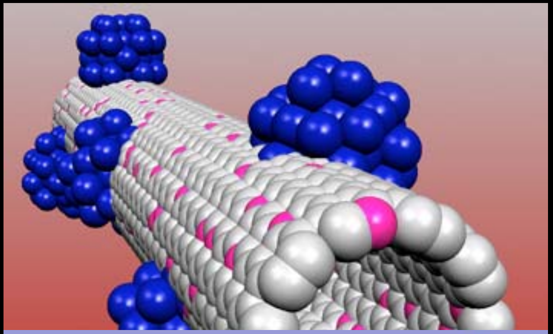
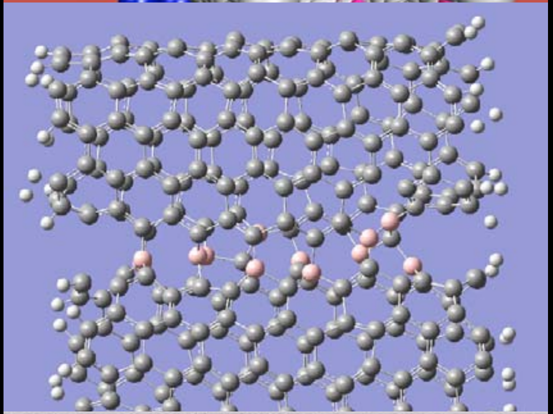
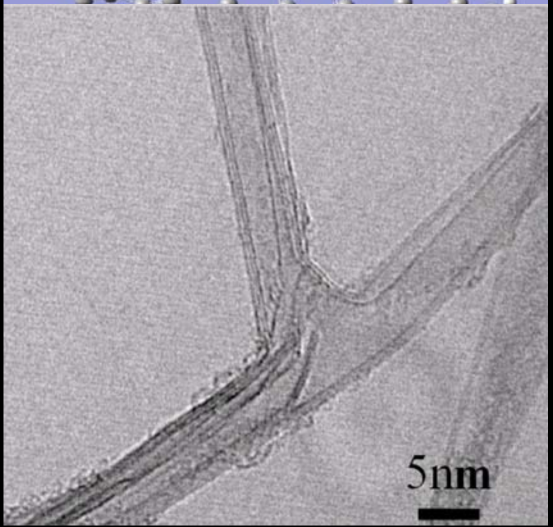
Importance of Defects and Dopants in Carbon Nanotubes: Emerging Applications







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INSTITUTO POTOSINO DE INVESTIGACIÓN CIENTÍFICA Y TECNOLÓGICA, A.C.
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- J. Y. Cavaillé (INSA, France)
- J-C. Charlier (UCLN, Louvain-la-Neuve, Belgium)
- M. S. Dresselhaus (MIT. USA)
- D. Golberg (NIMS, Japan)
- M. Endo (Shinshu, Japan)
- T. Hayashi (Shinshu, Japan)
- E. Hernández (Barcelona, Spain)
- A. Jorio (Minas Gerais, Brazil)
- Y.A. Kim (Shinshu, Japan)
- V. Meunier (Oak Ridge, USA)
- M. Pimenta (Minas Gerais, Brazil)
- M. Rühle (Max-Planck-Institut für Metallforschung, Germany)
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Ana Laura Elías-Arriaga (PhD)
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David Meneses (PhD)
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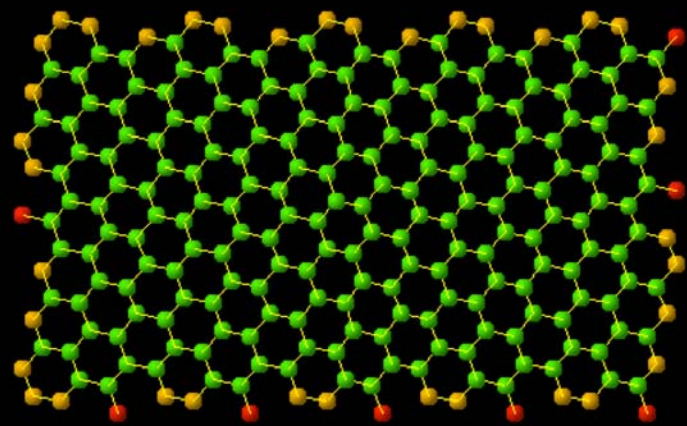
Eduardo Cruz Silva (PhD)
Leonardo Chávez Guerrero (PhD)
Eduardo Terrés (PhD)
Mariamne De Honor (PhD)
Benjamín Fragneaud (PhD)

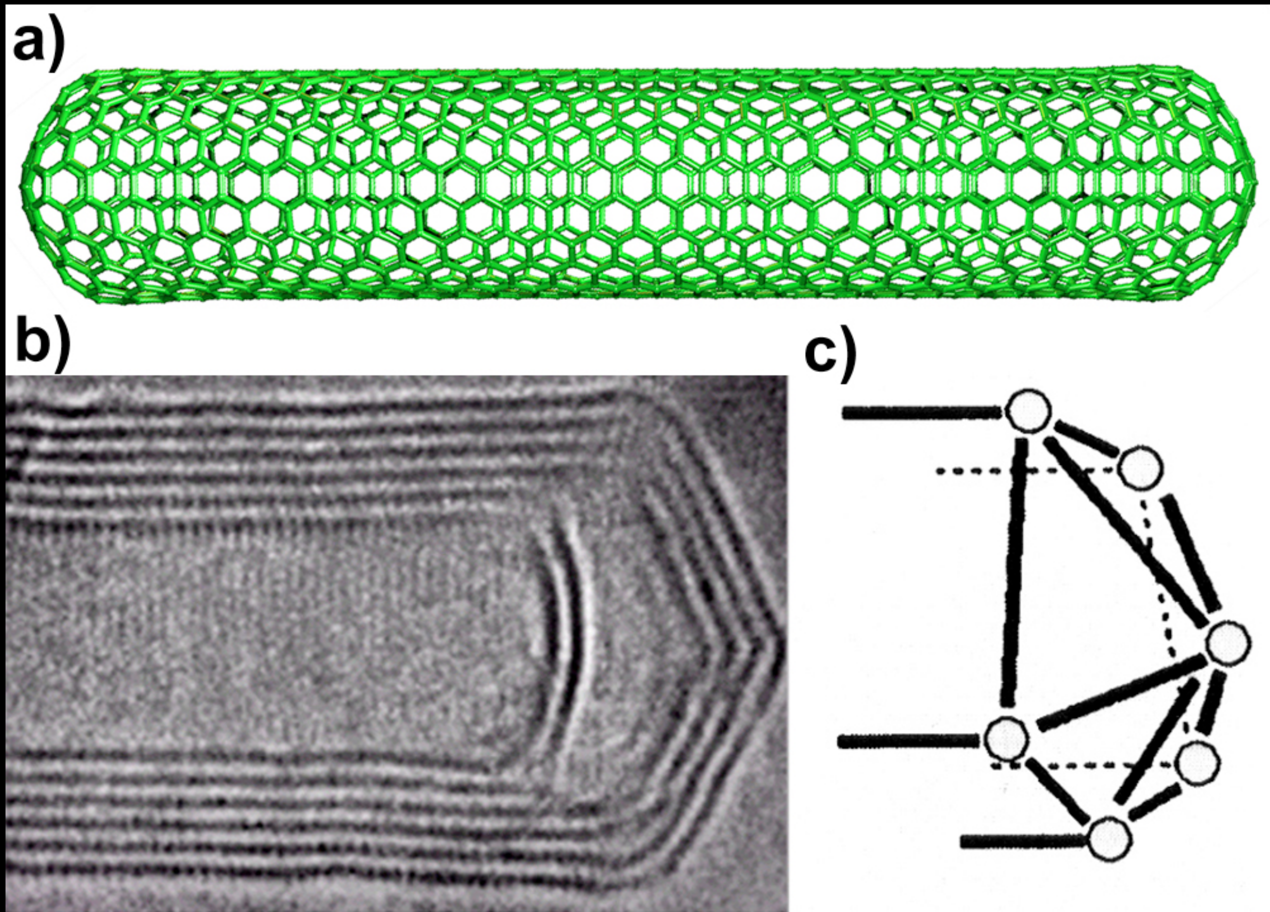
Defects in Graphene

1. Structural Defects, responsible of Curvature Changes (Pentagons, Heptagons, etc.)
2. Topological Defects (Bond Rotations, Stone-Wales Type Transformations)
3. Substitutional Atoms (Impurities, Doping)
4. Vacancies, Interstitials and Edges



1. STRUCTURAL DEFECTS

Positive Curvature in Nanotubes

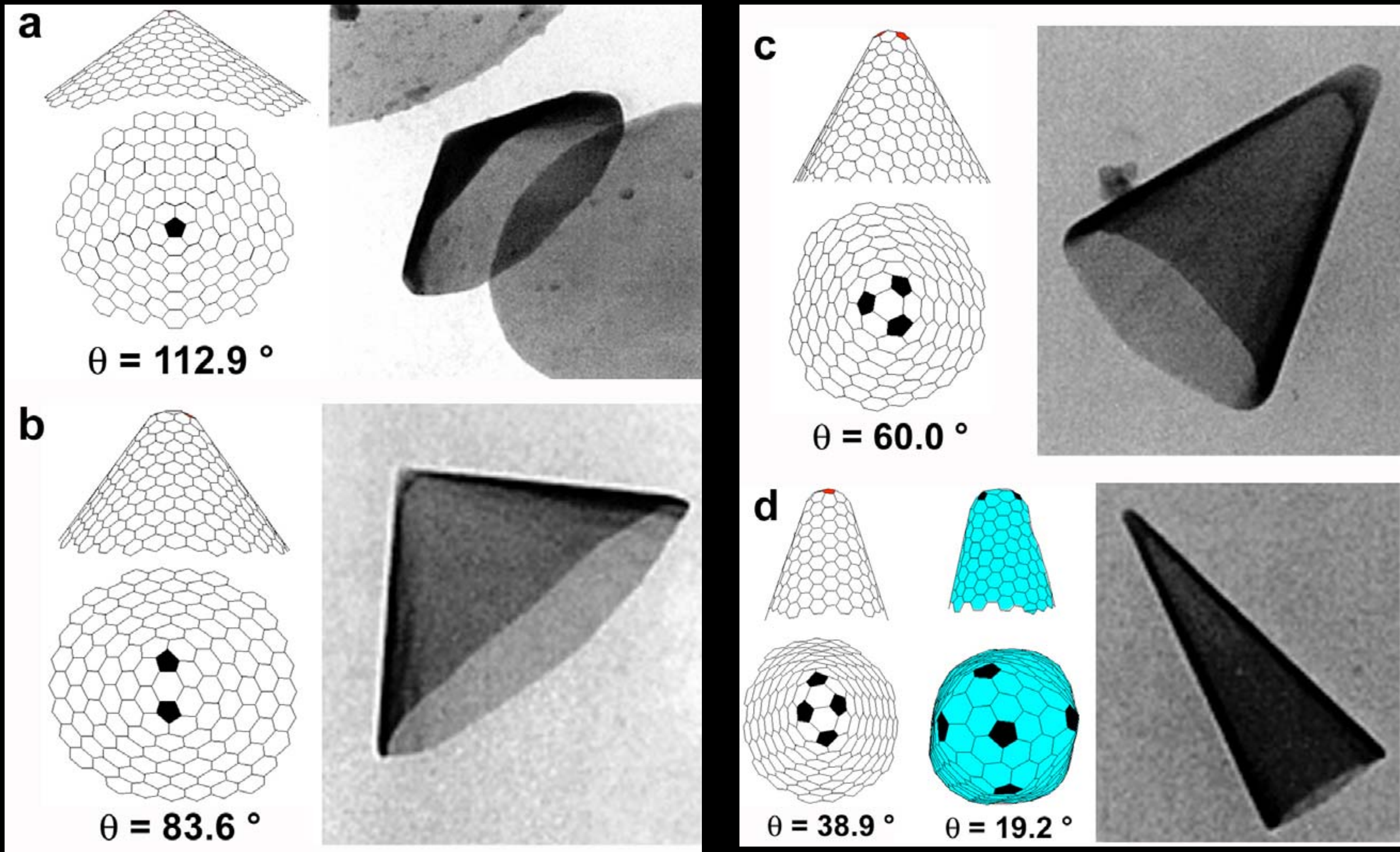


Iijima S. Mat. Sci. Engng. B 19, 172-80 (1993).

Closed Carbon Nanotubes due to pentagonal sites

Hexagons and Pentagons
Carbon Nano-Cones

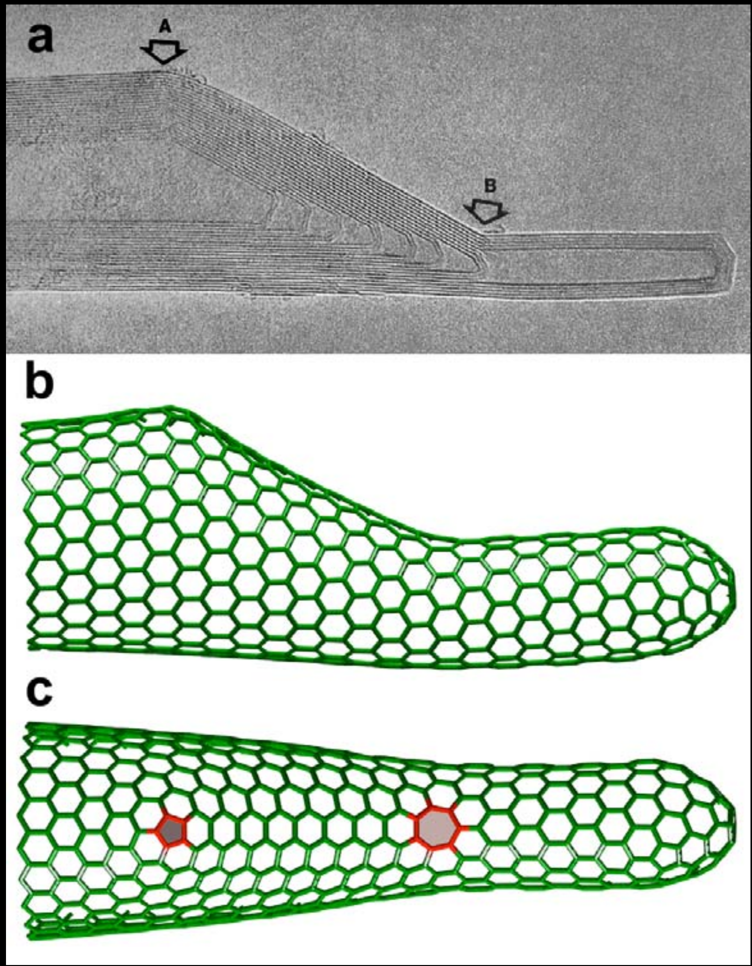
Positive Curvature: Graphite Cones



Krishnan, A., Dujardin, E., Treacy, M.M.J., Hugdahl, J., Lynum, S., Ebbesen, T.W. Nature, 1997, 388, 451-454. Models courtesy of M. Endo

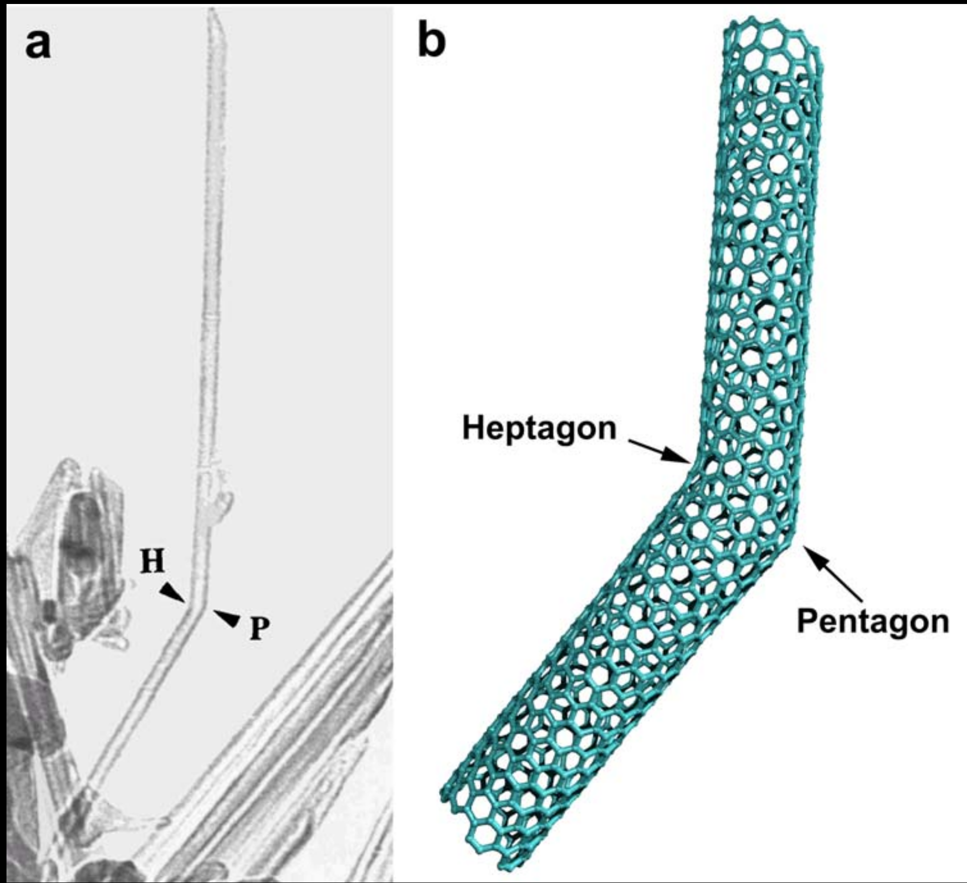
Hexagons, Pentagons and Heptagons

Negative Curvature in Nanotubes



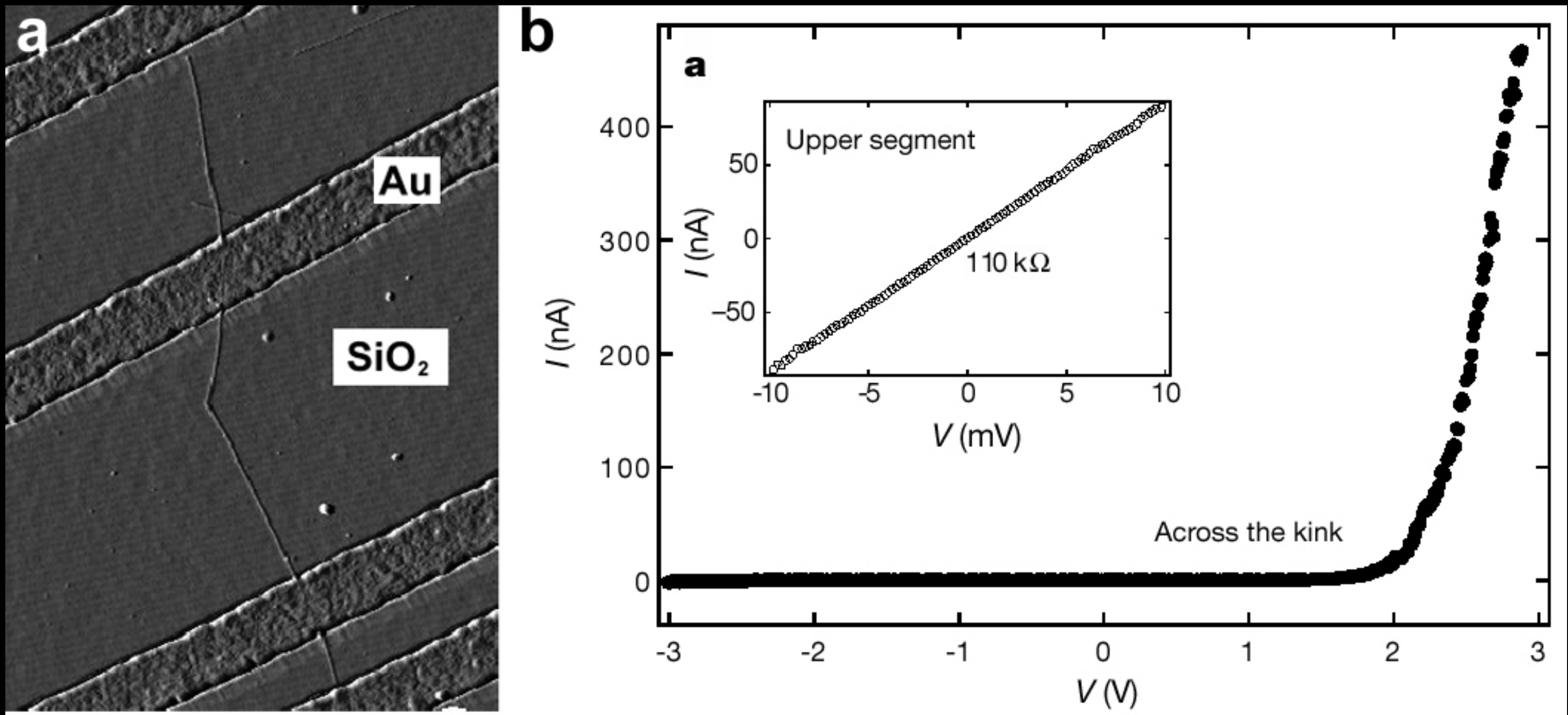
Mackay AL, Terrones H. 1991. Nature 352:762.
Iijima S, Ichihashi T, Ando Y- 1992. Nature 356:776-8.

