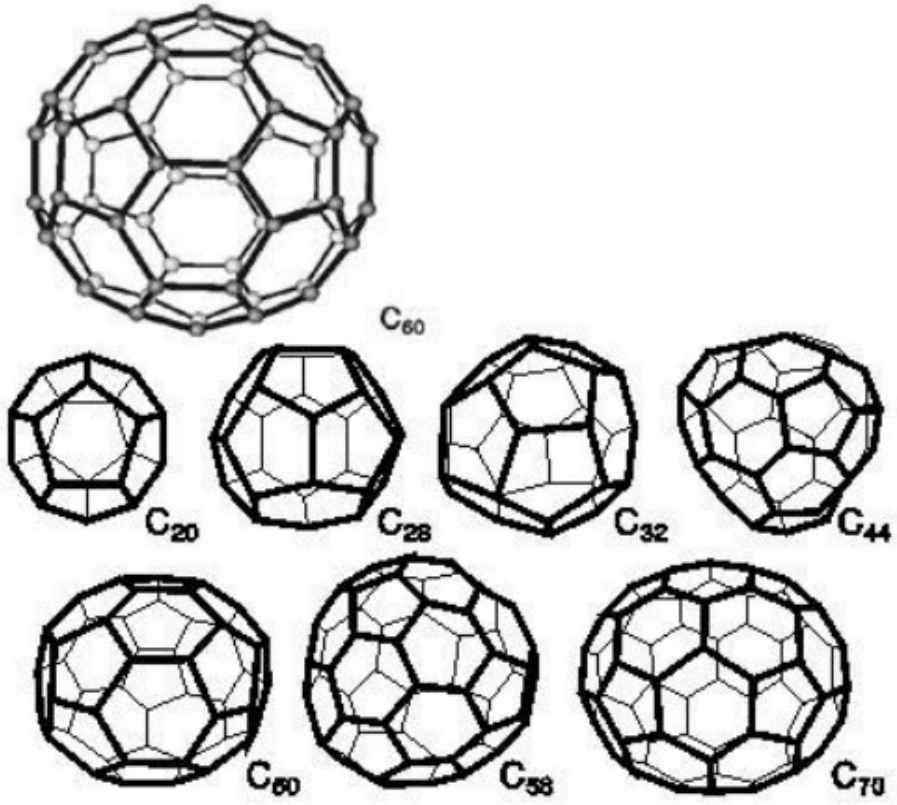


Fig. 6. GNR edges. (a) Zigzag edge, (b) armchair edge

Nanočástice: Fullereny

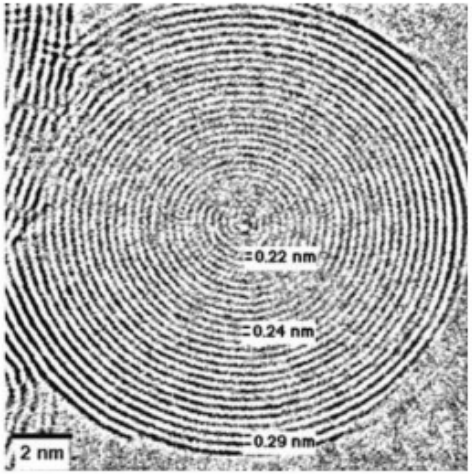
- sp^2, kulovitý tvar
- alternující
  - hexagony (bohaté na elektrony)
  - pentagony (chudé na elektrony)
- vynikající akceptory elektronů
- taktéž výborné klece



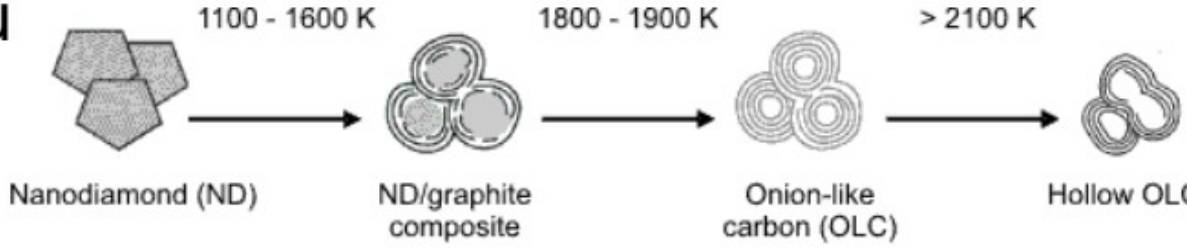
Kroto, H. W.; Heath, J. R.; Obrien, S. C.; Curl, R. F.; Smalley, R. E. C60-Buckminsterfullerene. Nature **1985**, 318, 162-163.

Fullereny

Uhlíkové cibule (onions)



