

# Nano-containers and nano-scaffolds

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# Wigner Research Centre for Physics Advanced Structural Laboratory



**FIR/MIR**



**MIR/NIR**



**Photoluminescence**

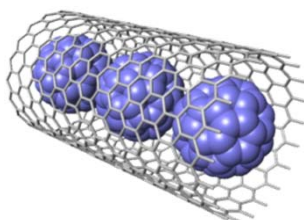


**Near field/SNOM**

# Hybrid structures from nanotubes

- **exceptional properties of nanotubes:**

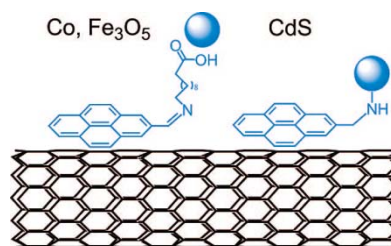
- mechanical stability
- electric conductivity



peapod

- **organic components:**

- selectivity
- function



adsorbed organic molecule

D. Eder:  
*Chem. Rev.* **110**,  
1348 (2010)

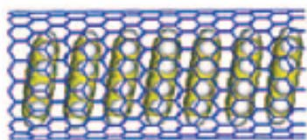
## Nano-containers

van der Waals interaction inside  
nanosize reaction vessel  
packaging of unstable, toxic molecules

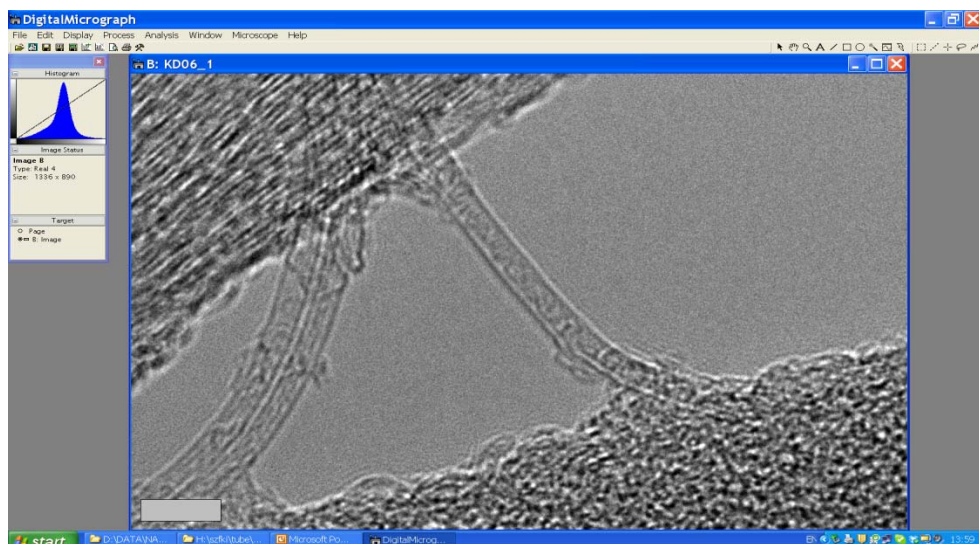
Incorporation of functional units

## Nano-supports

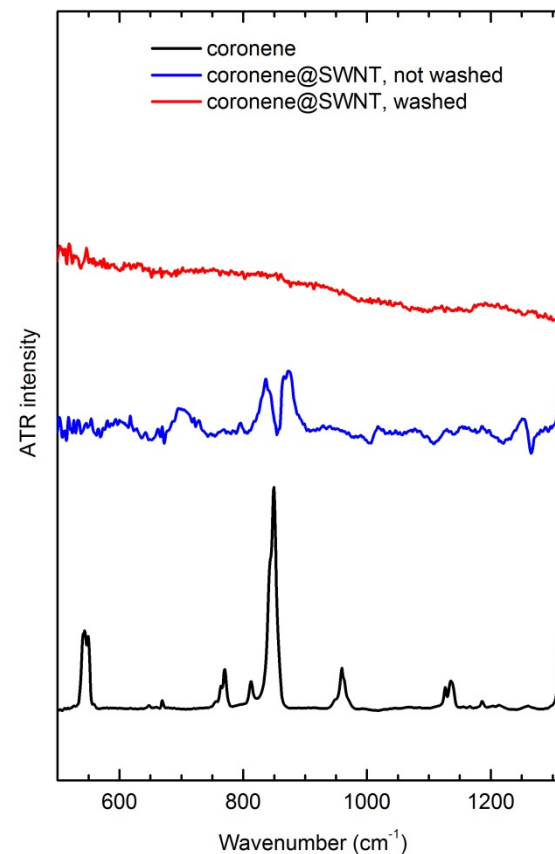
$\pi$ - $\pi$  interaction on surface  
increased solubility  
“glue”