Negative Curvature in Nanotubes



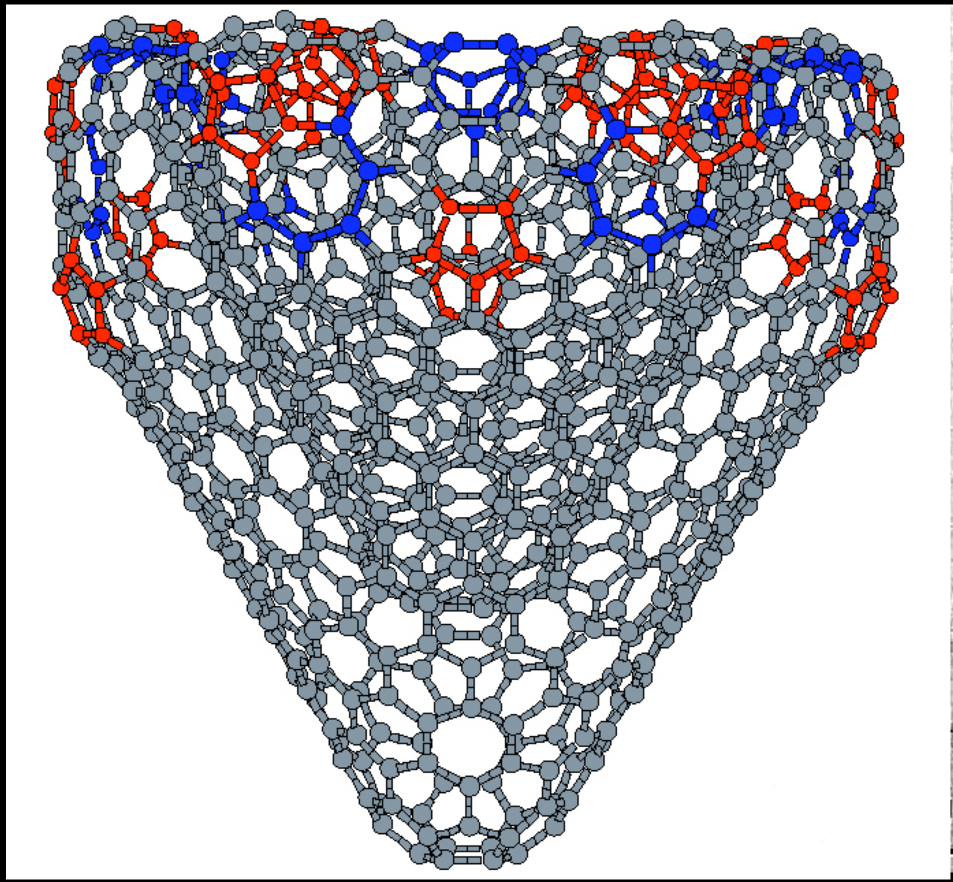
Mackay AL, Terrones H. 1991. Nature 352:762.
Iijima S, Ichihashi T, Ando Y- 1992. Nature 356:776-8.

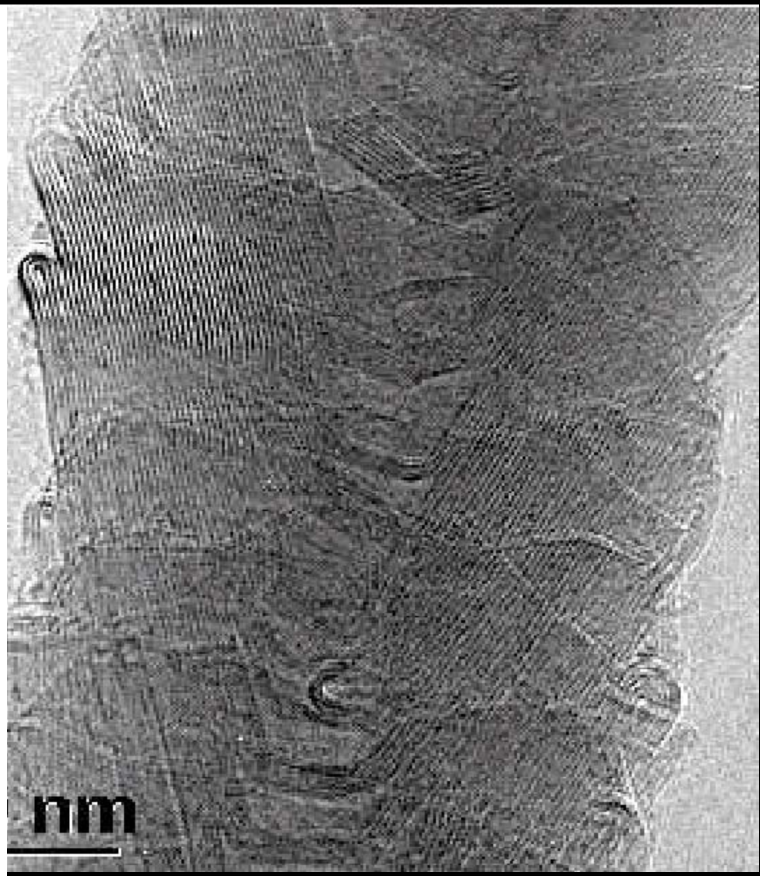
Bent Nanotubes as Nano-switches



Yao Z, Postma HWC, Balents L, Dekker C. 1999. Nature 402: 273-6.

Annealed Carbon Fibres (2800 °C)

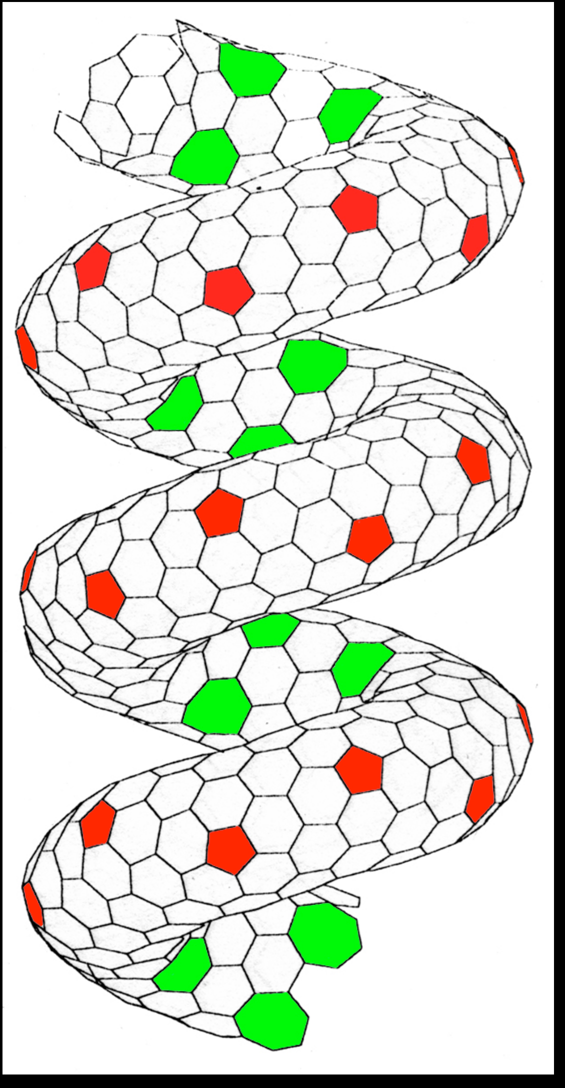


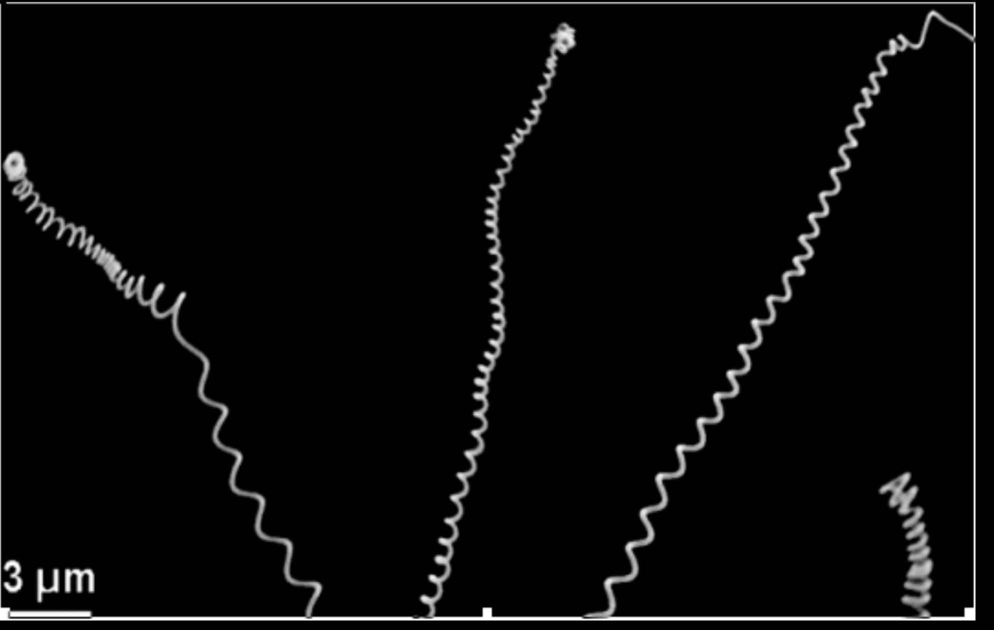


Muñoz-Navia, M., Dorantes-Dávila, J., Terrones, M., Hayashi, T., Kim, Y.A., Endo, M., Dresselhaus, M.S. Terrones, H.
Chemical Physics Letters 407, 327 (2005)

Carbon Helices, Toroids, etc.

Helix-shaped Carbon Nanotubes

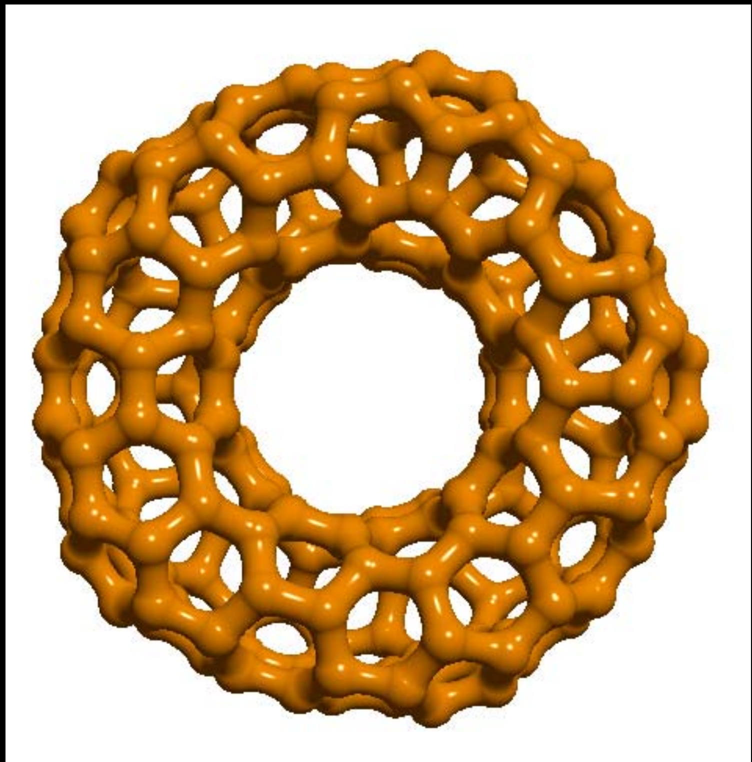




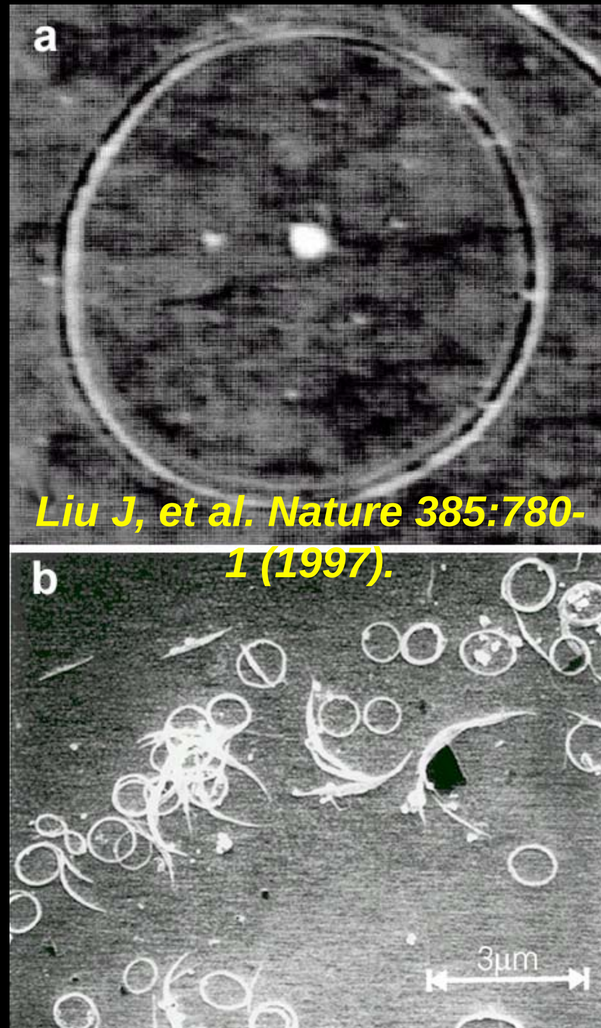
Carbon Helices produced by pyrolyzing melemine over CoO_x substrates

Itoh S, Ihara S, Kitakami J. Phys Rev B 47:1703-4 (1993).

Carbon Toroids



Carbon Nanotoroids:
Molecular Model, AFM image
and SEM image

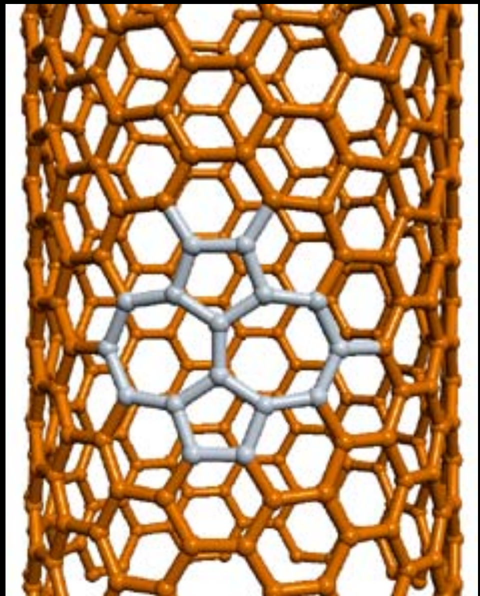


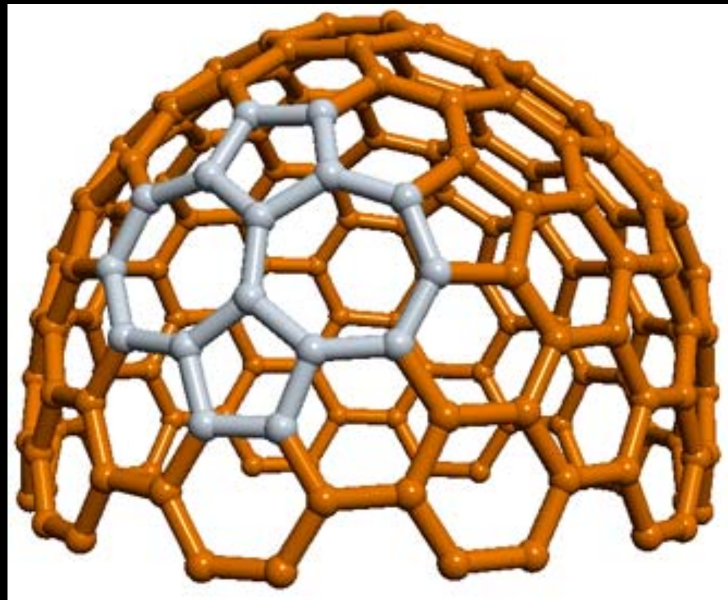
Liu J, et al. Nature 385:780-1 (1997).

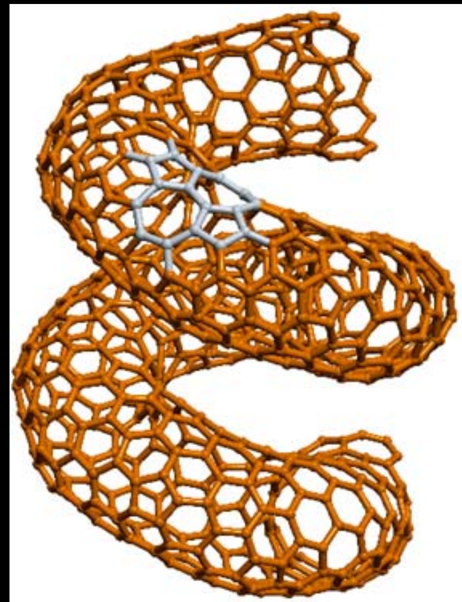
Martel R, et al Nature 398:299 (1999).