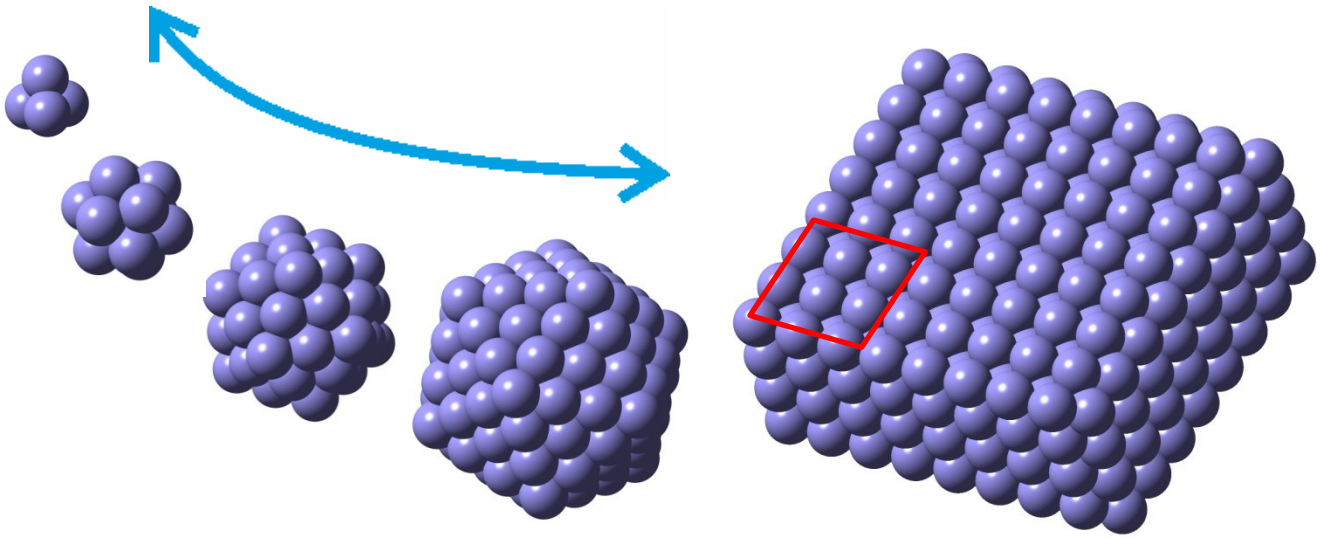
- několikavrstevné fullereny
- příprava
  - el. oblouk ve vodě
  - z nanodiamantů



- použití
  - nanoreaktory
  - superkondenzátory (200 V/s, ~200 Wh/kg)

Butenko YV et al.Photoemission of onionlike carbons produced by annealing nanodiamonds *Physical Review* B 71,7, (2005)
Pech, D. et al. Ultrahigh-power micrometre-sized supercapacitors based on onion-like carbon *Nature Nanotechnology* **5,** 651–654 (2010)
Sun L and Banhart F, Graphitic onions as reaction cells on the nanoscale. Appl Phys Lett 88:1931211–3 (2006).

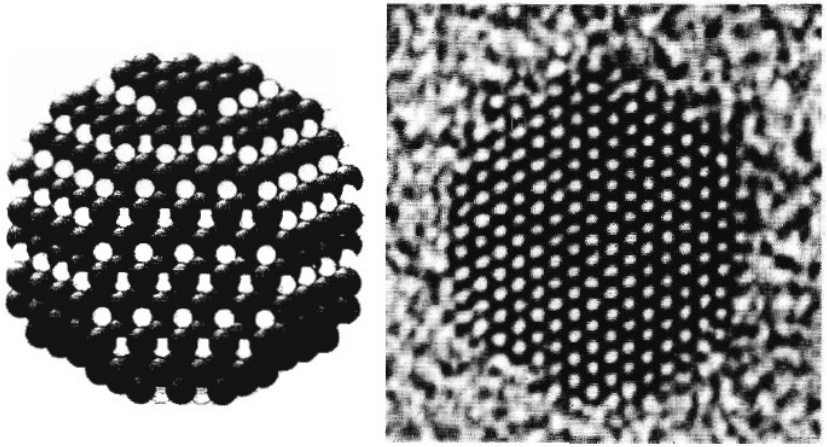
Nanočástice: kovové nanočástice



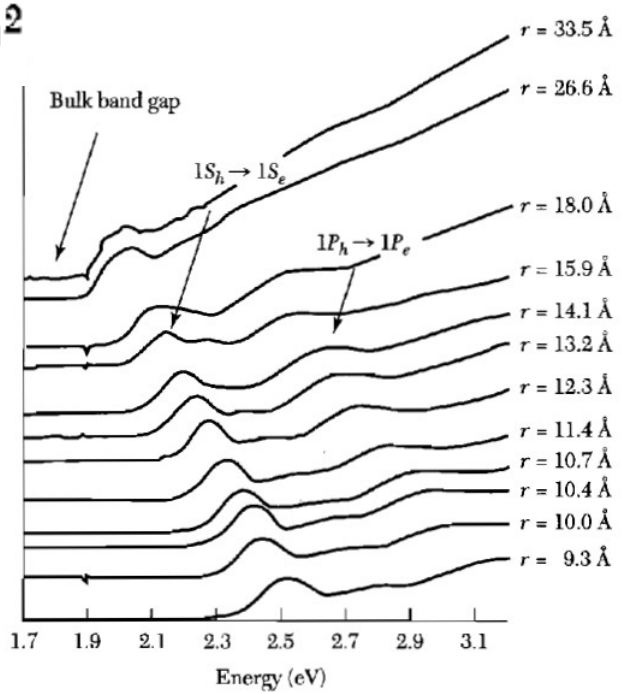
Další 0D systémy

- Všechny 3 směry limitovány – diskrétní elektronické hladiny (3D potenciálová jáma)
- Tzv. kvantové tečky (Quantum dots)
- Př. Polovodičové nanokrystaly CdSe
  - El. hladiny $\varepsilon_{n,l} = (2.9\ \mathrm{eV}/R^2)(\beta_{n,l}/\beta_{0,0})^2$

R - průměr nanokrystalu v nm,β – nuly Besselových funkcí



Model CdSe a transmisní elektronová mikroskopie (TEM).



Optická absorpční spektra nanokrystalů CdSe o různých velikostech.