# Coronene@SWNT



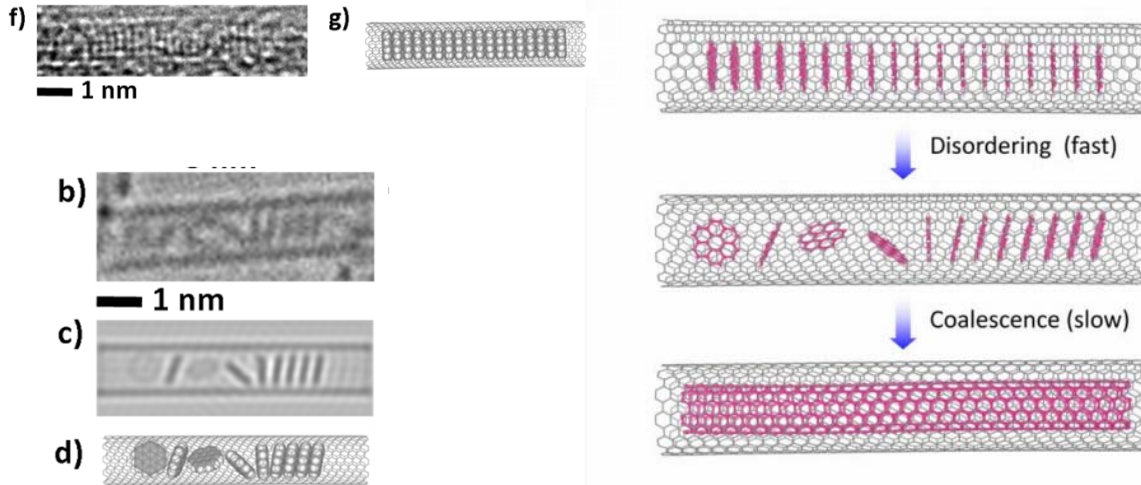
## ATR-IR



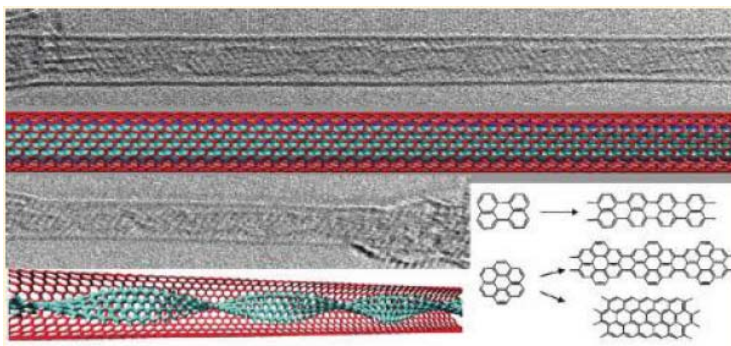
coronene both encapsulated and adsorbed  
adsorbed coronene dissolves in toluene

# Reactions inside nanotube

low-temperature filled nanotubes: no side reactions on adsorbed molecules  
 surface can be cleaned by toluene washing  
 adsorbed molecules do not obscure encapsulated ones

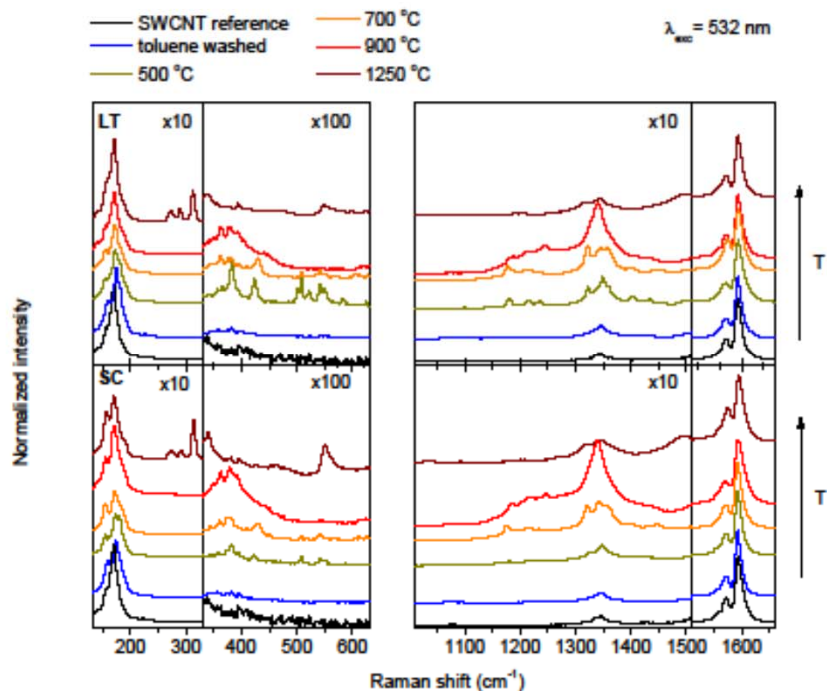


Can we stop the process at the nanoribbon stage?

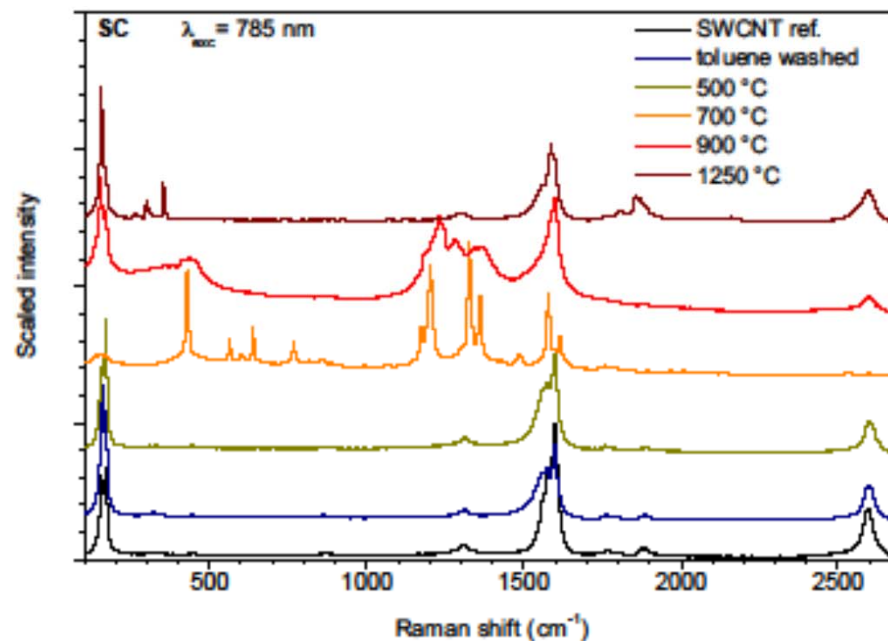


A.V. Talyzin, I.V. Anoshkin,  
 A.V. Krasheninnikov, R.M. Nieminen,  
 A.G. Nasibulin, H. Jian, E.I. Kauppinen:  
*Nano Lett.* **11**, 4352 (2011)