2. TOPOLOGICAL DEFECTS

Nanotube defects and SW-type Transformations

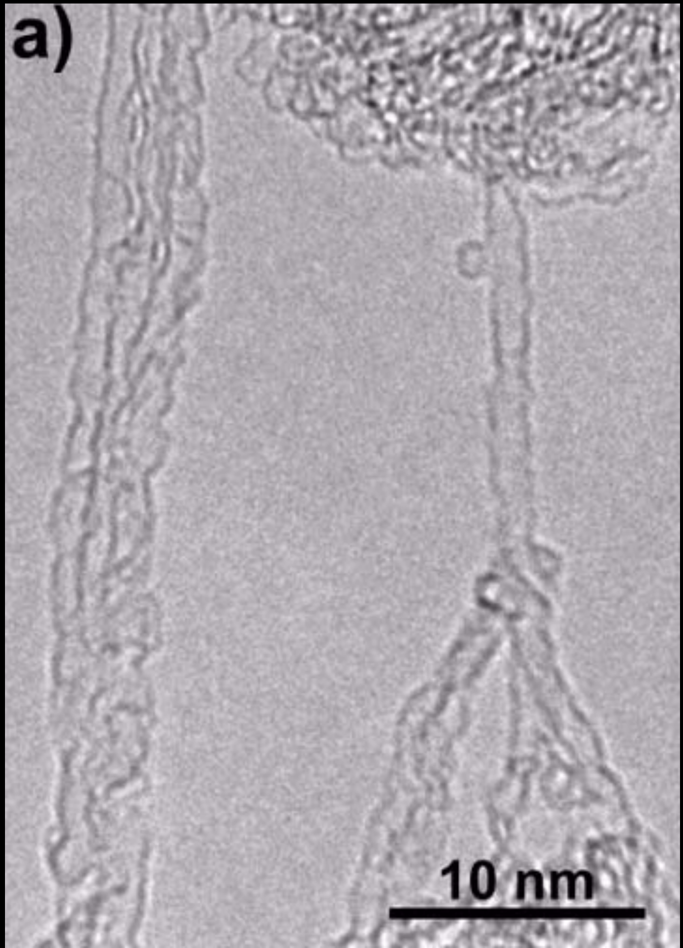




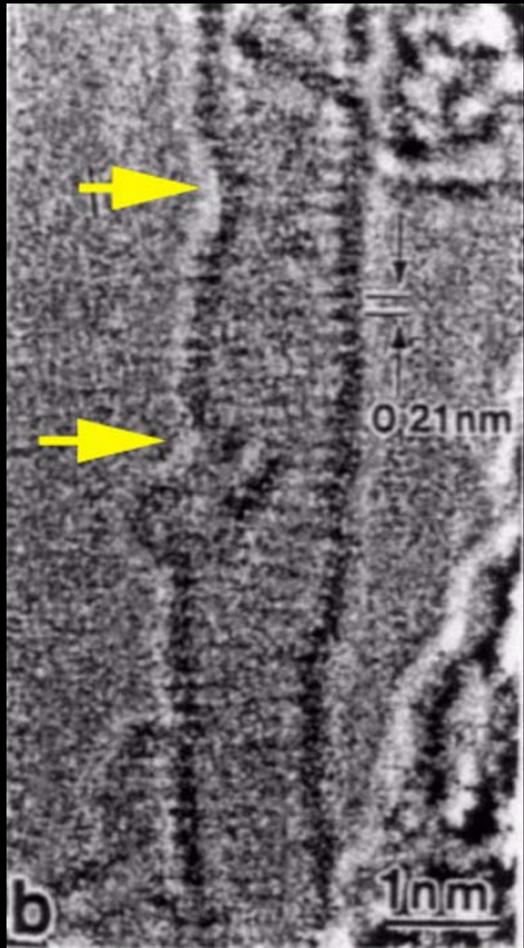


M. Terrones & H. Terrones
Fullerene Science and Technology 4, 517-533 (1996)

Nanotube defects in SWNTS

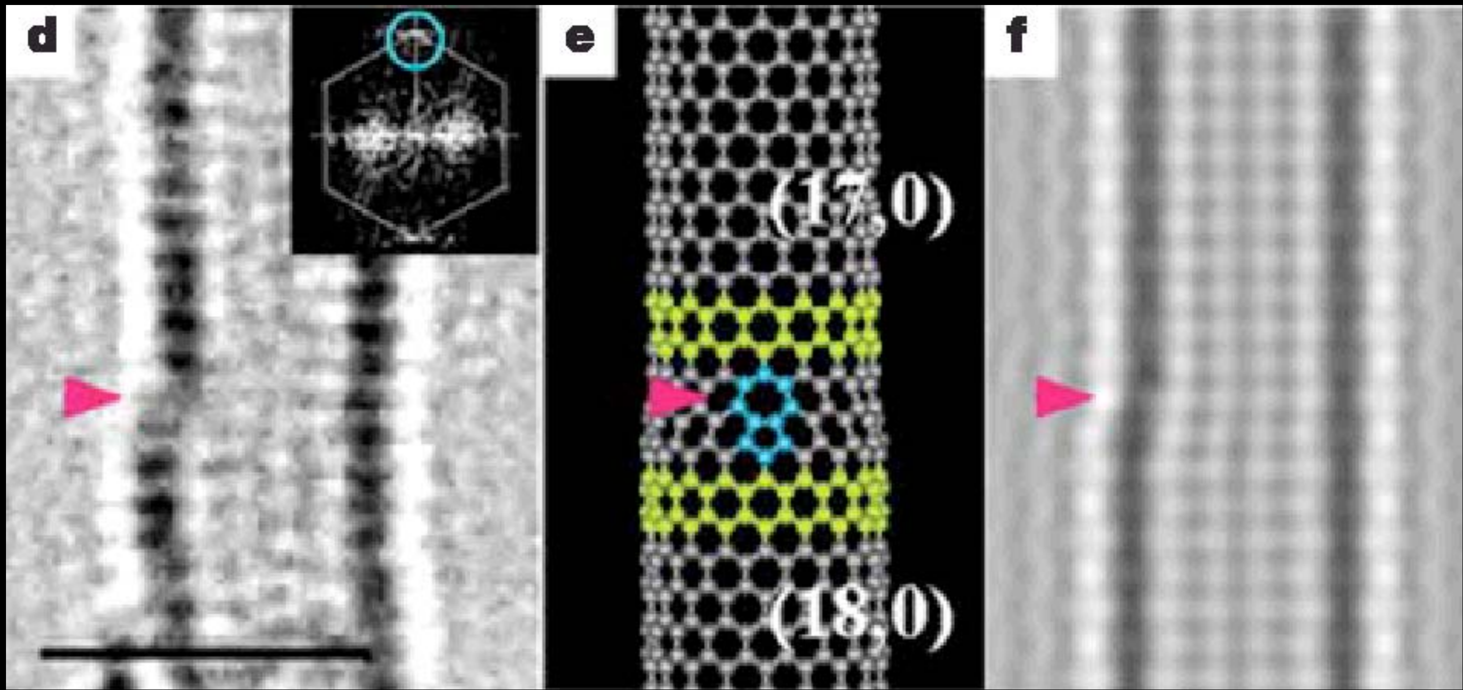


M. Terrones, et al. Unpublished



D. Golberg, Y. Bando, L. Bourgeois, K. Kurashima
Carbon 37 (11): 1858-1860 1999

Topological defects in SWNTS

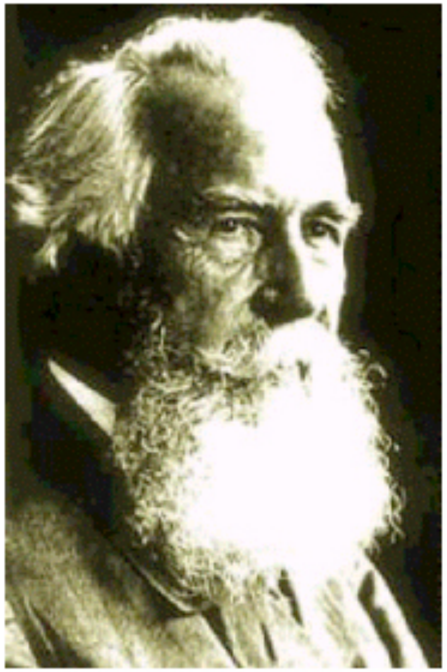


Hashimoto, A., Suenaga, K., Gloter, A., Urita, K., Iijima, S.
Nature 430, 870 (2004)

Hexagons, Pentagons & Heptagons: New Carbon Allotropes

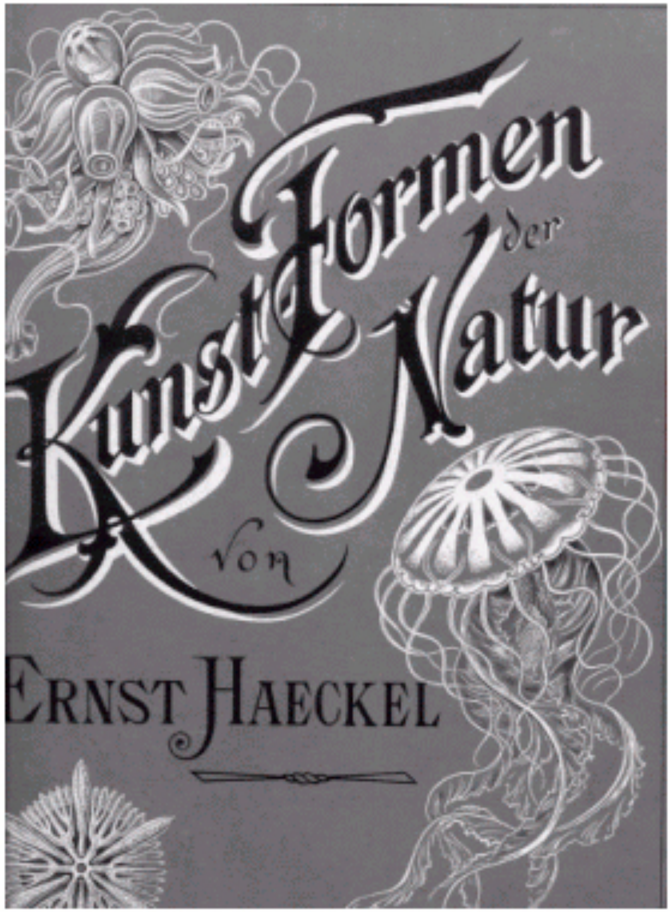
V. Crespi, et al. Phys. Rev. B 53, 13303 (1996)
H. Terrones, et al. Phys. Rev. Lett. 84, 1716 (2000)

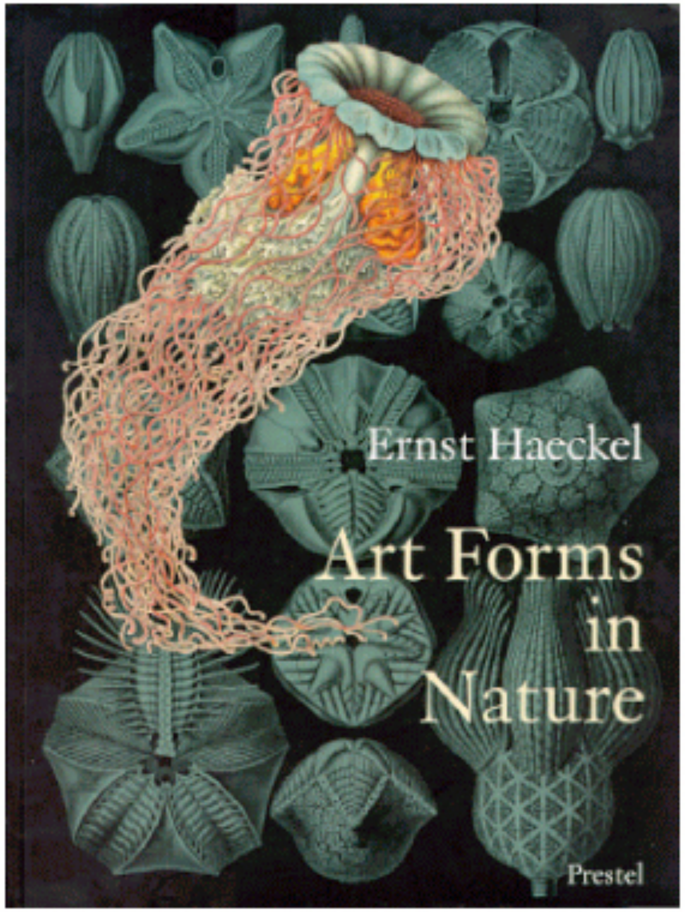
Haeckelites: Origin of the name ?



Ernst Haeckel
(1834-1919)

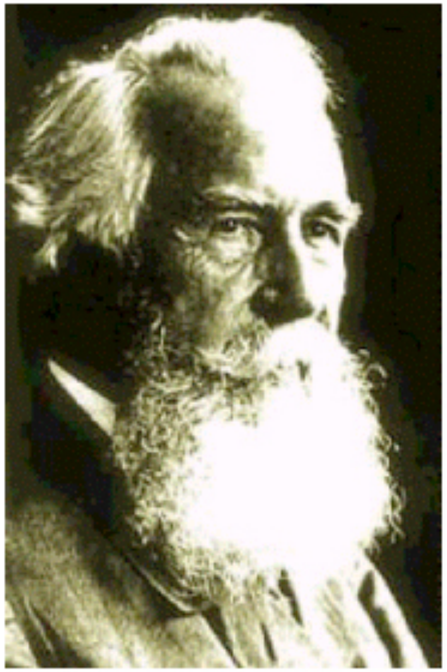
Prof. of Biologie and Zoology, Philosopher
University of Jena, Germany



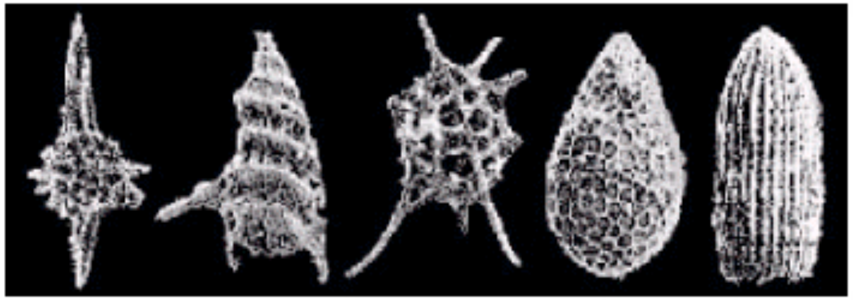


http://www.fh-augsburg.de/~harsch/germanica/Chronologie/19Jh/Haeckel/hae_intr.html

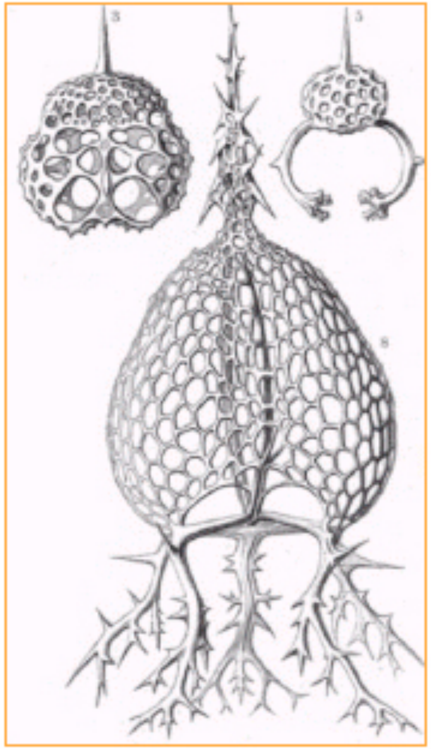
Topology of Radiolarias

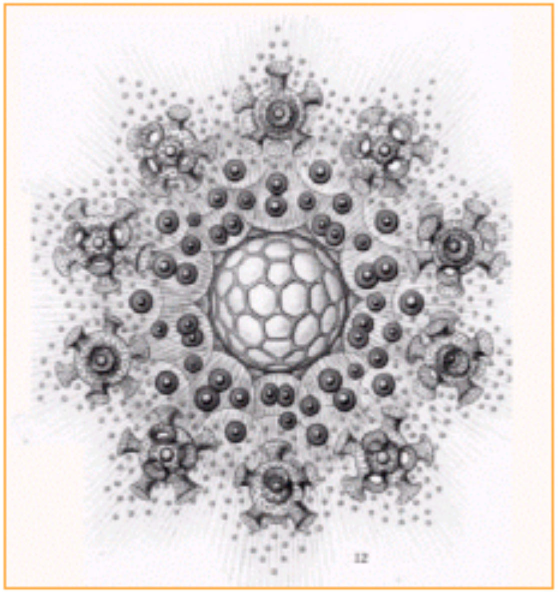


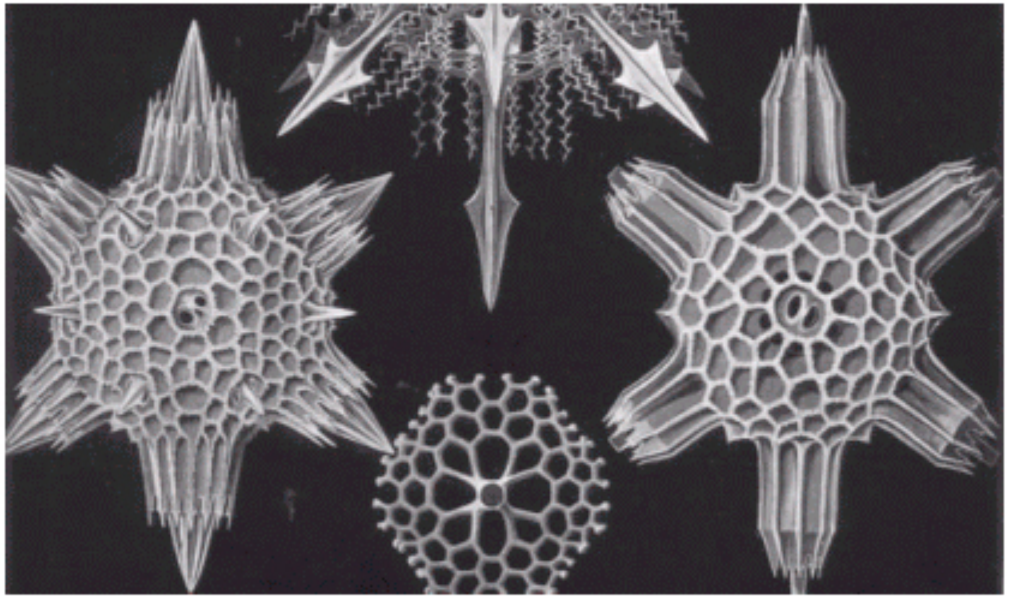
Ernst Haeckel



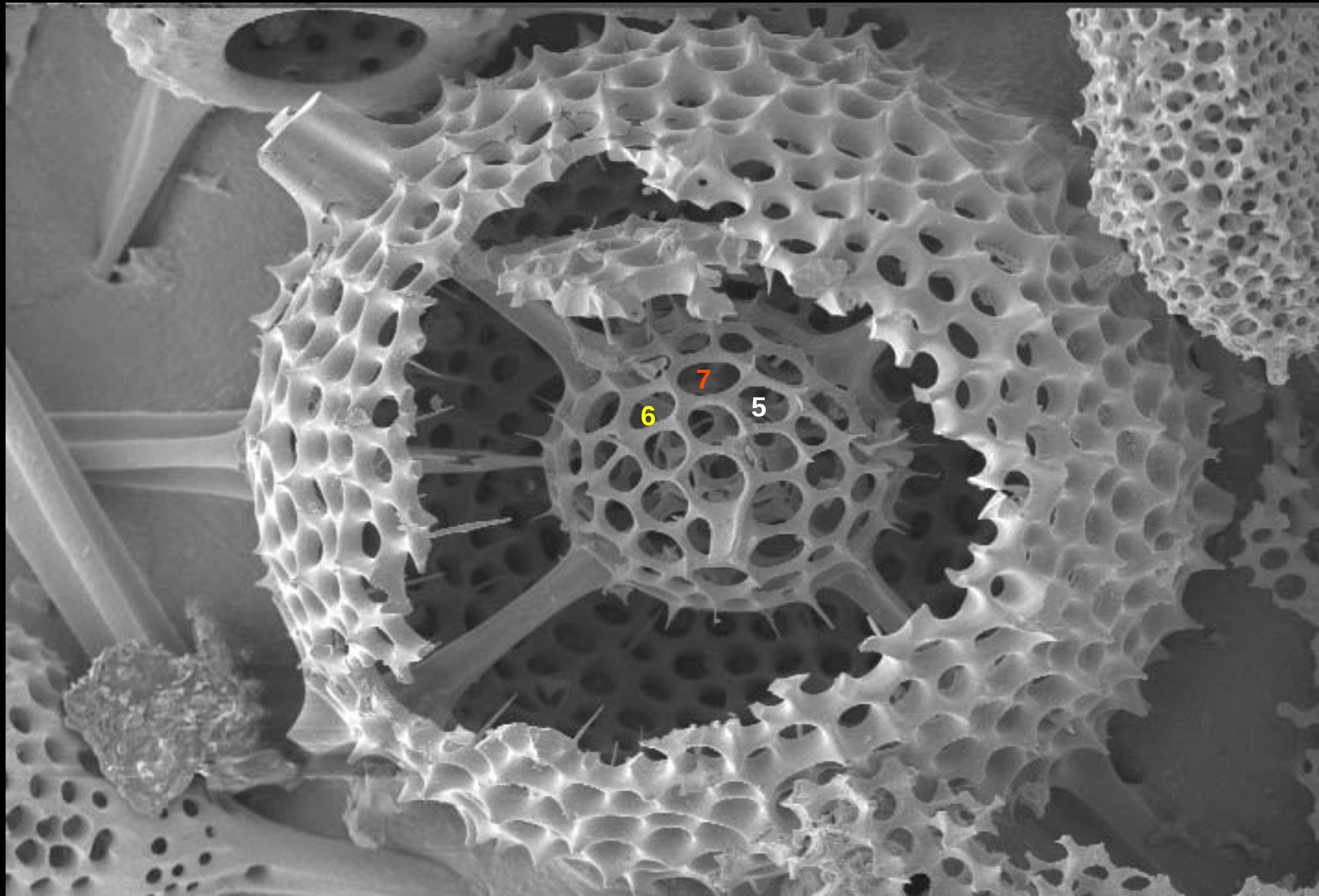
Small unicell organism
absorbing silica from the sea in order
to create a skeleton (dimension: 1/10 mm)
which possesses a specific architecture.



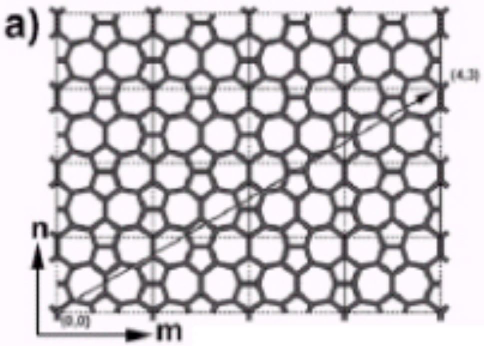




SEM Image of the skeleton of a Radiolaria



Haeckelites: theoretical predictions of a NEW family planar and cylindrical carbon structures with sp^2 type

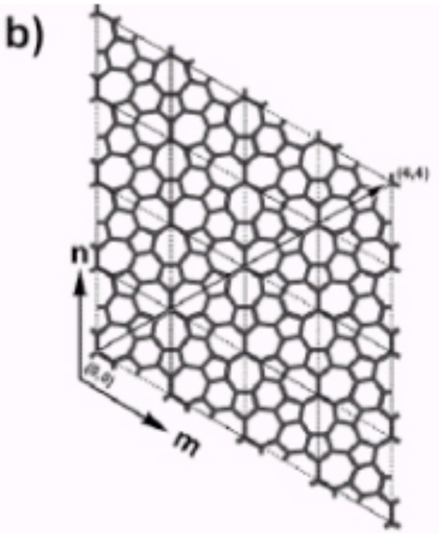


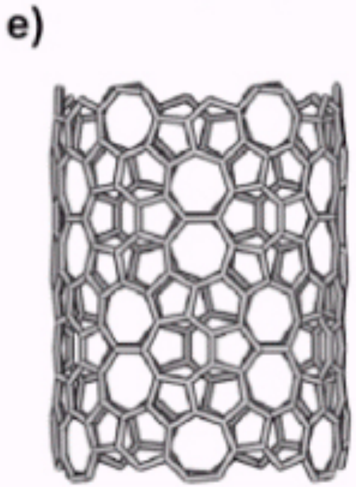
V. Crespi, et al. Phys. Rev. B 53, 13303 (1996)

0.307 eV/atom

$R_{5,7}$ (6,0)

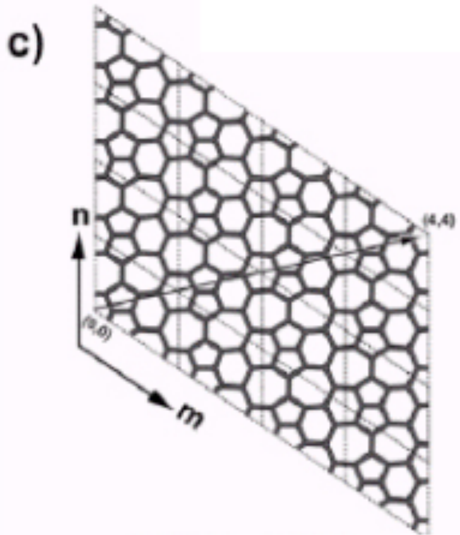
The most favorable nonclassical fullerene clusters (i.e., those which may contain other types of rings, such as heptagons, as well as pentagons and hexagons) are those that minimize the number of pentagon-pentagon pairs and maximize the number of pentagon-heptagon pairs.





0.304 eV/atom

$H_{5,6,7}$ (6,0)



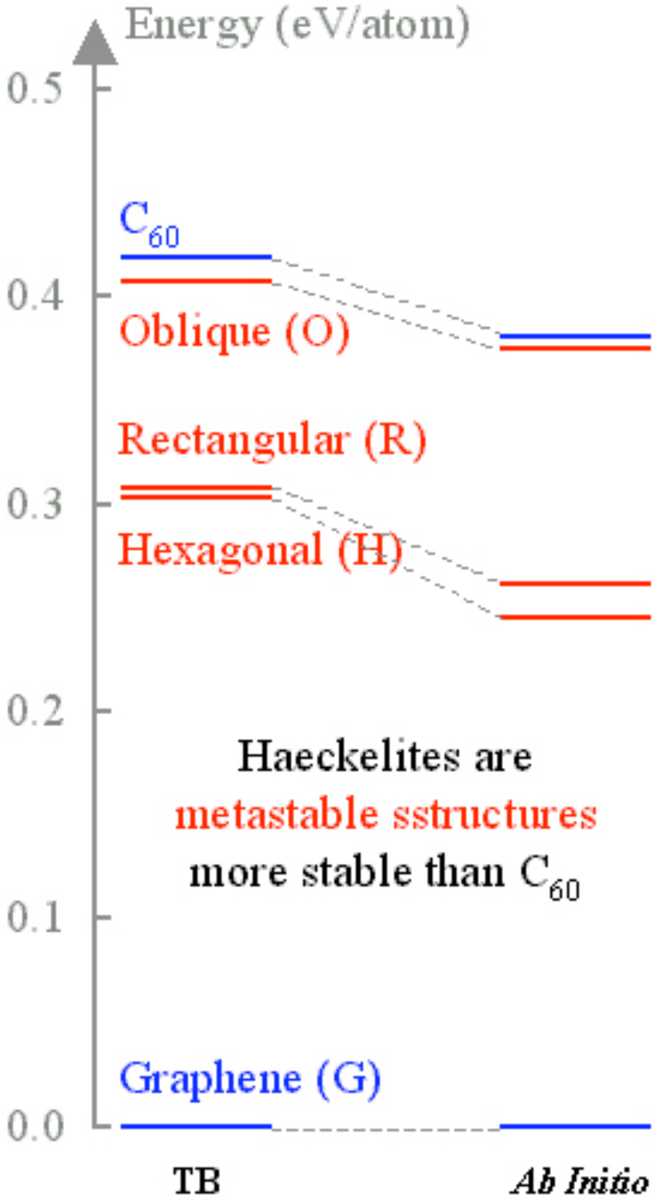
0.408 eV/atom

$O_{5,6,7}$ (0,8)

H. Terrones, et al. Phys. Rev. Lett. 84, 1716 (2000)

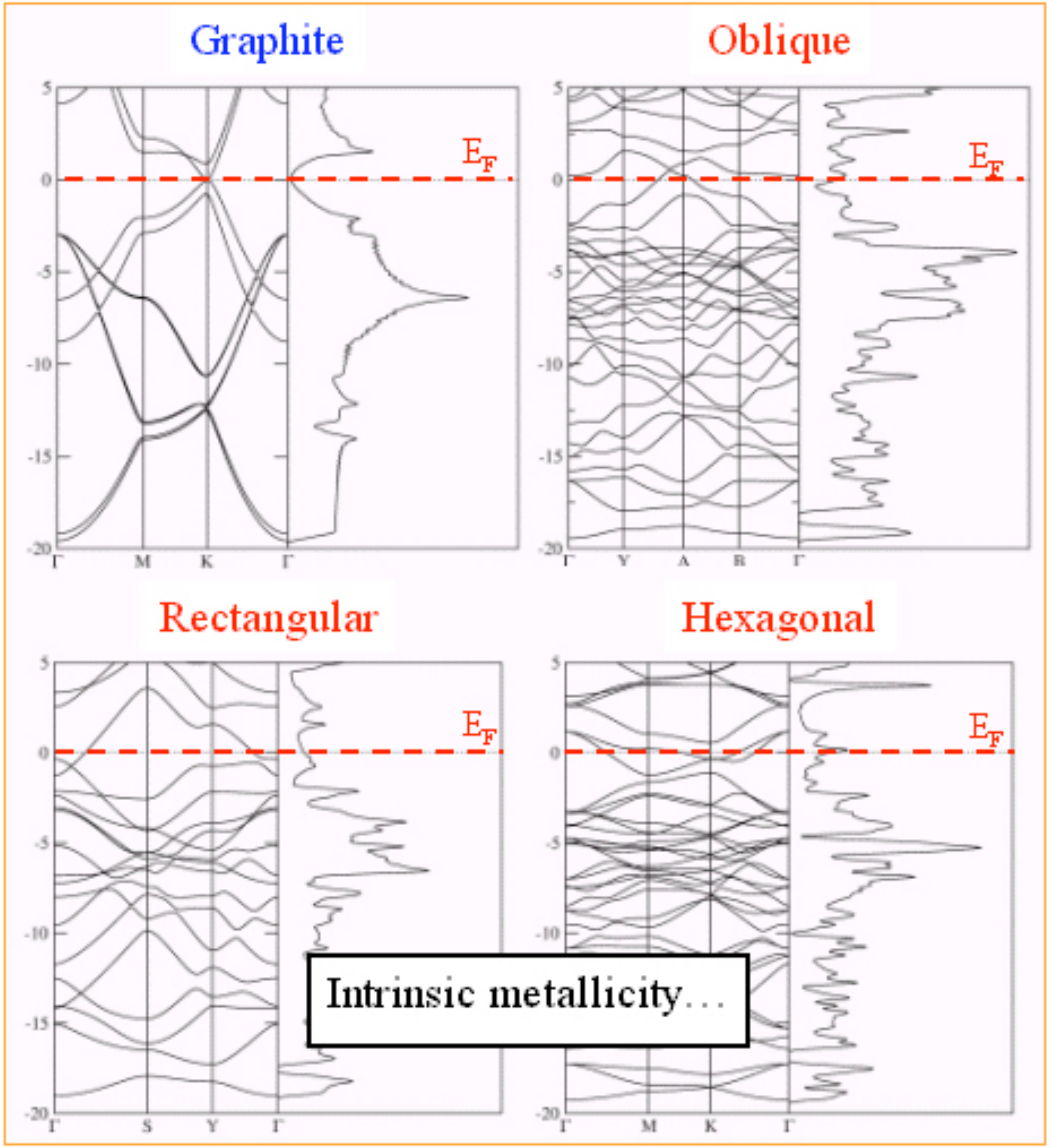
PRL **84**, 1716 (2000)

Ab initio calculations for the planar structures



Haeckelites are
metastable sstructures
more stable than C_{60}

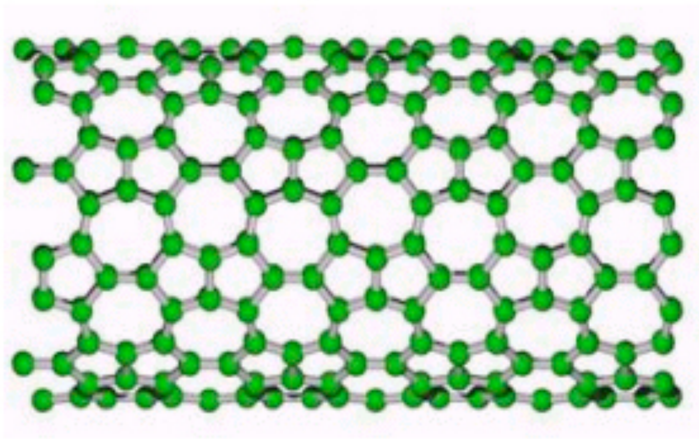
Electronic properties

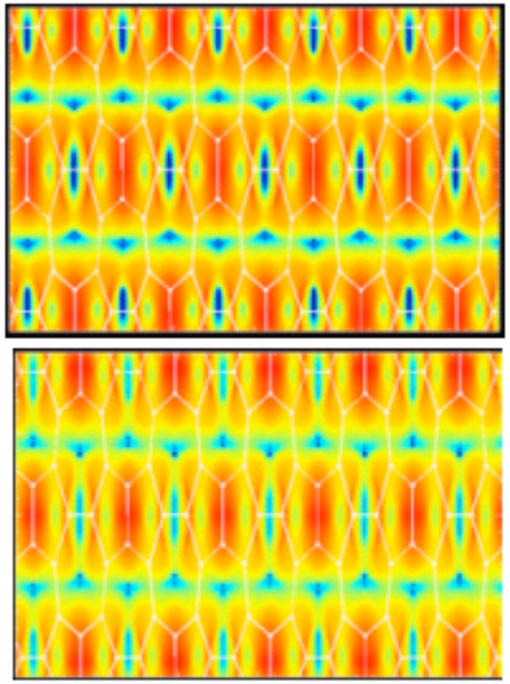


Where are the defects ??

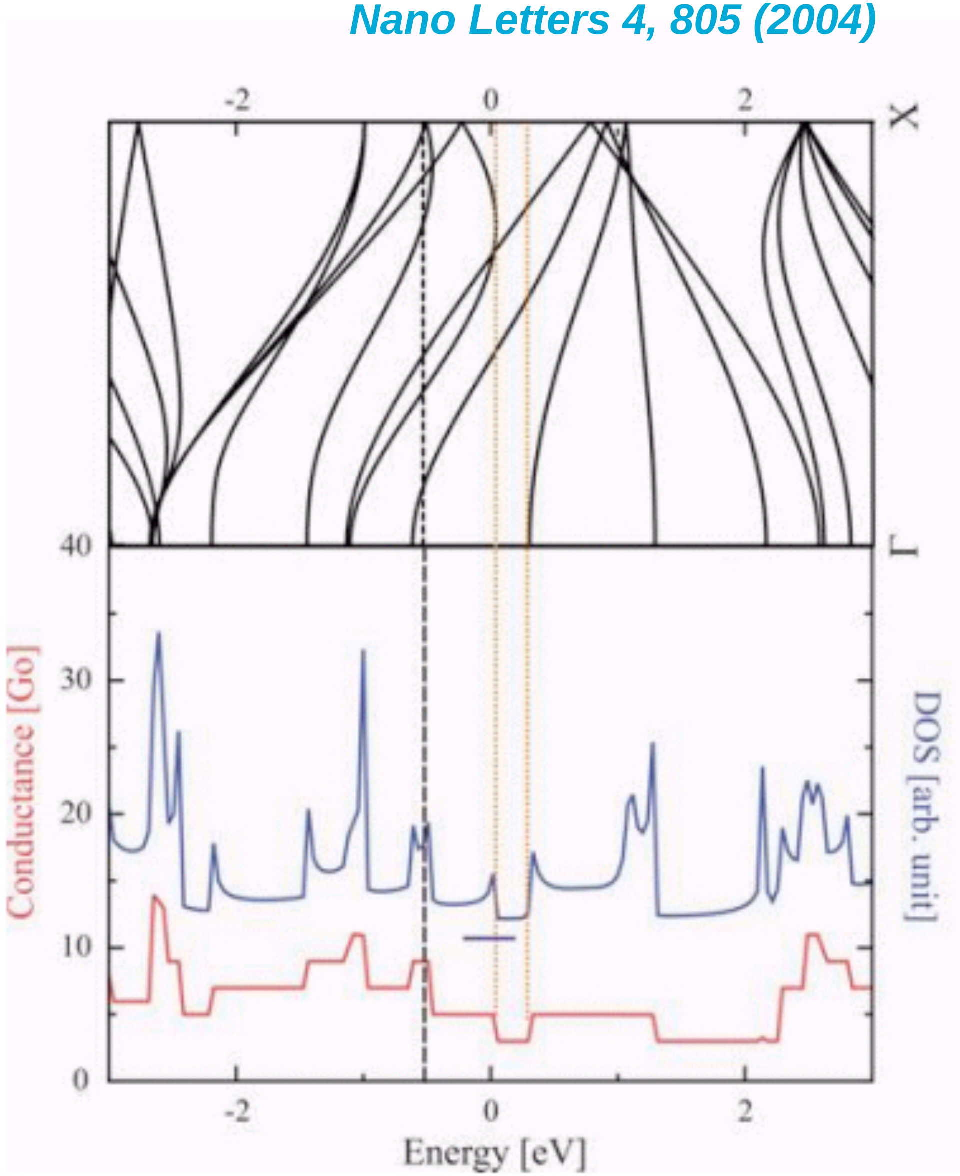
$R_{5,7}$

X. Rocquefelte, G.-M. Rignanese, V. Meunier, H. Terrones, M. Terrones& J.-C. Charlier
Nano Letters 4, 805 (2004)





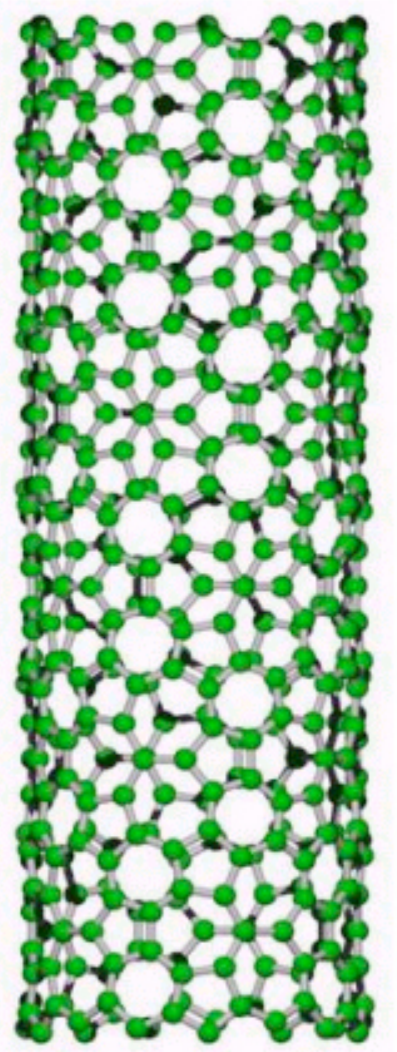
STM image

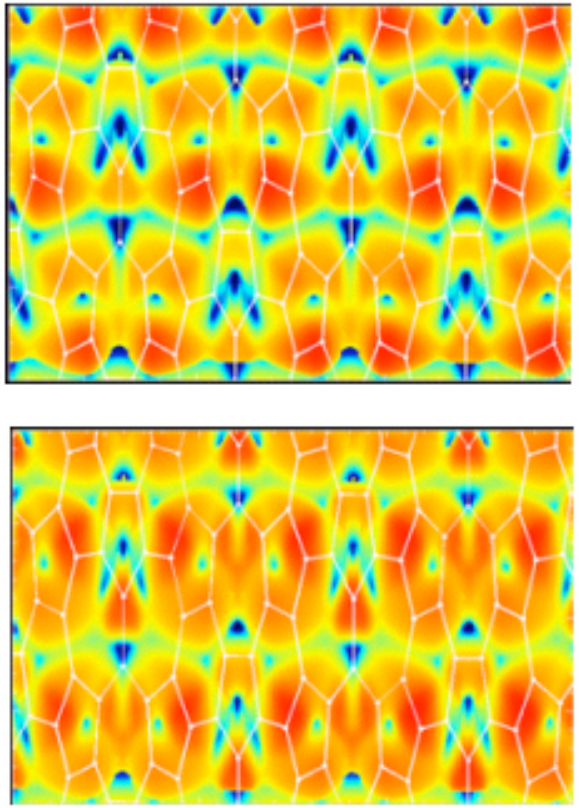


Defects are the hexagons…

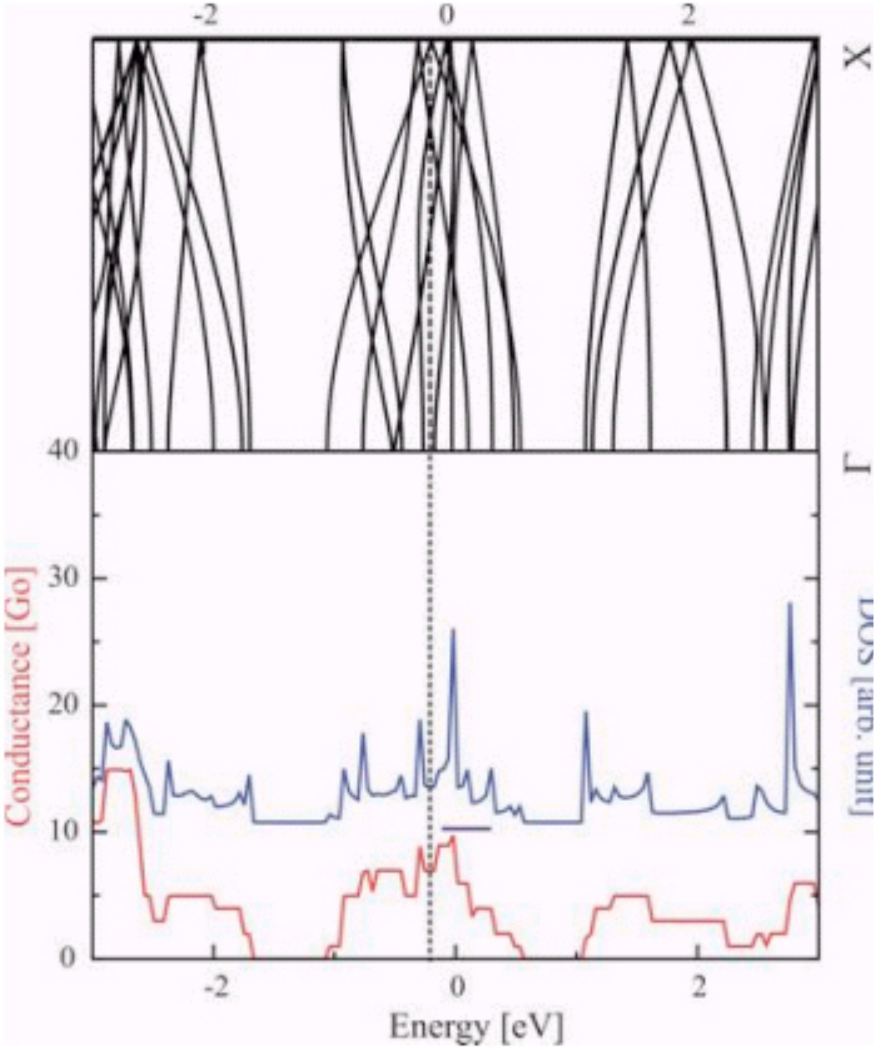
X. Rocquefelte, G.-M. Rignanese, V. Meunier, H. Terrones, M. Terrones& J.-C. Charlier
Nano Letters 4, 805 (2004)

$H_{5,6,7}$





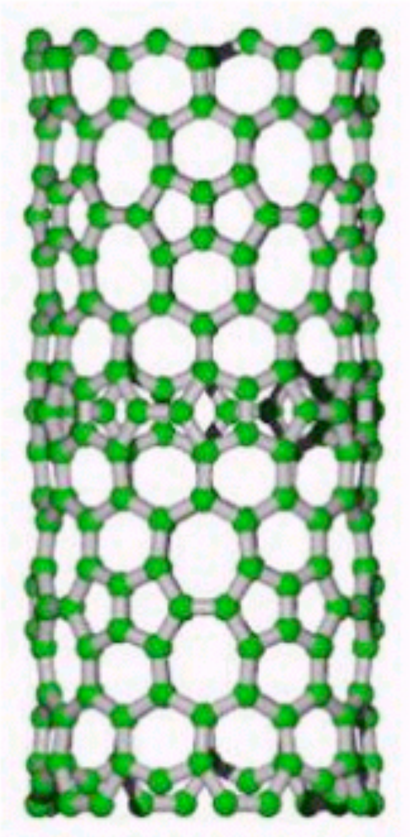
STM image

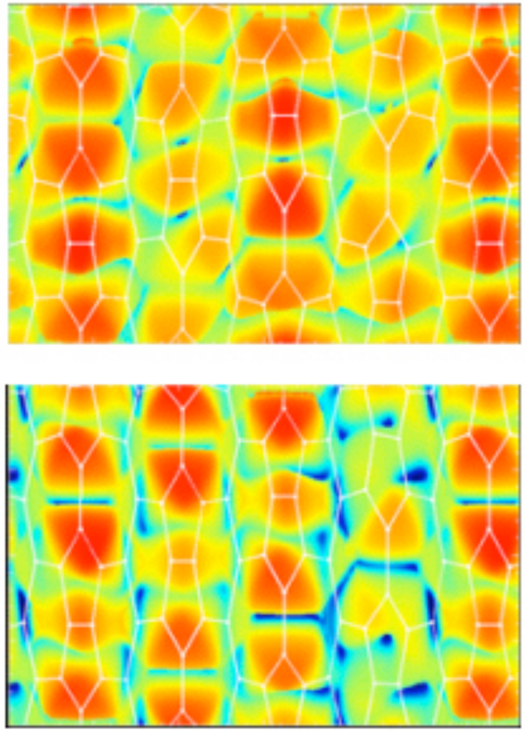


Semiconducting structures are possible !