# Following reactions by Raman spectroscopy



Resonance with nanoribbons:  
500, 700, 900 °C

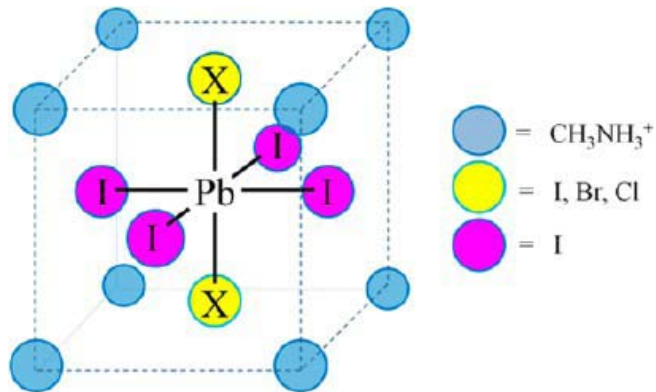


Resonance with nanoribbons:  
700, 900 °C

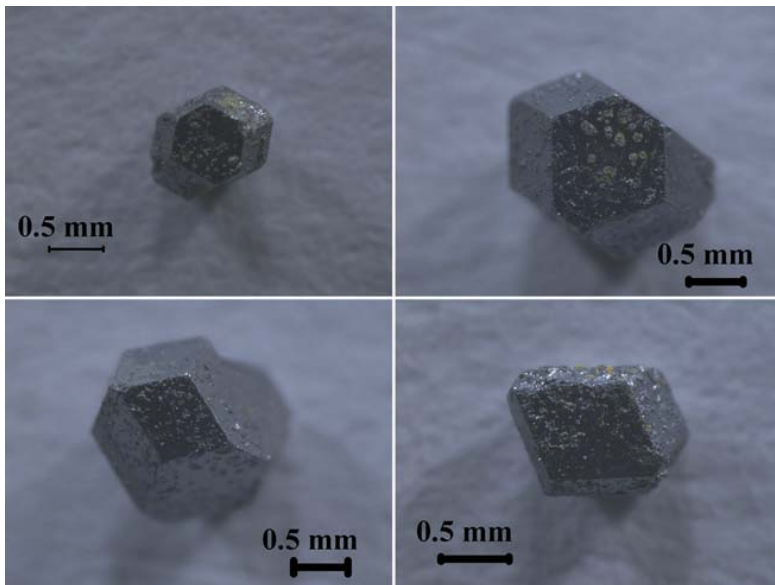
DWNT formation: 1250 °C

# Lead halide perovskites

the solar cells of the future



E. Mosconi, A. Amat, Md.K. Nazeeruddin,  
M. Grätzel, F. De Angelis:  
*J. Phys. Chem. C* **117**, 13902 (2013)

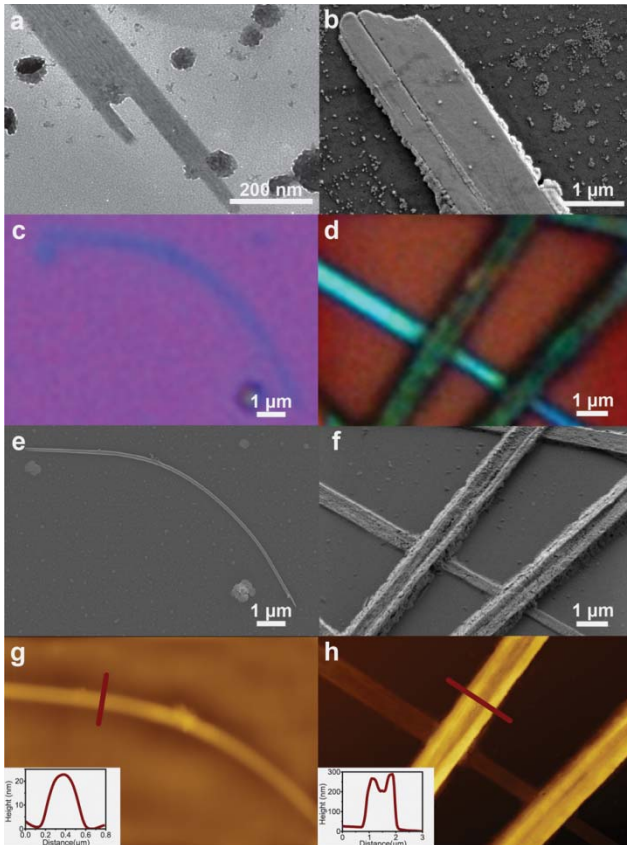


T. Baikie, Y. Fang, J.M. Kadro, M. Schreyer, F. Wei,  
S.G. Mhaisalkar, M. Grätzel, T.J. White:  
*J. Mater. Chem. A* **1**, 5628 (2013)

# Lead halide perovskites: nanoscale

E. Horváth, M. Spina, Zs. Szekrényes, K. Kamarás,  
R. Gaal, D. Gachet, L. Forró:

*Nano Lett.* **14**, 6761-6766 (2014)