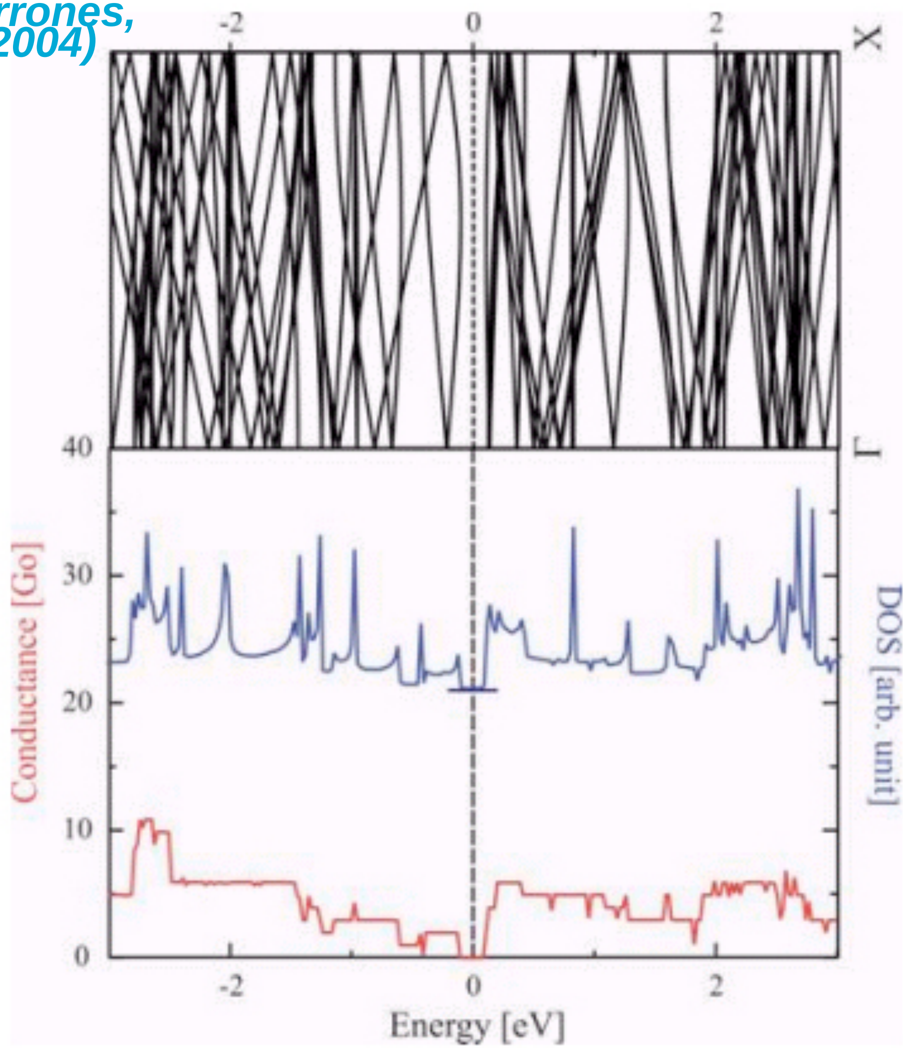
O$_{5,6,7}$

X. Rocquefelte, G.-M. Rignanese, V. Meunier, H. Terrones, M. Terrones& J.-C. Charlier Nano Letters 4, 805 (2004)





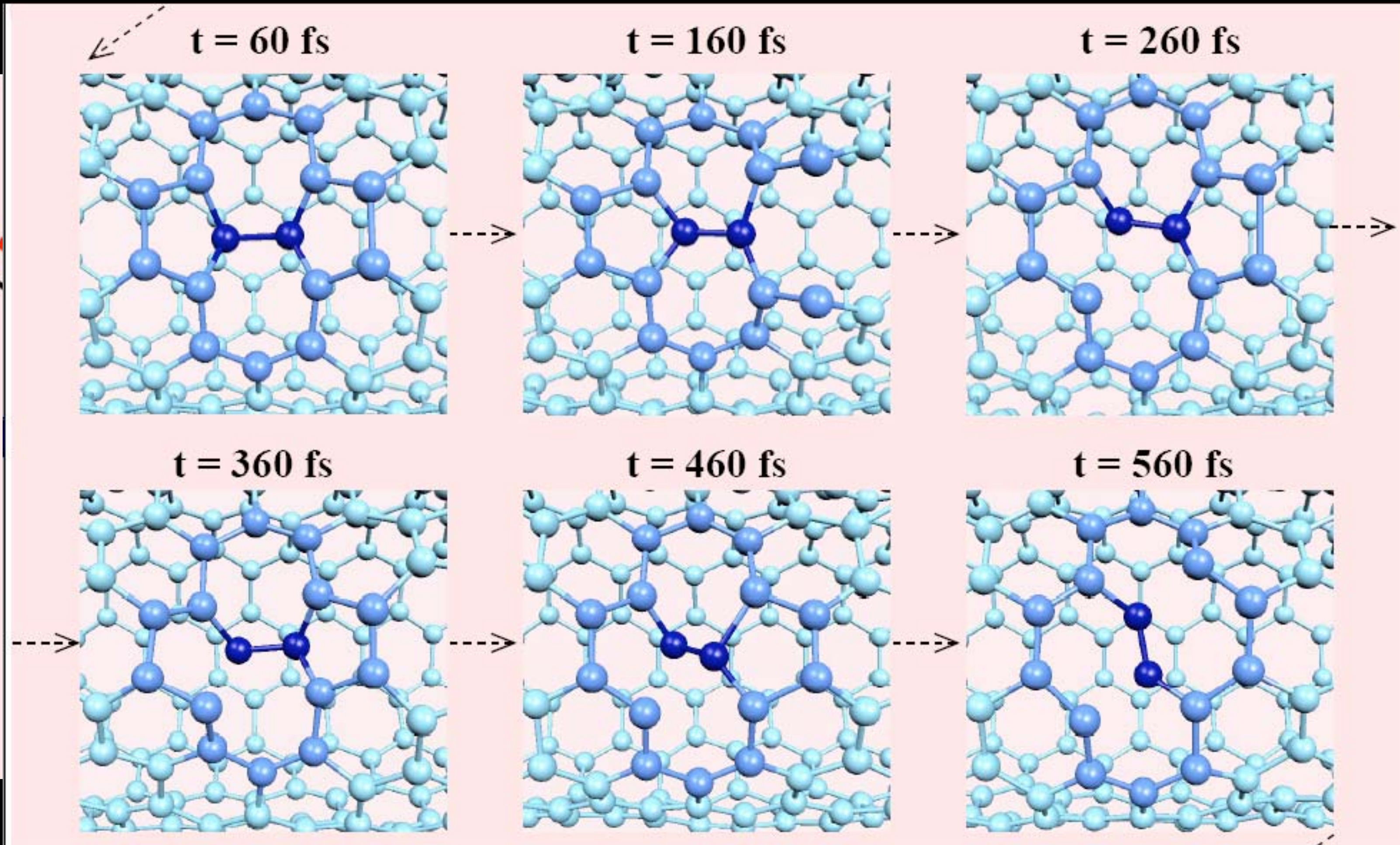
STM image



Nanosurgery:

Removing SW defects Selectively

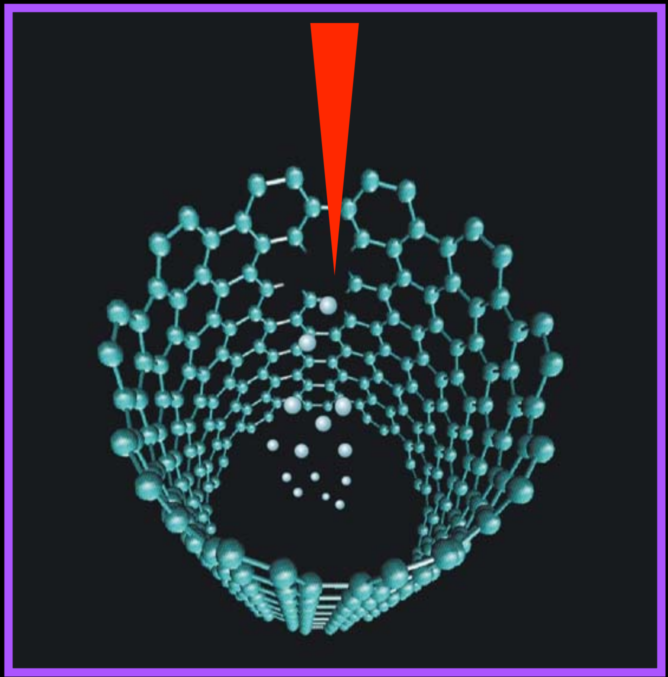
Using Femtosecond Lasers to Remove Defects: A New Approach



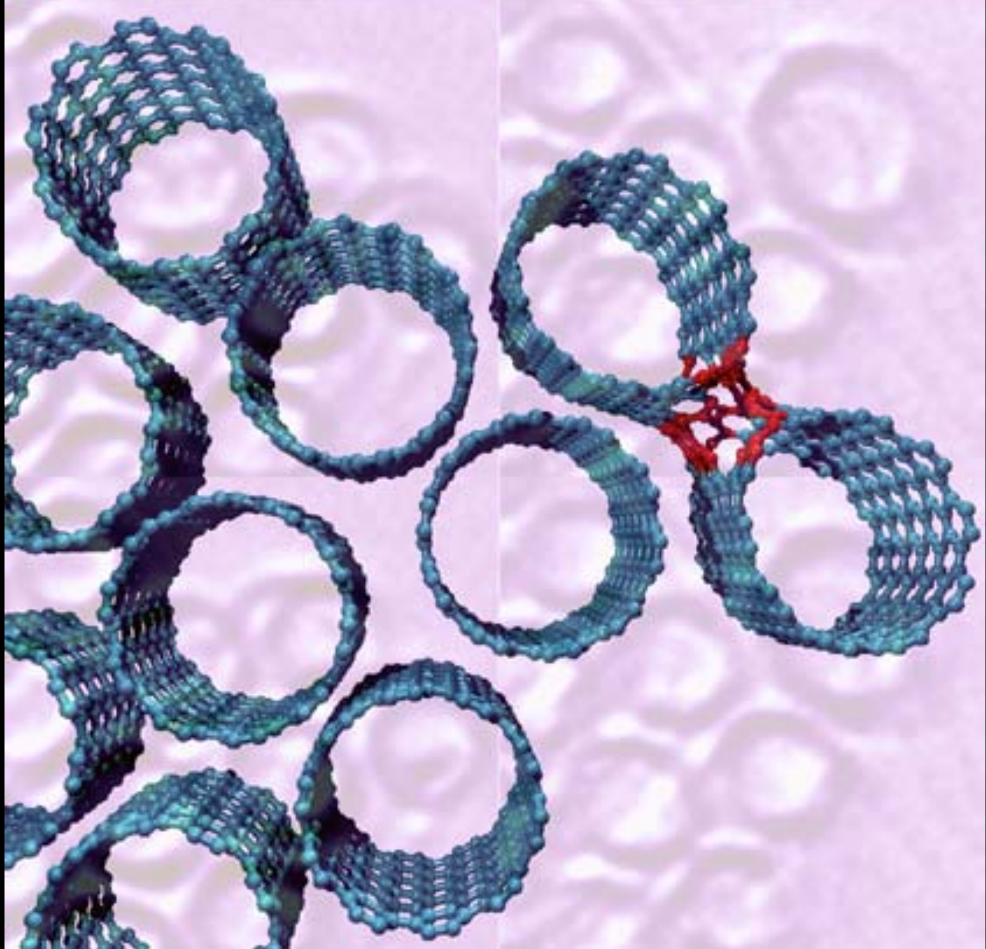
A.H. Romero, M. García, F. Valencia, H. Terrones, M. Terrones, H. Jeschke.
Nano Letters 5, 1361 (2005)

Defects & Carbon Nanotube Electronics

3. VACANCIES AND INSTERSTITIALS!!

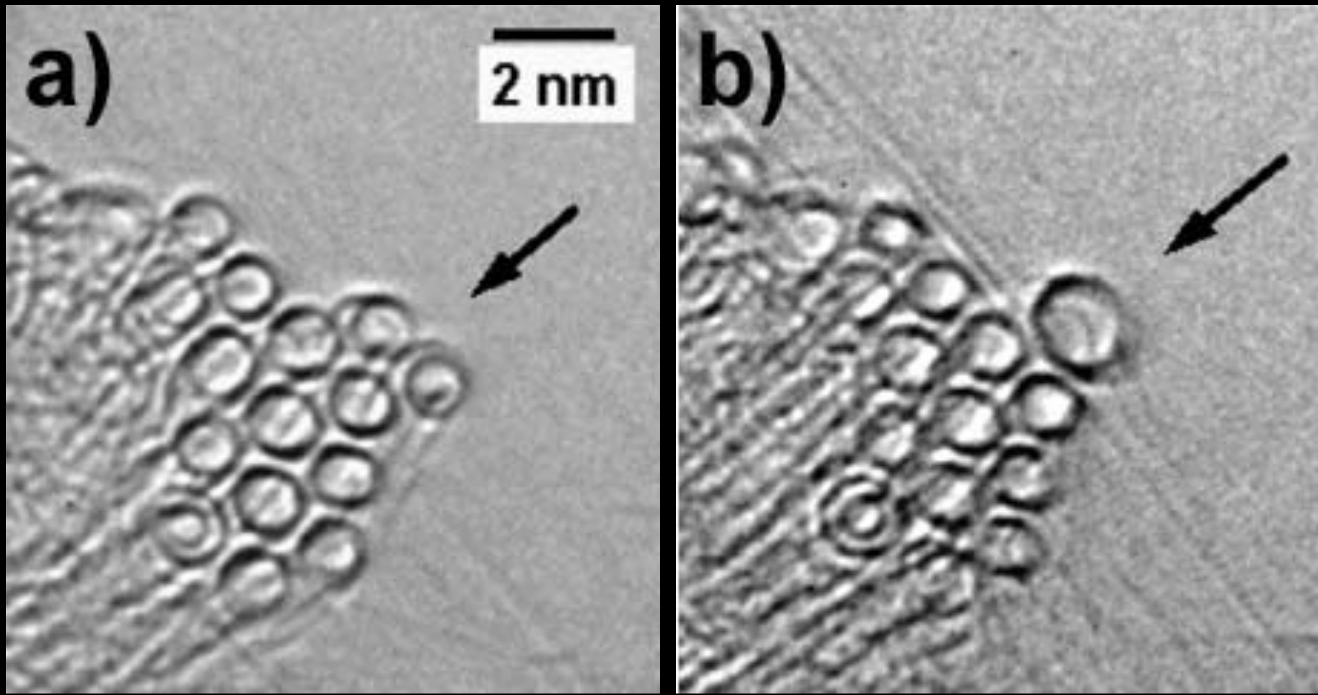


Joining Nanotubes



Coalescence of single-walled carbon nanotubes

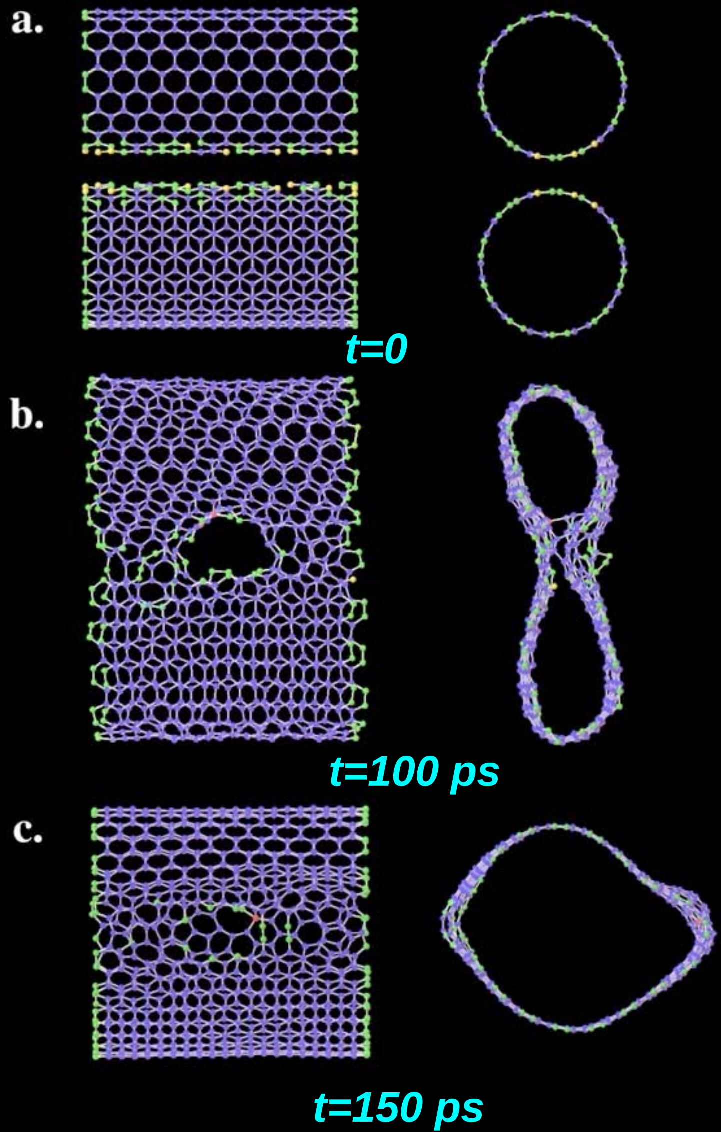
Coalescence of Carbon Nanotubes



(a) SWNT bundle; (b) bundle after a few seconds of high intensity electron irradiation (1.25 MeV) at 800 °C, exhibiting the coalescence of two tubes (arrow).

Terrones M, Terrones, H, Banhart F, Charlier JC, Ajayan PM. Science 288, 1226 (2000)

Nanotube Coalescence

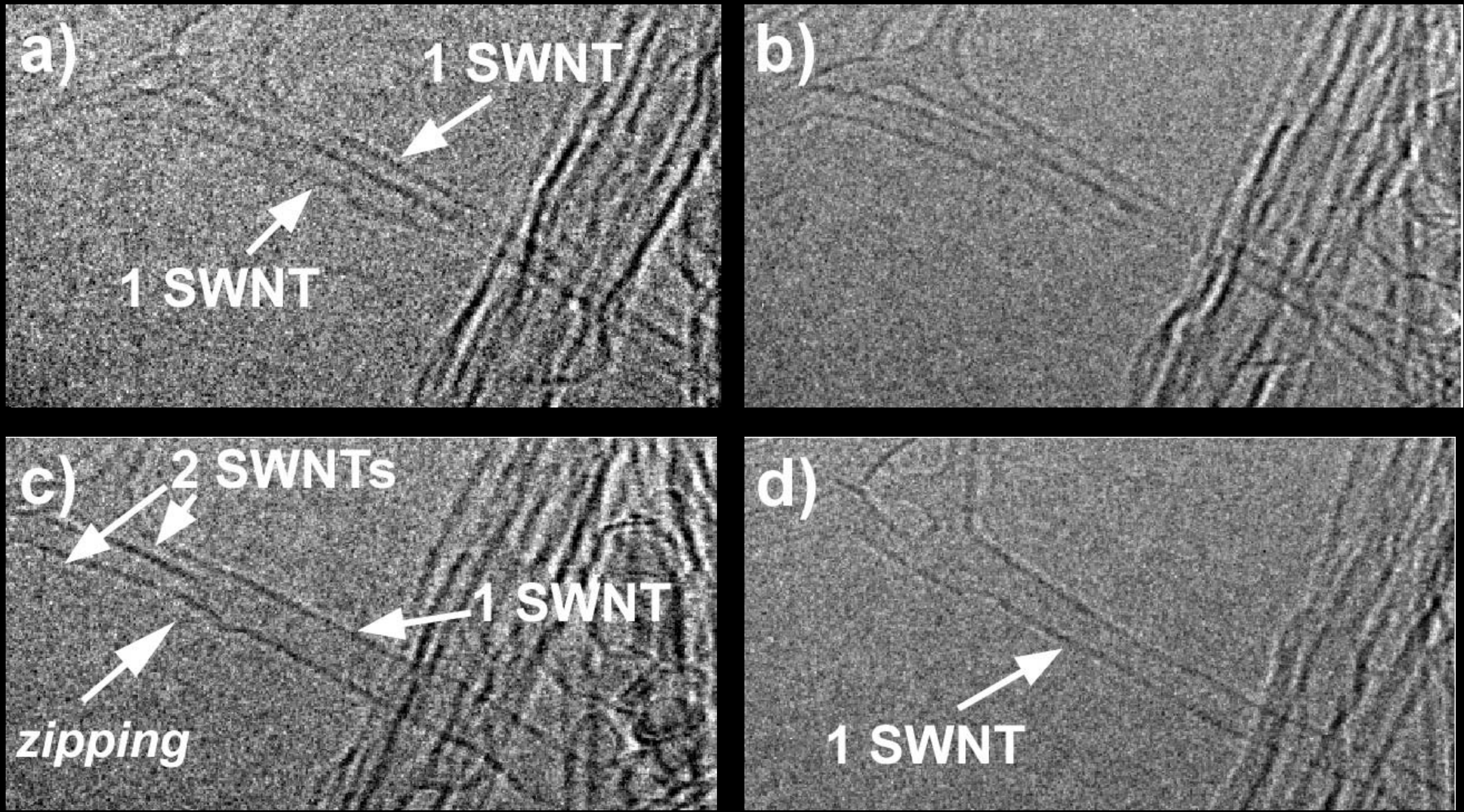


The Importance of Vacancies and Interstitials

(a-c) Sequences of coalescence between two adjacent (10,10) carbon nanotubes (diameter: 1.36 nm) (two-coordinated atoms in green, four-coordinated in red –only one).

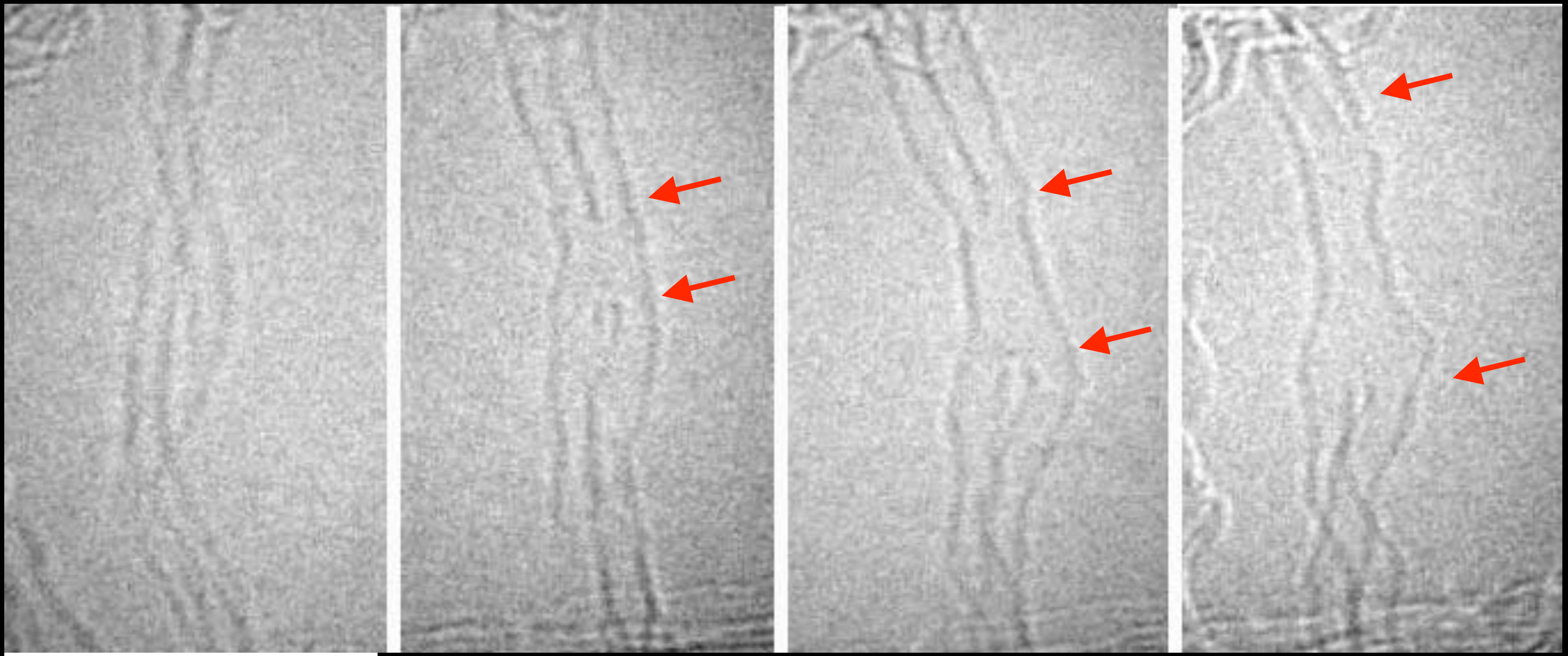
Terrones M, Terrones, H, Banhart F, Charlier JC, Ajayan PM. Science 288, 1226 (2000)

Nanotube Coalescence



Zipping Mechanism

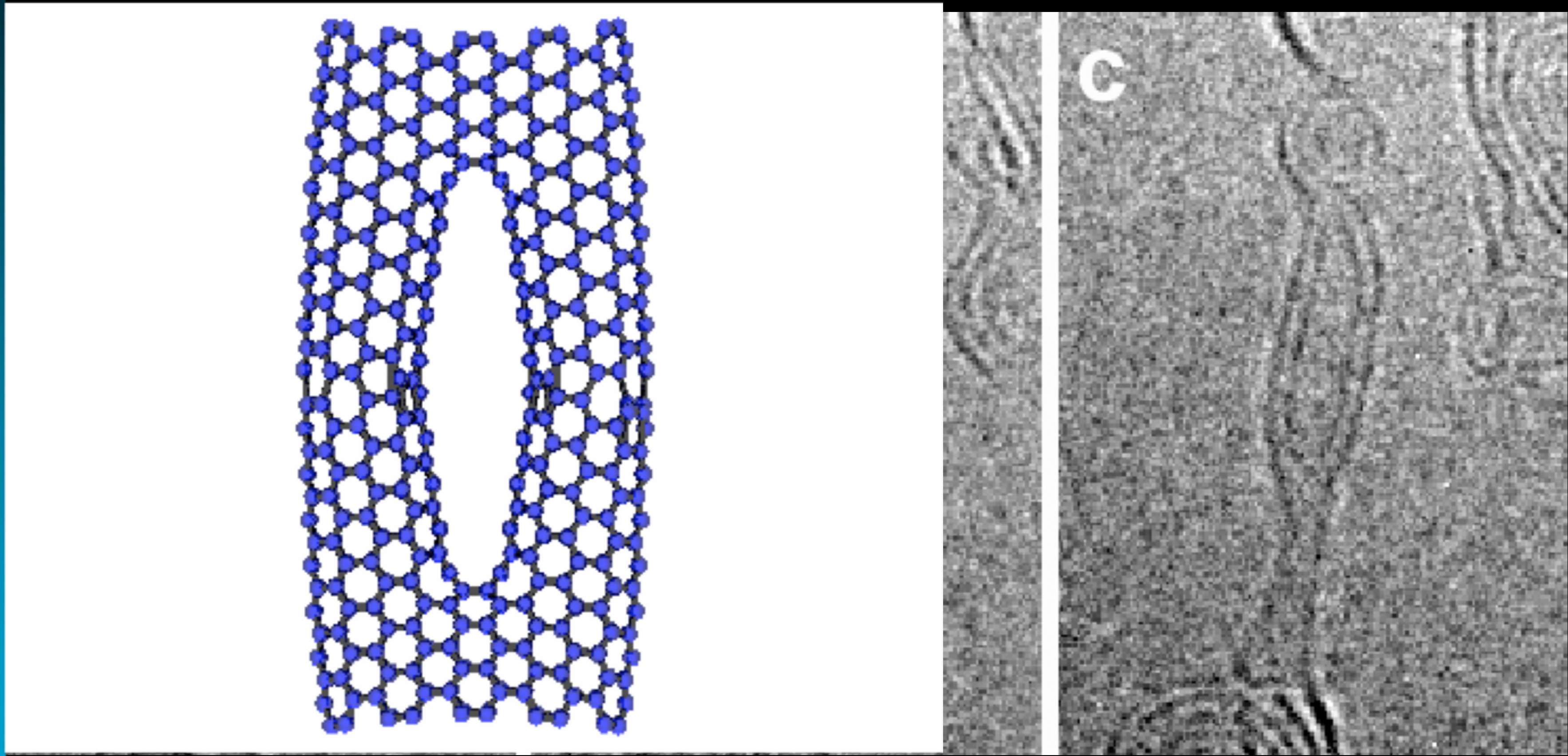
Nanotube Coalescence



Zipping Mechanism

M. Yoon, et al. Physical Review Letters 92, 075504 (2004)

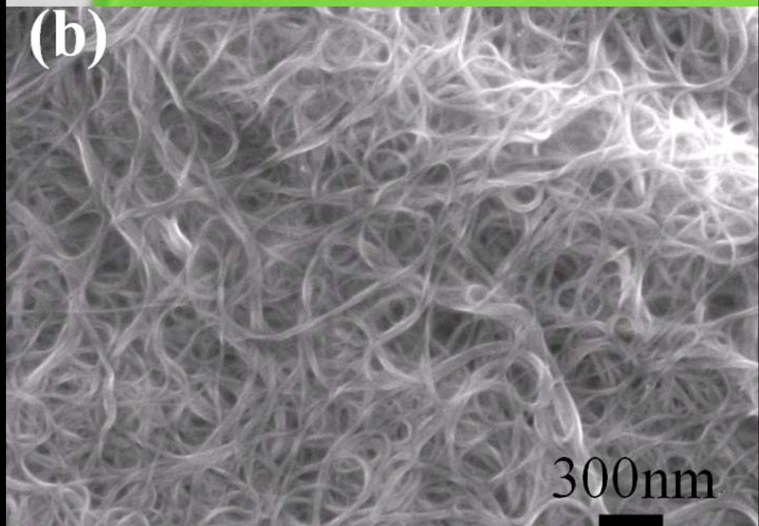
When the Zipper does not work!



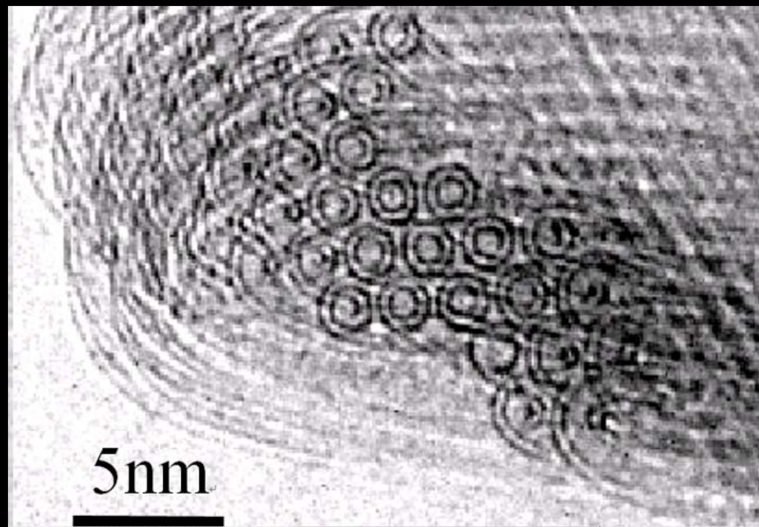
Due to chirality defects in the tubes the zipper stops working!!

M. Yoon, et al. Physical Review Letters 92, 075504 (2004)

NEW TYPE OF NANOTUBES: DOUBLE-WALLED

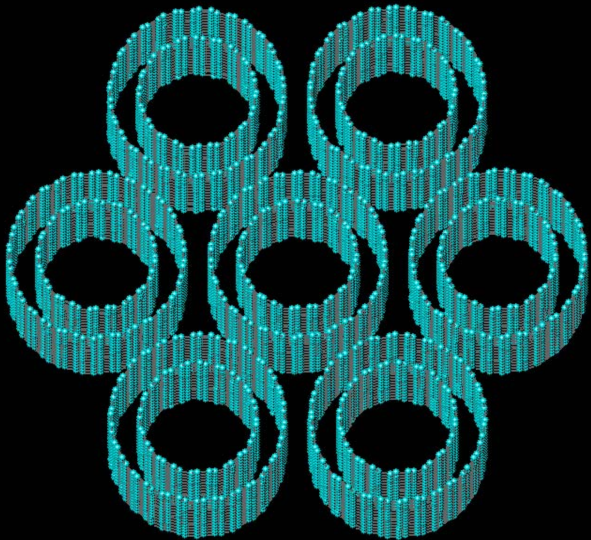


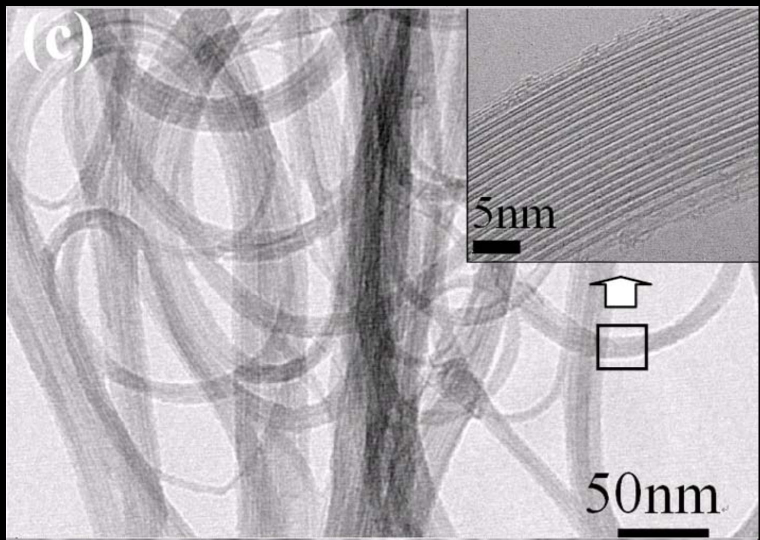
Bundles of Double-walled Nanotubes (DWNTs)

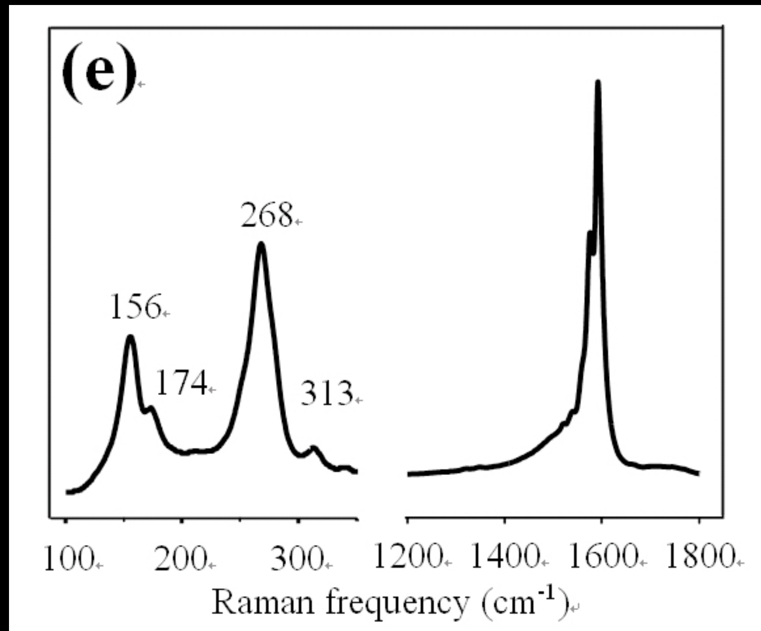


Endo, Y.A., Muramatsu, H., Kim, Y.A., Hayashi, T., Terrones, M., Dresselhaus, M. Nature 433, 476 (2005)

Bundles of Double-walled Nanotubes (DWNTs)

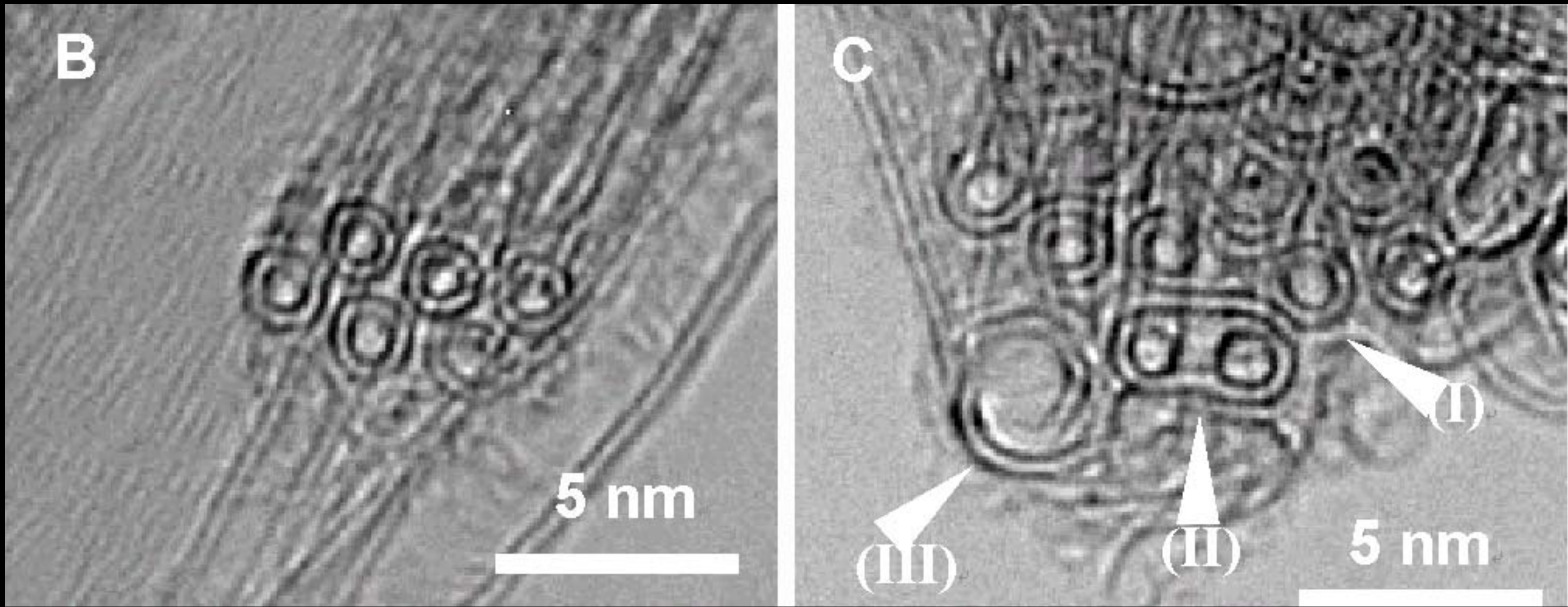






Endo, Y.A., Muramatsu, H., Kim, Y.A., Hayashi, T., Terrones, M., Dresselhaus, M. Nature 433, 476 (2005)