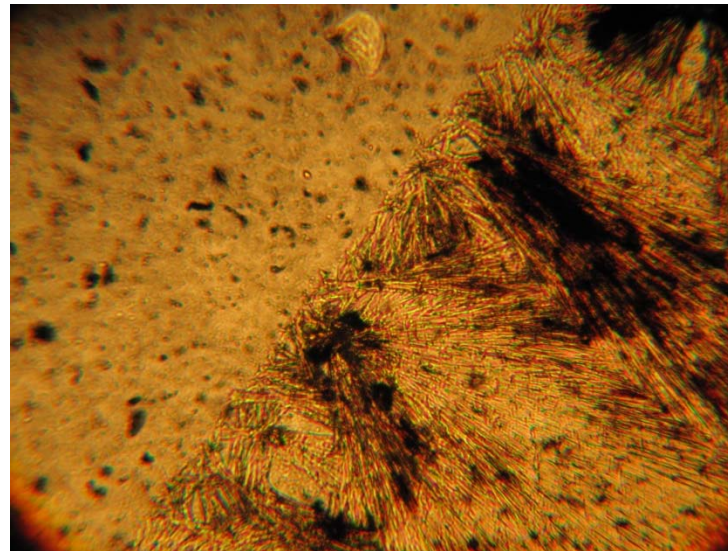


$\text{CH}_3\text{NH}_3\text{PbI}_3$  nanowires with 50 – 200 nm diameter



# Perovskite nanowires: using carbon nanotubes as scaffolds

Transparent CNT film



$\text{CH}_3\text{NH}_3\text{PbI}_3$  nanowire

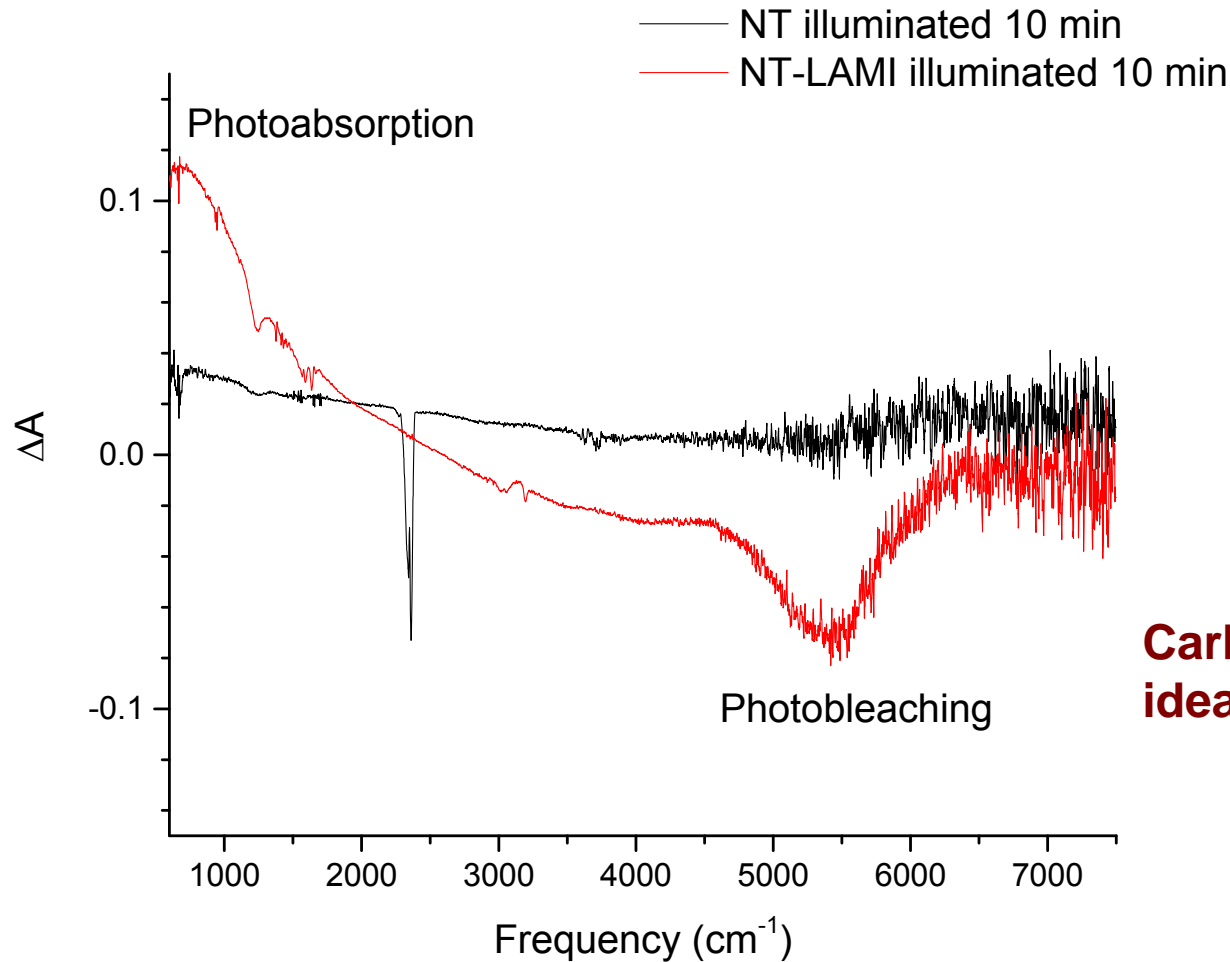
M. Spina, B. Náfrádi,  
H.M. Tóháti, K. Kamarás,  
E. Bonvin, R. Gaal,  
L. Forró, E. Horváth:  
*Nanoscale* **8**, 4888  
(2016)