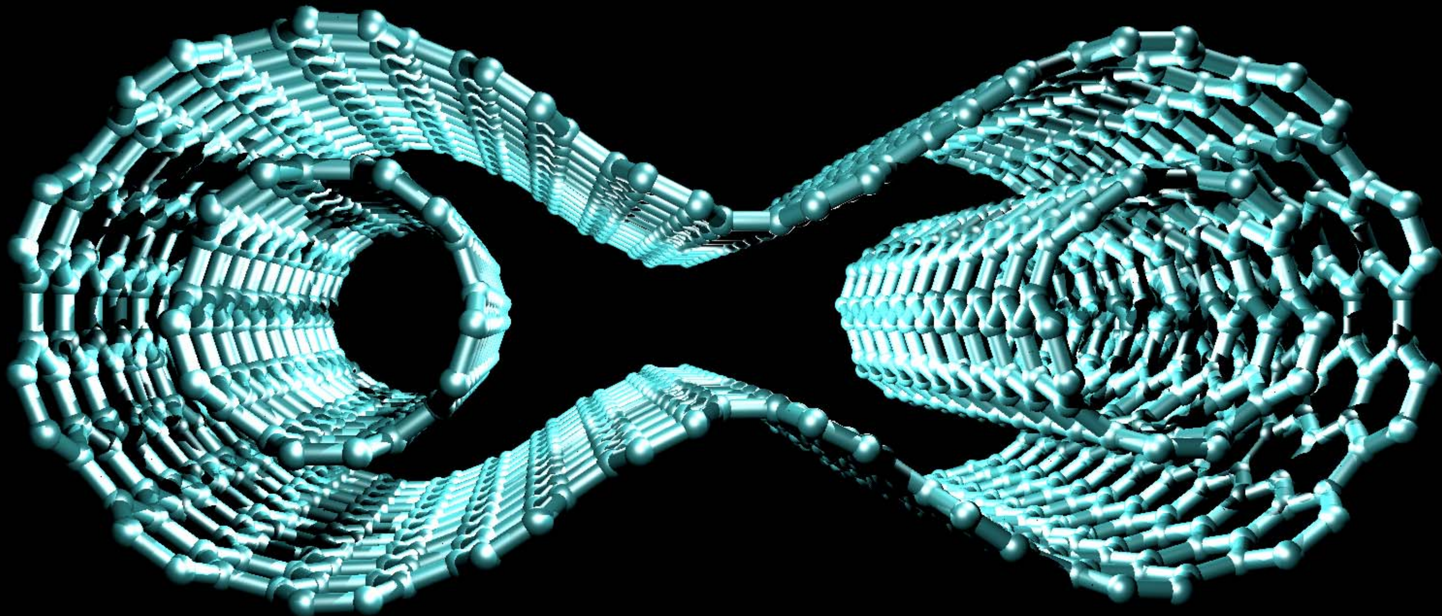
Coalescence of DWNTs: Bi-cable formation



(a) DWNT bundle; (b) bundle after a heat treatment at 2000 °C, exhibiting the coalescence of two tubes (arrow).

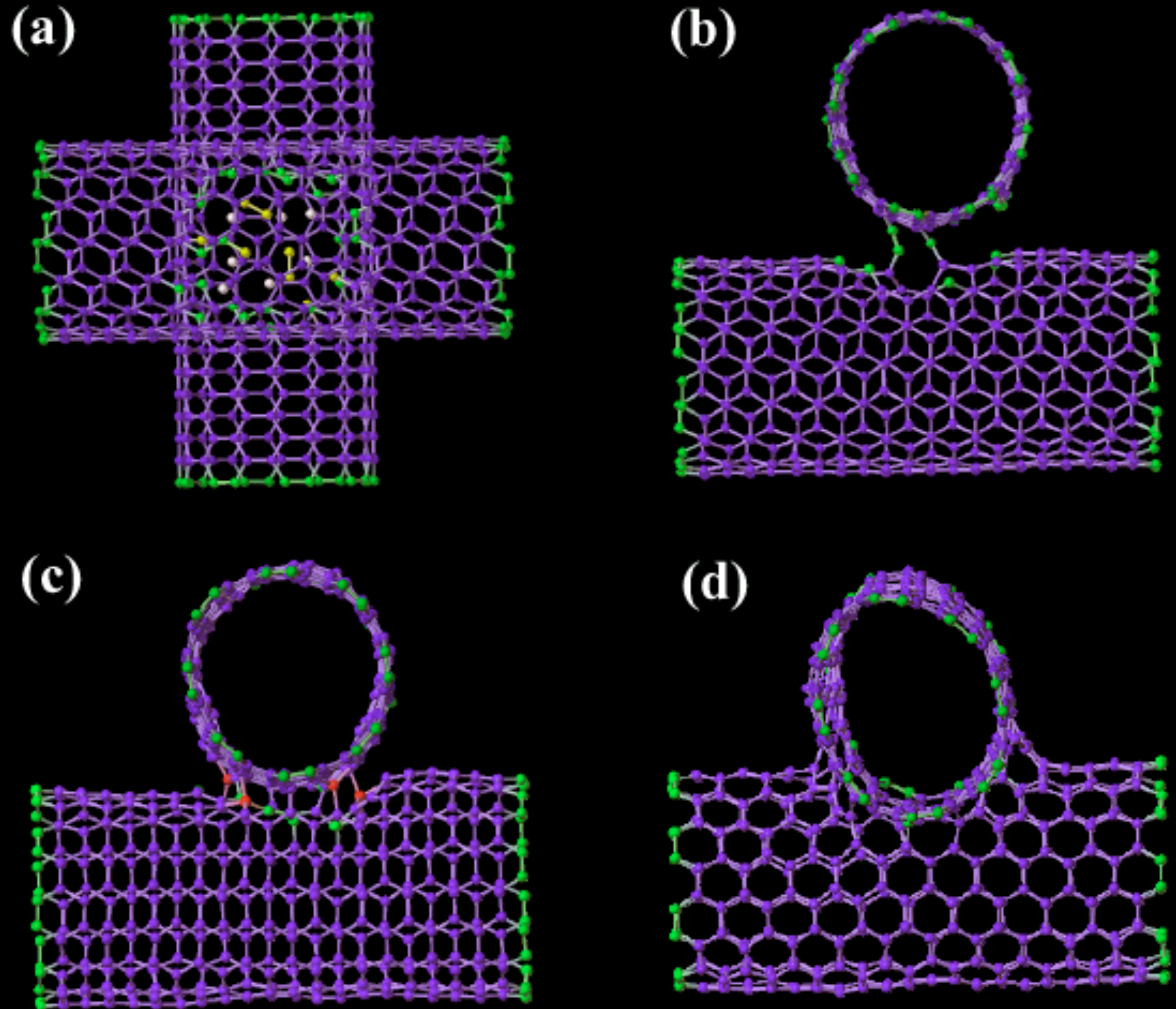
Endo, M., Hayashi, T., Muramatsu, H., Kim, Y.A., Terrones, H., Terrones, M., Dresselhasu, M.S. Nano Letters 4, 1451 (2004)

Coalescence of DWNTs



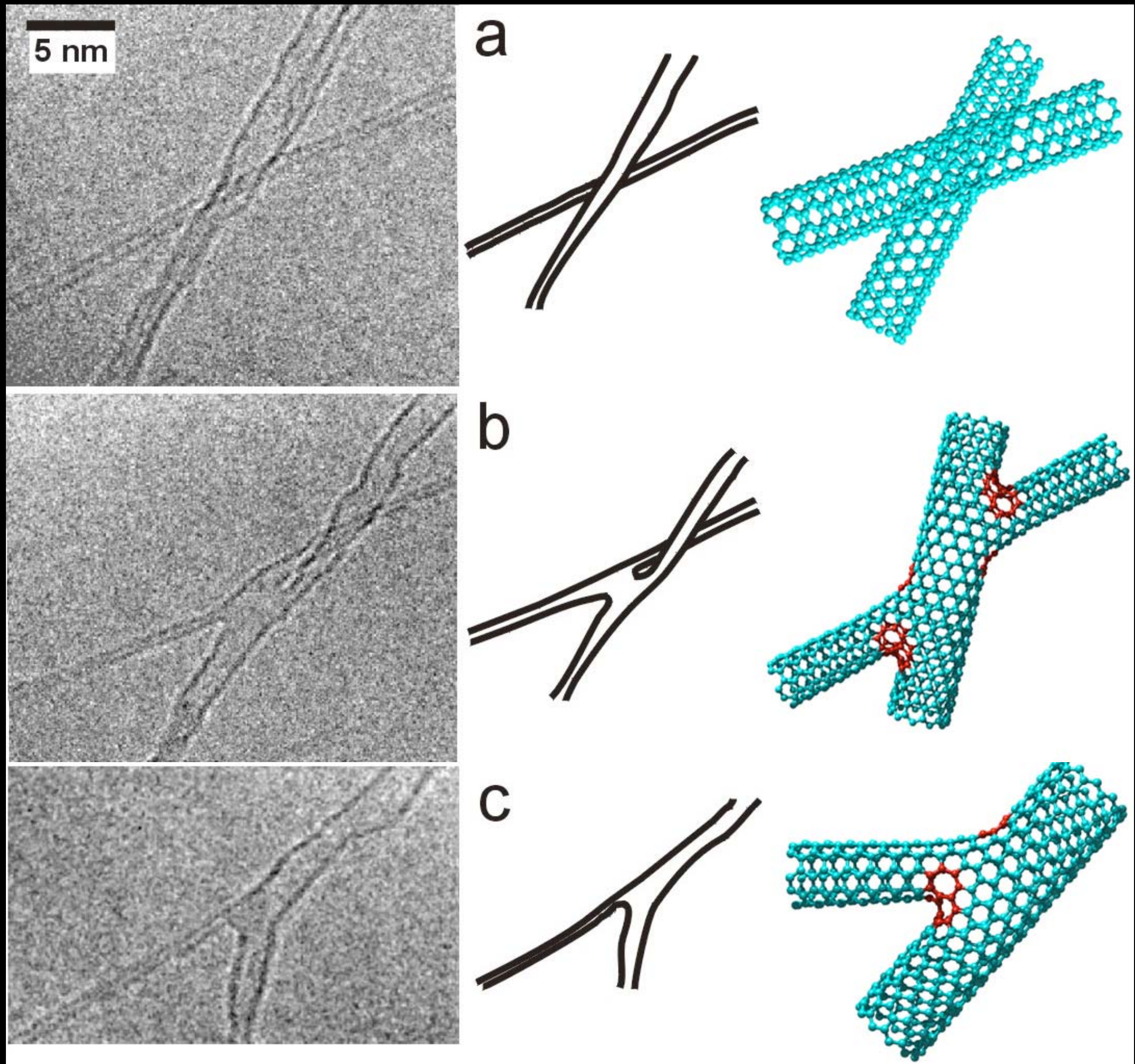
Endo, M., Hayashi, T., Muramatsu, H., Kim, Y.A., Terrones, H., Terrones, M., Dresselhasu, M.S. Nano Letters 4, 1451 (2004)

Connecting Nanotubes



M. Terrones, F. Banhart, N. Grobert, J. C. Charlier, H. Terrones, P.M. Ajayan.
Physical Review Letters 89, 07505 (2002)

Creating Nanotube "X" and "Y" Junctions

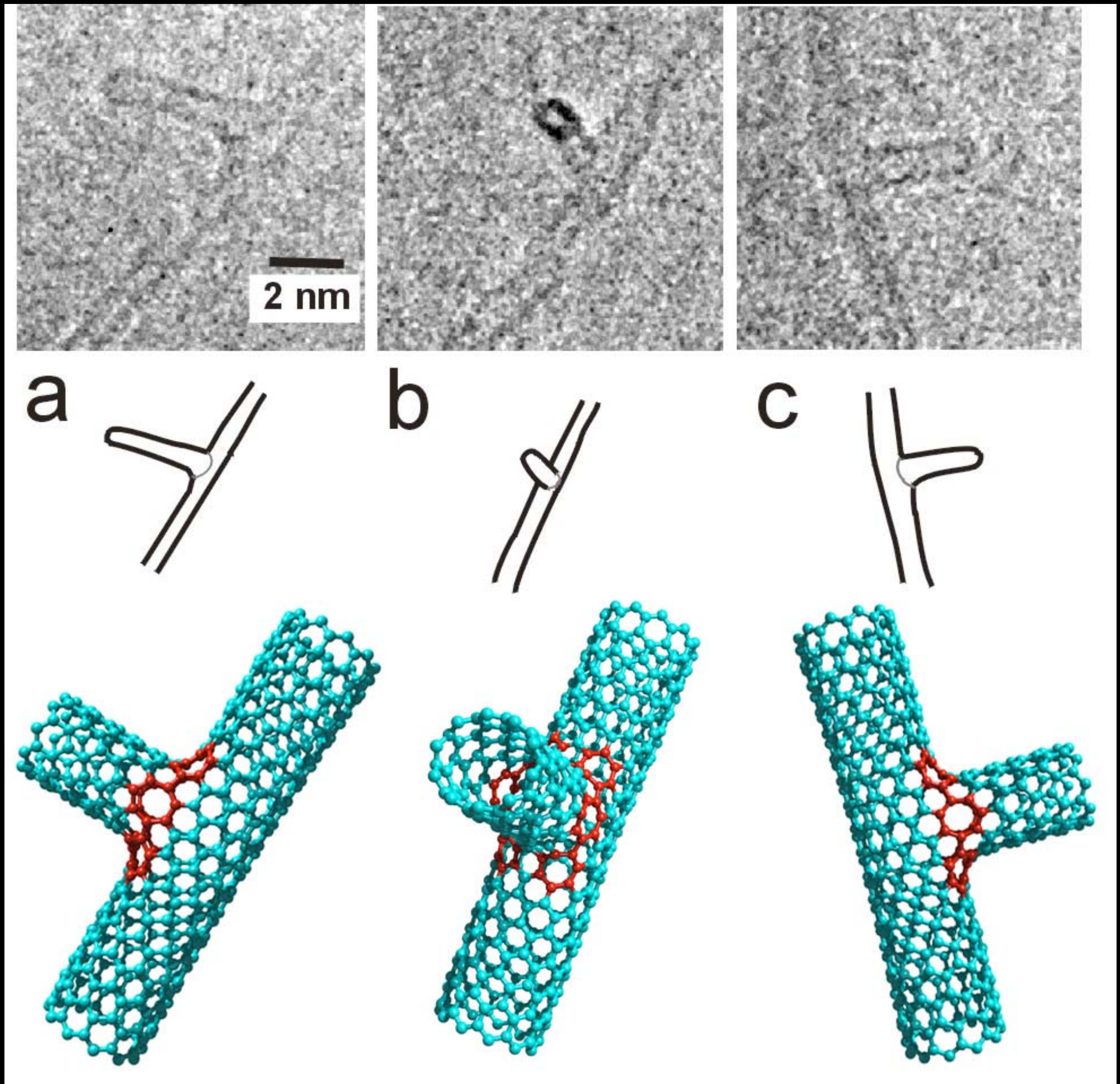


The Importance of Vacancies and Interstitials

M. Terrones, F. Banhart, N. Grobert, J. C. Charlier, H. Terrones, P.M. Ajayan.

Physical Review Letters 89, 07505 (2002)

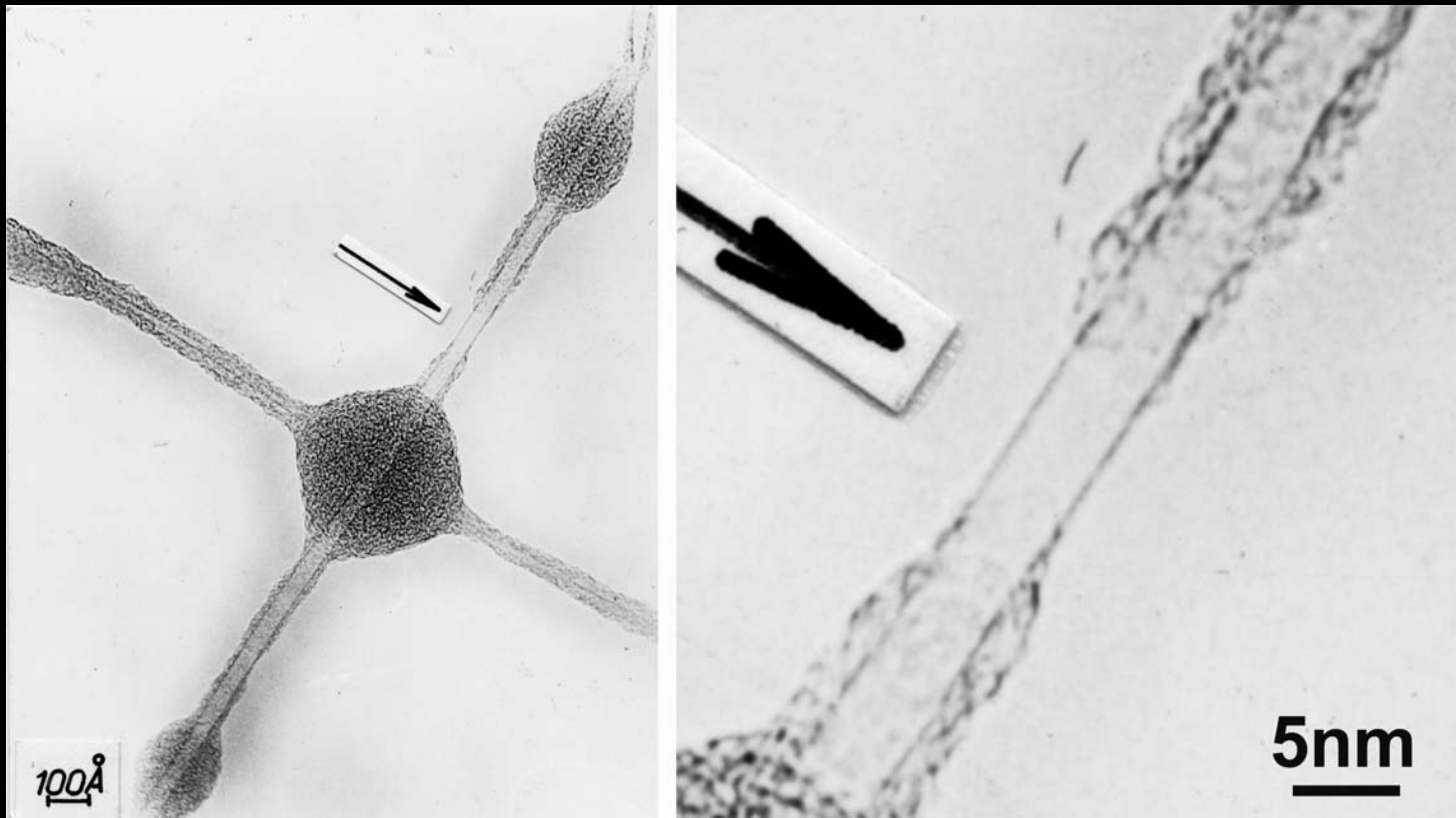
Creating a Nanotube "T" Junction



M. Terrones, F. Banhart, N. Grobert, J. C. Charlier, H. Terrones, P.M. Ajayan.

Physical Review Letters 89, 07505 (2002)

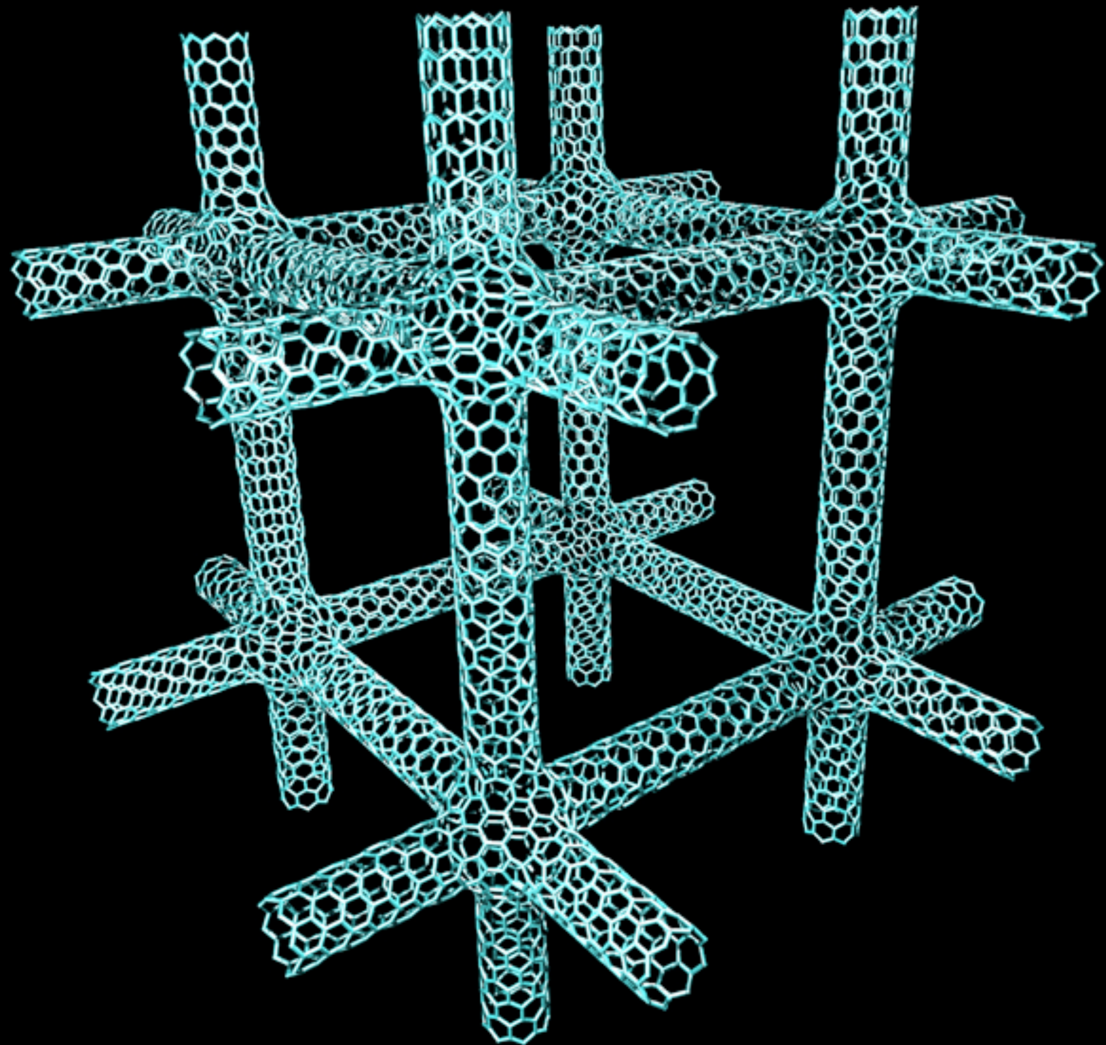
The First SWNT device



Oberlin, A., Endo, M., Koyama, T.