- strong
- transparent
- chemically inert? **yes**

# Photoinduced spectral changes

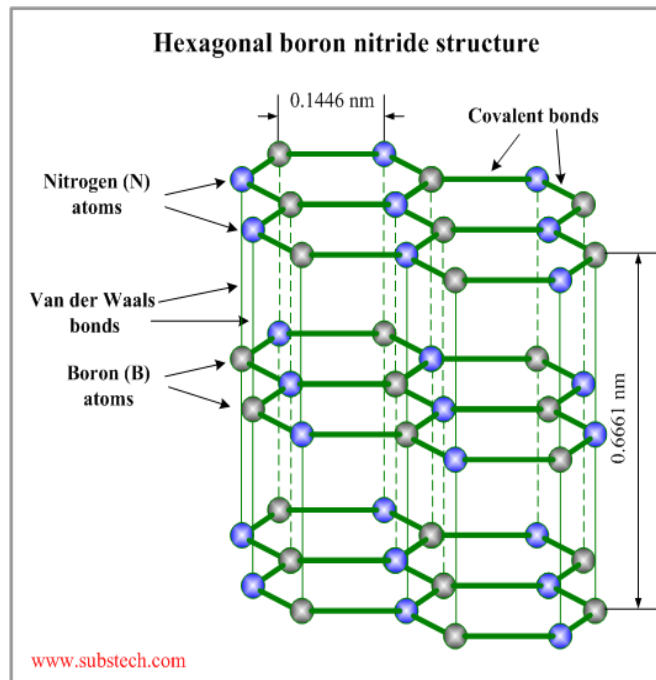
Illumination by 633 nm light

$$\text{Presented as } \Delta A = \frac{T_{\text{dark}} - T_{\text{illum}}}{T_{\text{dark}}}$$



**Carbon nanotubes are ideal hole transport layers!**

# Boron nitride nanotubes

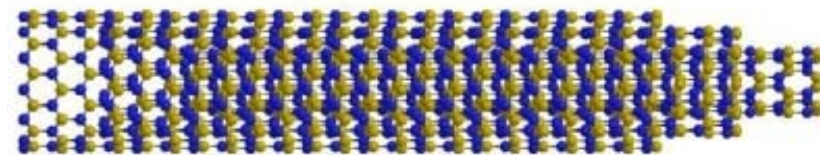


Both covalent and van der Waals bonds have ionic character

electrons are less delocalized

h-BN is an insulator with a bandgap of 6 eV

folding  
→



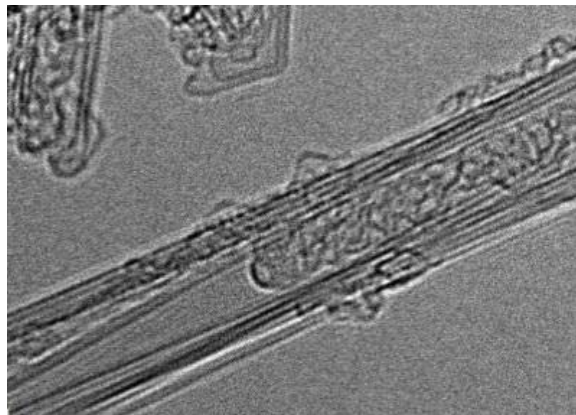
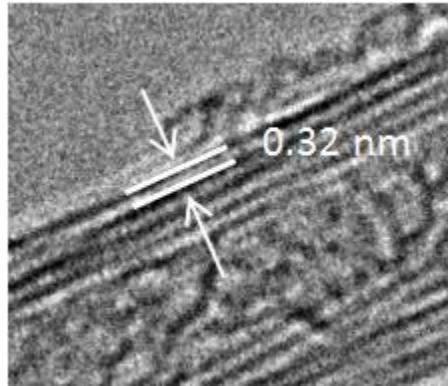
BNNT nanotube

Z. Gao et al.: *Nanobiomedicine*, 2014, 1:7.

# Electron microscopy of BNNT



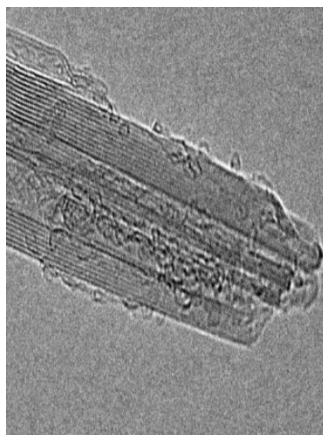
external diameter  $5.62 \pm 2.16$  nm  
internal diameter  $2.61 \pm 1.05$  nm  
interlayer spacing 0.32 nm (h-BN)



Samples: BNNT LLC  
Measurements: Andrei N. Khlobystov

# Filling of BNNT

BNNT as is



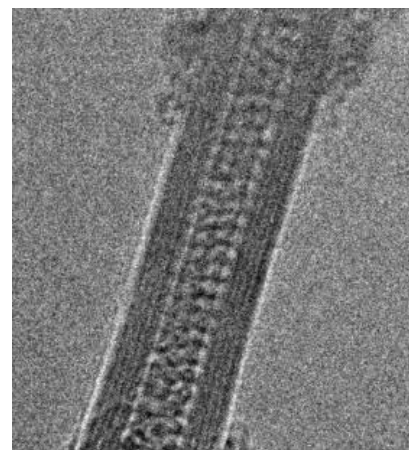
shortening ( $\sim 2 \mu\text{m} \rightarrow \sim 500 \text{ nm}$ )  
opening  
purification (ammonia, annealing)

BNNT open

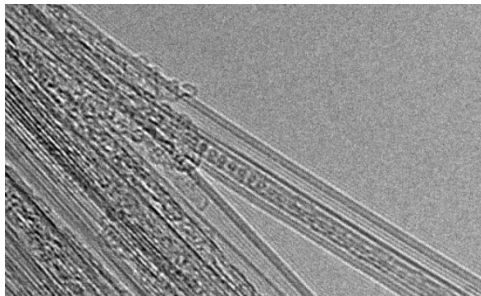


sublimation filling  $600 \text{ }^\circ\text{C}$   
W. Mickelson, S. Aloni, W.-Q. Han, J. Cumings,  
A. Zettl: *Science* **300**, 467 (2004)

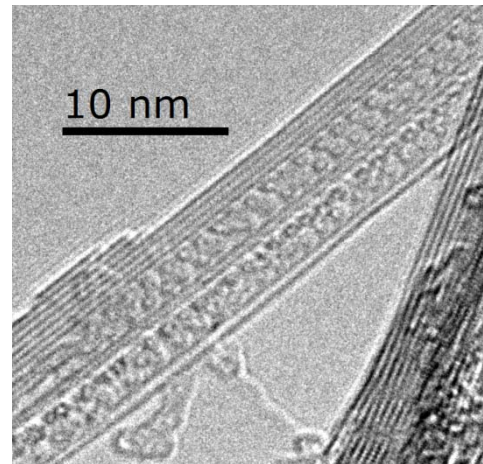
$\text{C}_{60}$ @BNNT



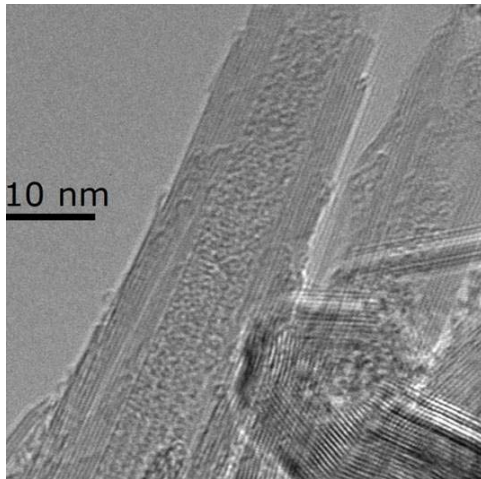
# Microscopy of BNNT peapods



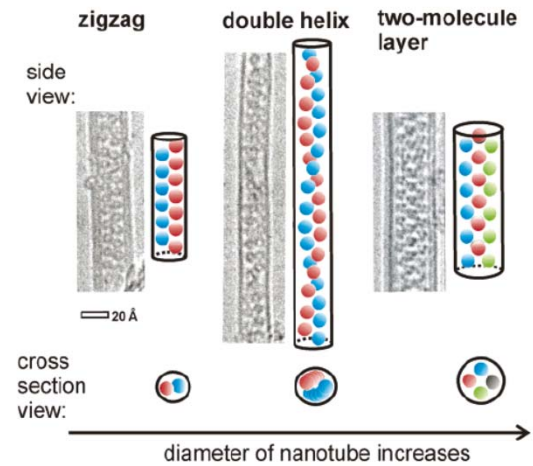
linear chain



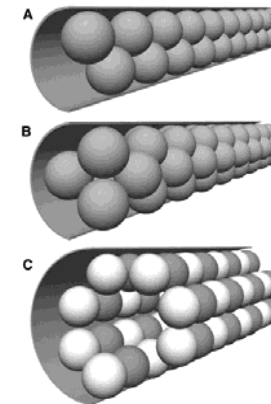
zigzag



two-molecule layer

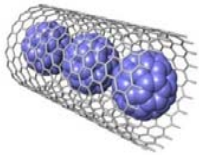
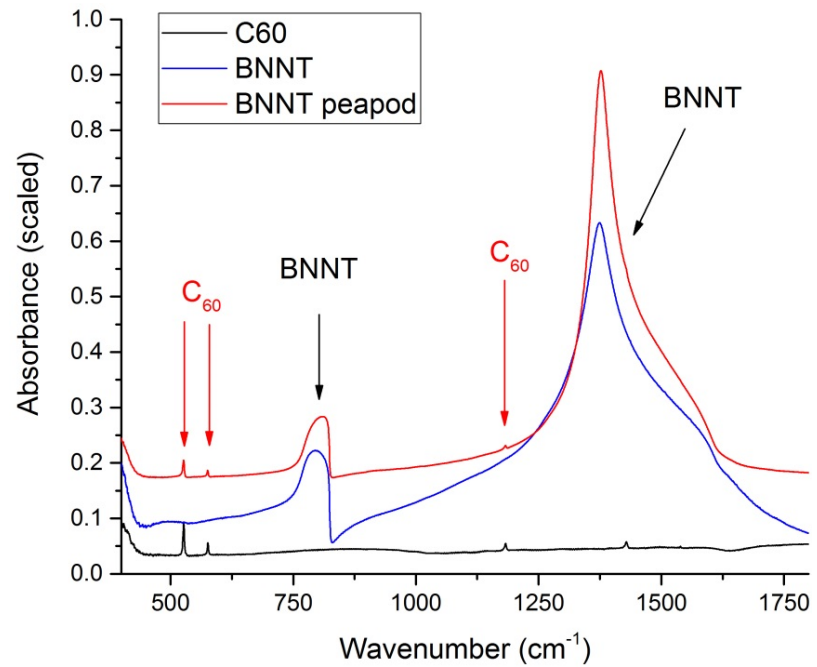
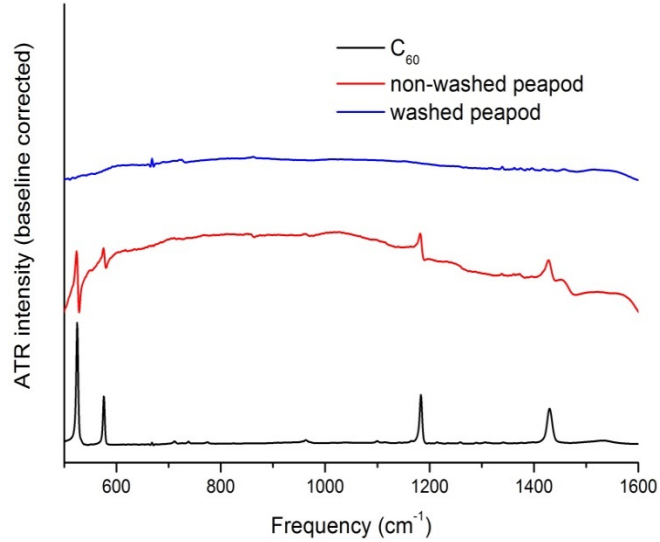


A.N. Khlobystov, D.A. Britz, J. Wang, S.A. O'Neil, M. Poliakoff, G.A.D. Briggs: *J. Mater. Chem.* **14**, 2852 (2004)



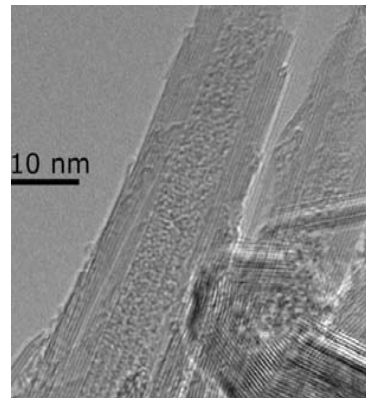
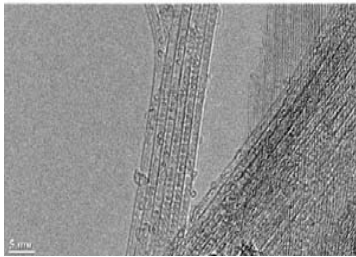
W. Mickelson, S. Aloni, W.-Q. Han, J. Cumings, A. Zettl: *Science* **300**, 467 (2004)

# Infrared spectra of peapods



## CNT

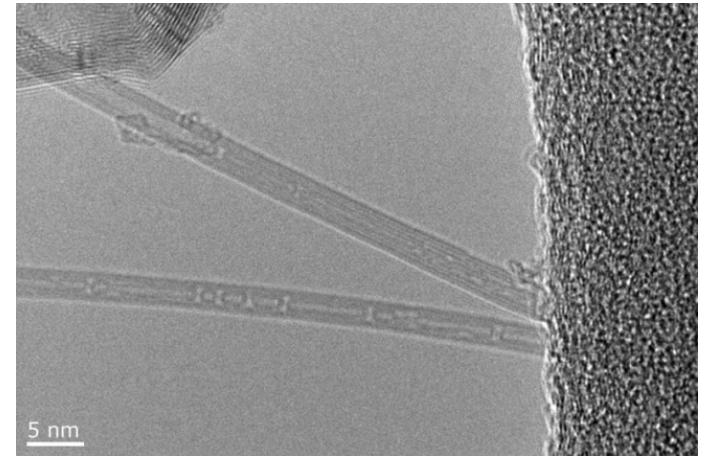
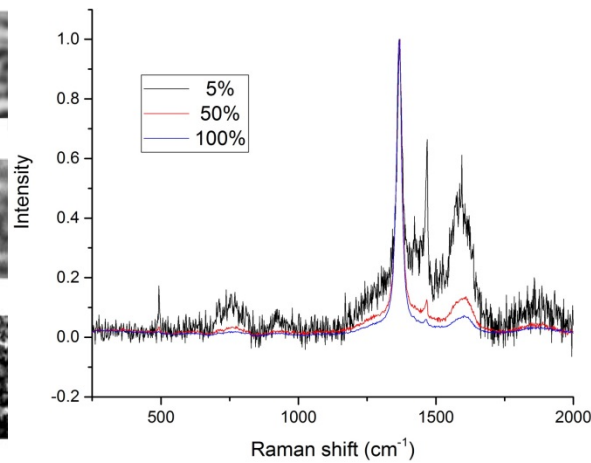
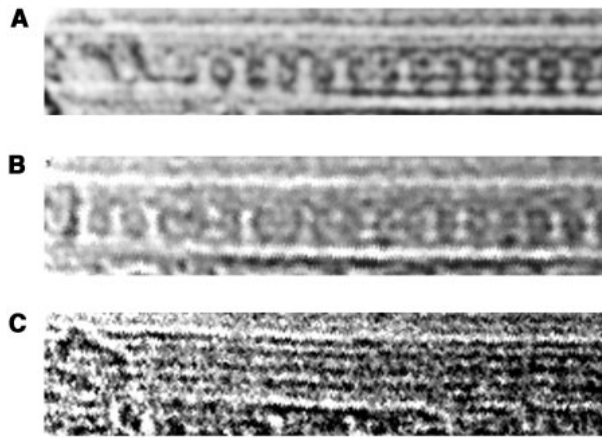
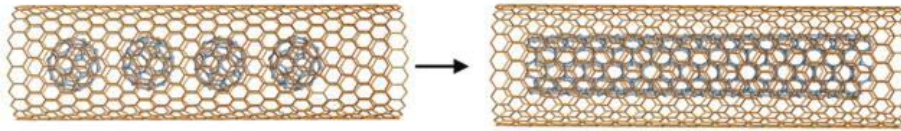
Infrared spectra  
of  $C_{60}$  shielded



## BNNT

$C_{60}$  vibrations can be  
clearly seen  
 $C_{60}$  retains  $I_h$  symmetry  
(no splitting of  
vibrational bands)  
free rotation at room  
temperature

# Formation of inner nanotube

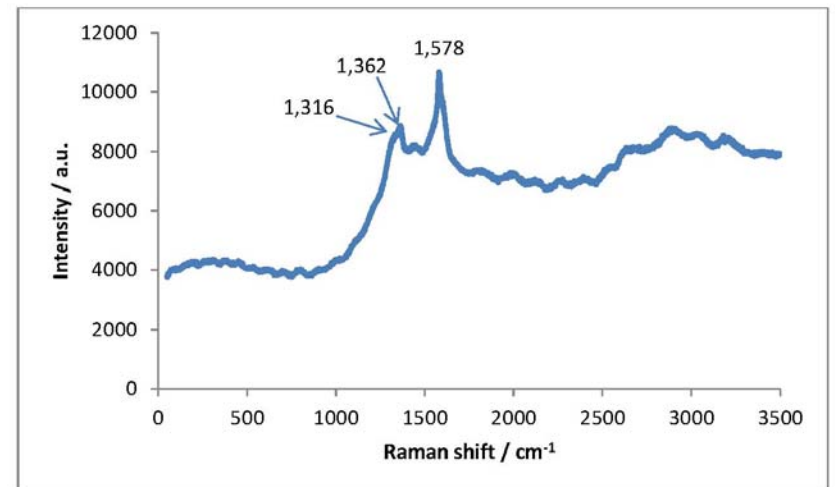


annealing 1200 °C

electron beam

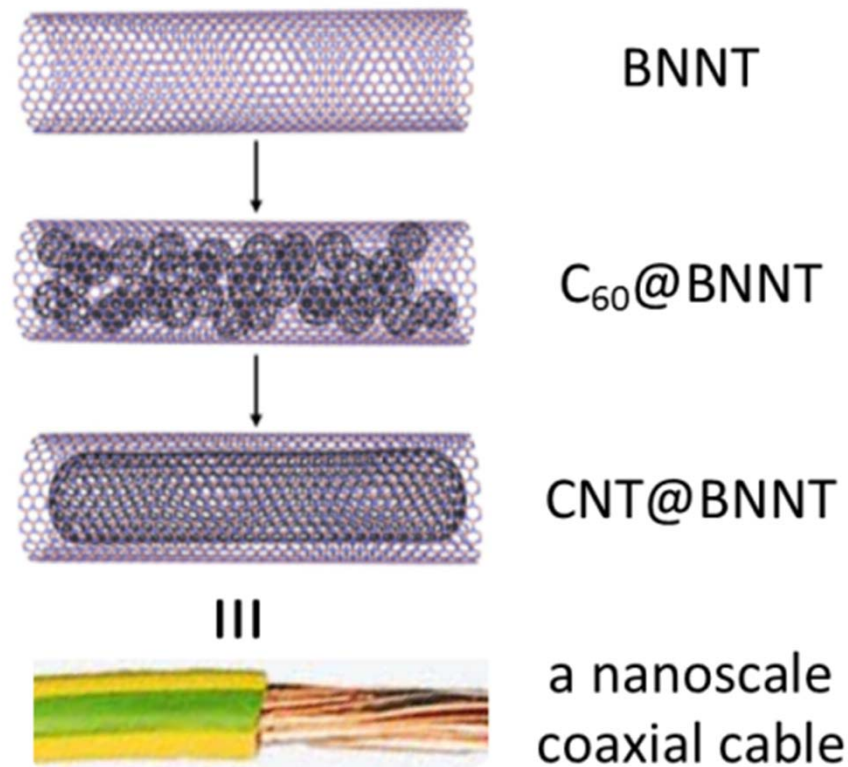
W. Mickelson, S. Aloni, W.-Q. Han, J. Cumings,  
A. Zettl: *Science* **300**, 467 (2004)

laser 355 nm





# “Towards the world’s smallest coaxial cable”



K.E. Walker, G.A. Rance, Á. Pekker, H.M. Tóháti, M.W. Fay, R.W. Lodge, C.T. Stoppiello, K. Kamarás, A.N. Khlobystov:  
*Small Methods*, published online, DOI: 10.1002/smtd.201700184

# Collaborators



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Ákos Botos  
Melinda Füstös  
Áron Pekker  
Zsolt Szekrényes  
Hajnalka M. Tóháti  
Miklós Veres



ÉCOLE POLYTECHNIQUE  
FÉDÉRALE DE LAUSANNE

Endre Horváth  
Bálint Náfrádi  
László Forró



The University of  
Nottingham

Kate E. Walker  
Graham A. Rance  
Thomas W. Chamberlain  
Andrei N. Khlobystov

**Funding:**



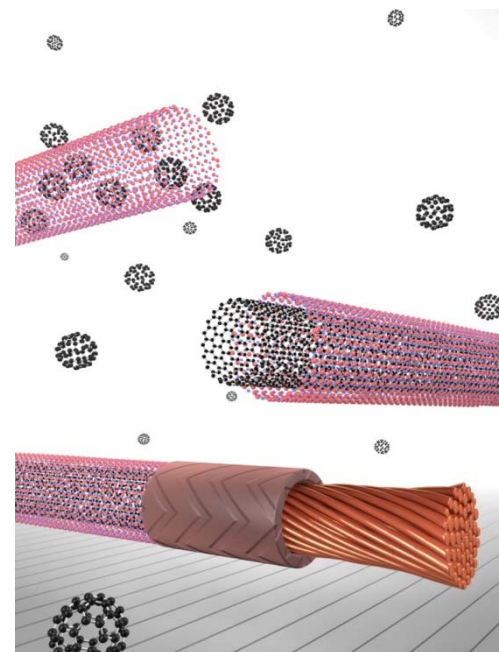
EU PITN-GA 2008-215399  
FINELUMEN



VEKOP 2.3.2-16-2016-00011  
VEKOP 2.3.3-15-2016-00001



NK 105691  
SNN 118012



September 3, 2017



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