J. Cryst. Growth 32, 335-349 (1976)

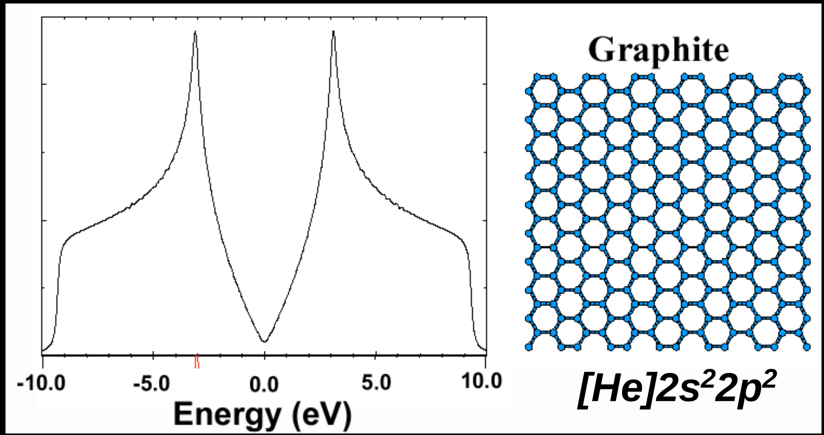
Building 3D Nanotube Networks



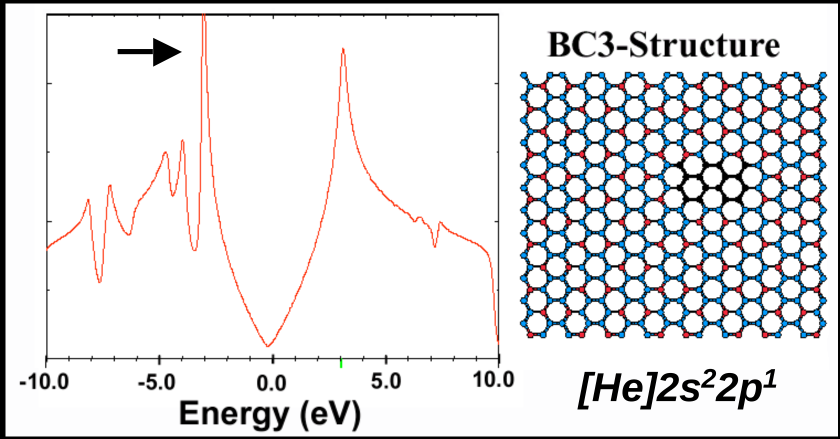
More Defects in Carbon Nanotubes

4. IMPURITIES AND DOPING!!

Changing Electronic Properties by doping



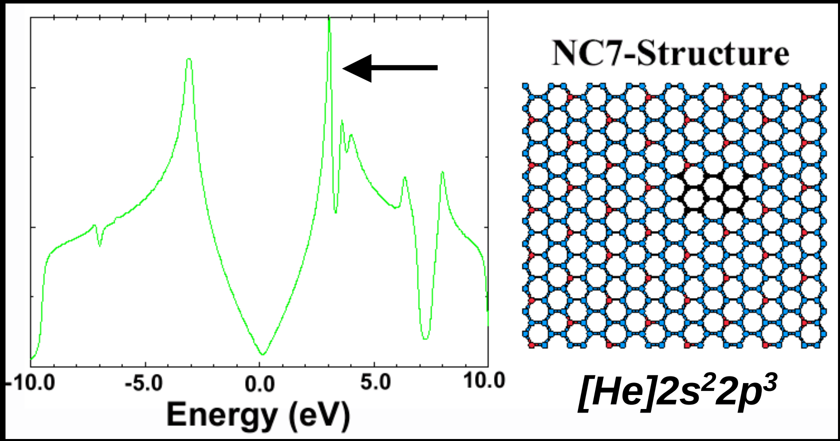
Semi-metal
(symmetric LDOS)



New features in the valence band

B atoms behave as acceptors in the graphene sheet

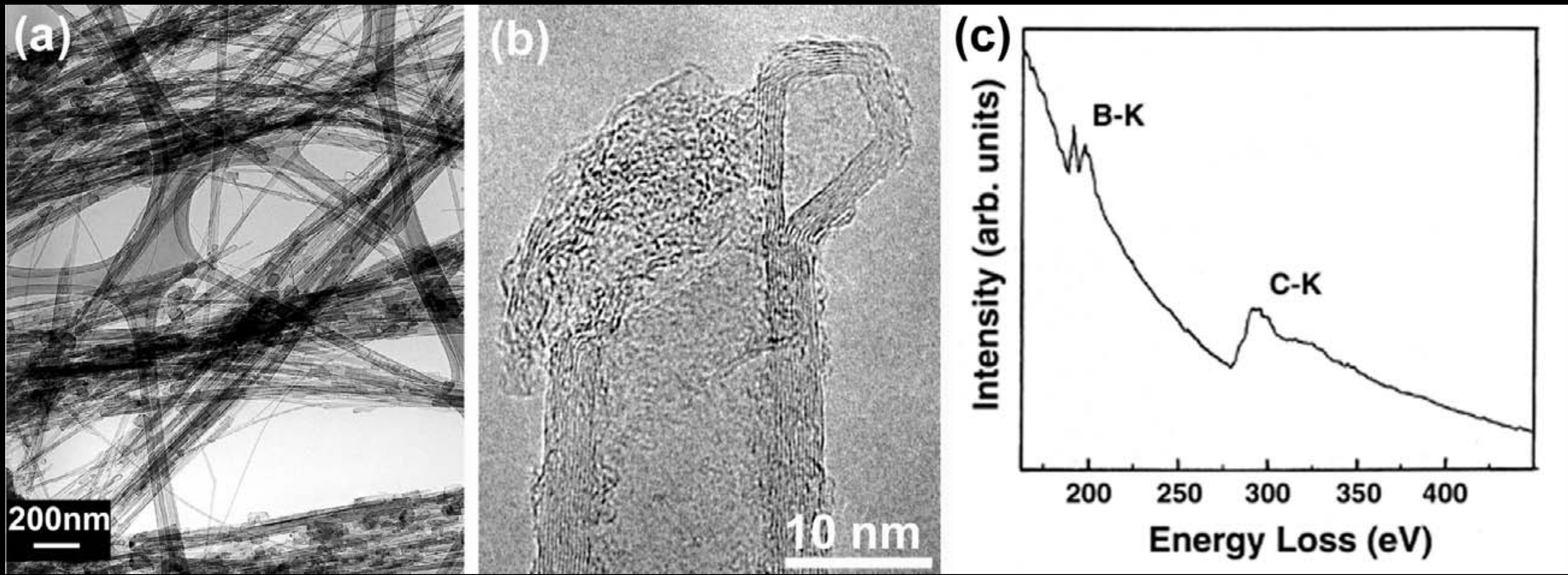
N atoms behave as donors in the graphene sheet



New features in the conduction band

Boron Doped Carbon Nanotubes

B-doped Carbon Nanotubes



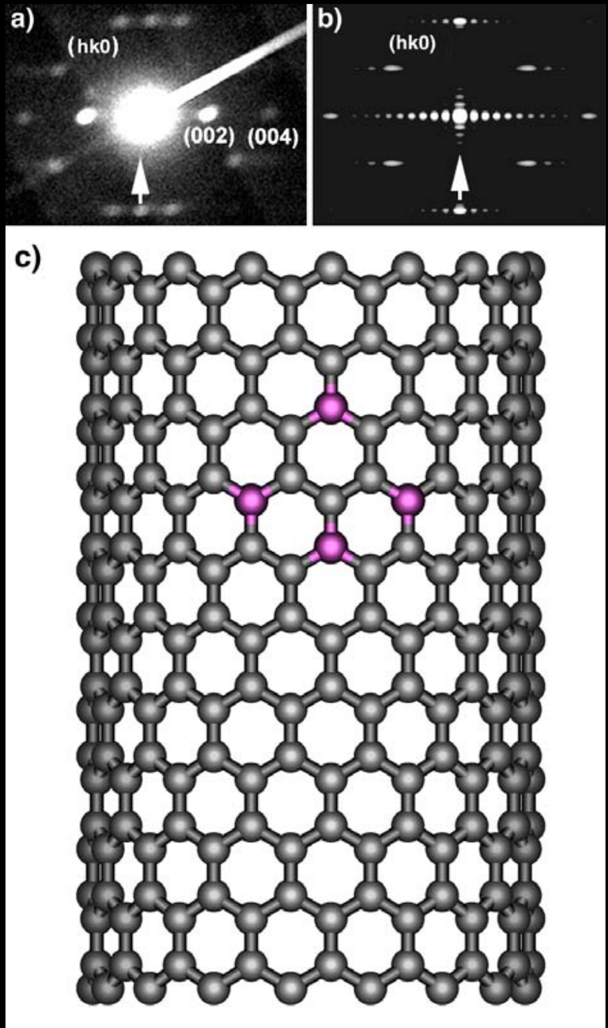
Long tubes
< 200 nm

Amorphous Tips

EELS spectrum of a
Nanotube tip

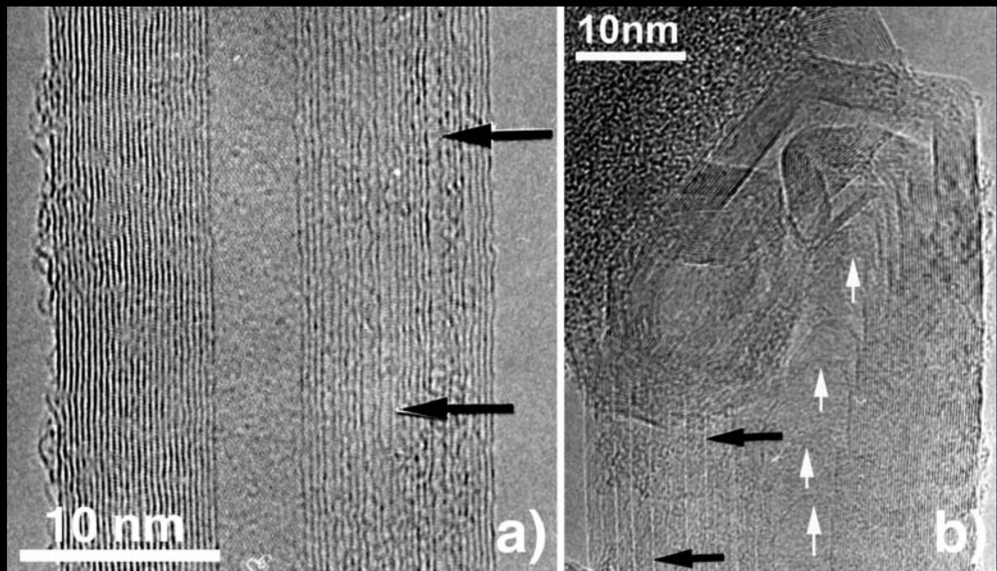
M. Terrones, et al. Full Sci & Tech 6, 787-800 (1998)
J.-C. Charlier, et al. Nanoletters 2, 1191 (2002)

Zig-zag chirality in B-doped Carbon Nanotubes

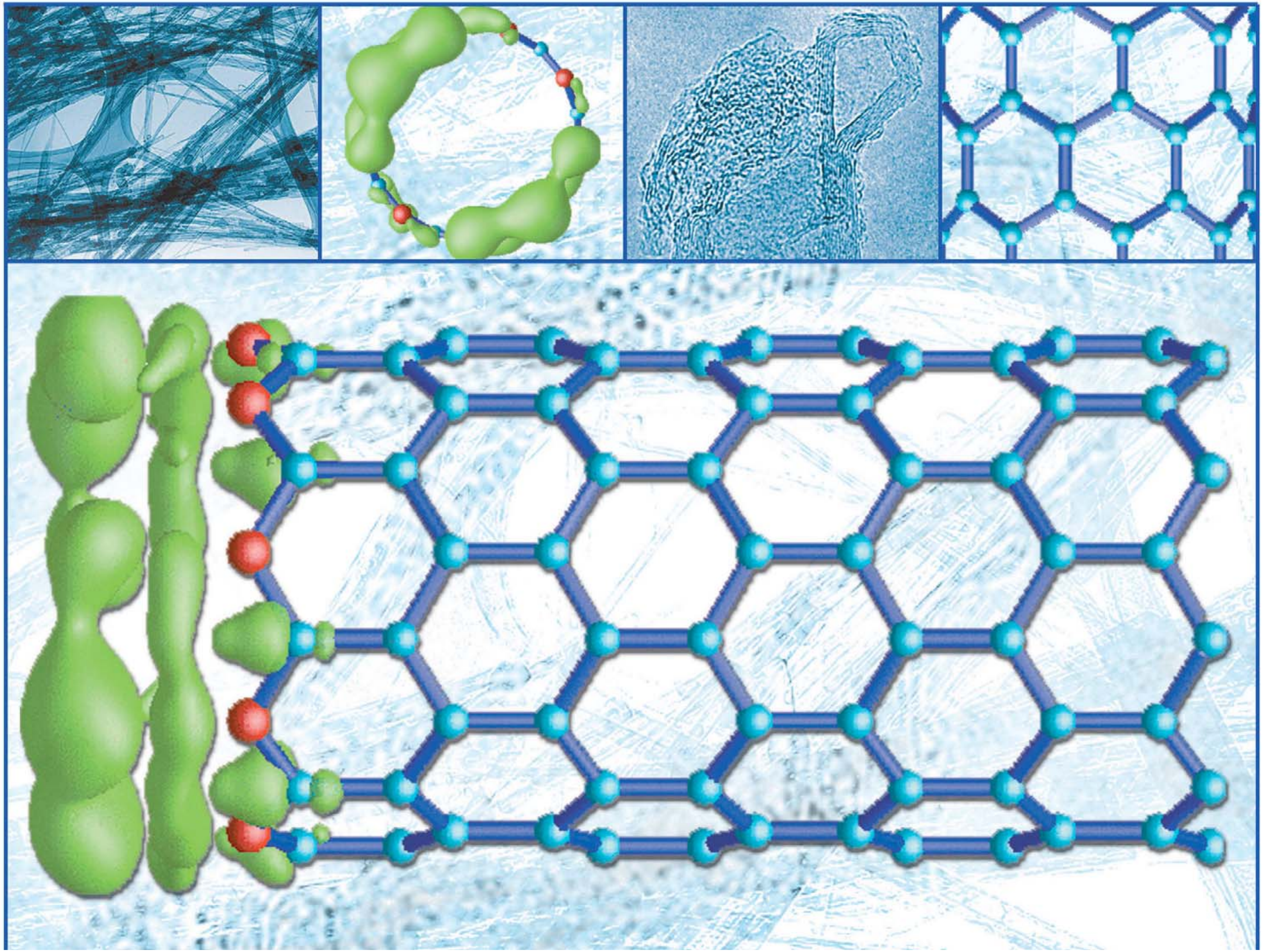


Electron diffraction patterns show that the majority of the tubes exhibit zigzag chirality

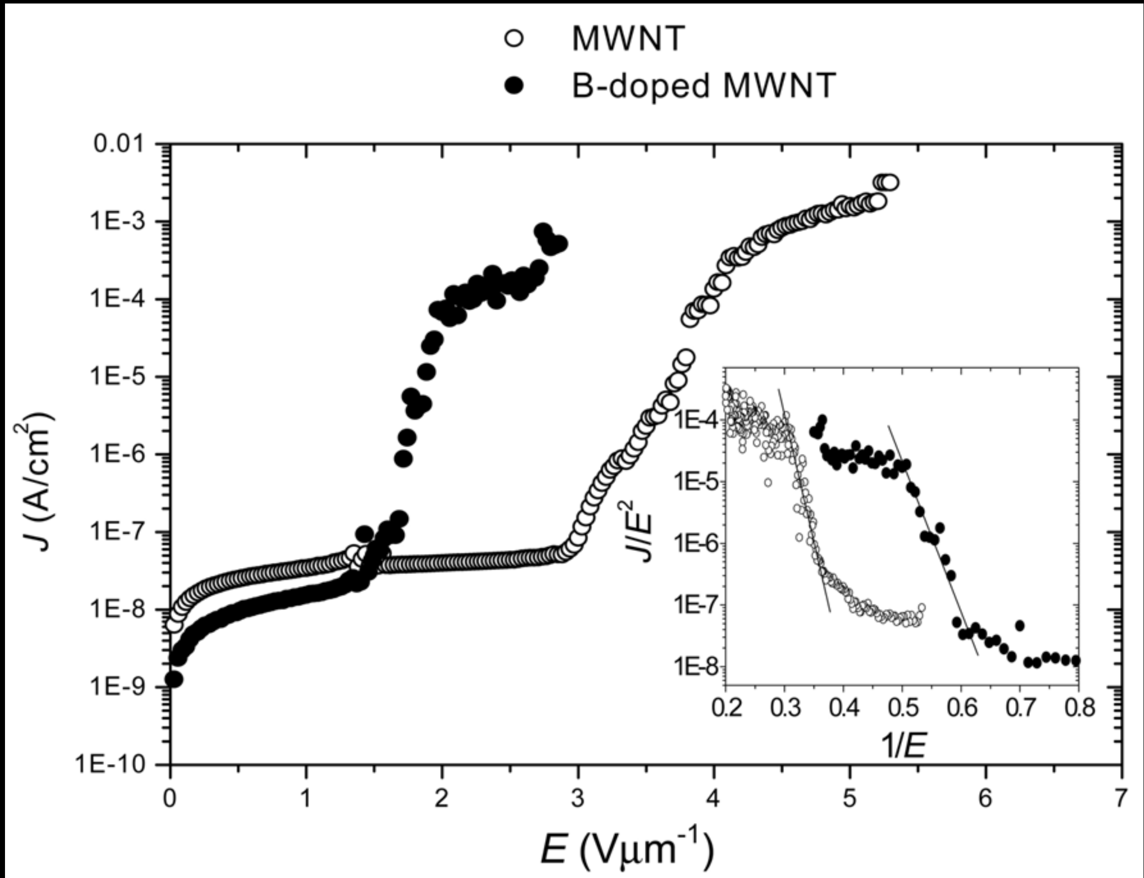
The tubes contain more than 10-20 layers and are polygonazied



X. Blase, et al. Phys. Rev. Lett. 83,5078-5081 (1999)
M. Terrones, et al. Carbon 40, 1665 (2002)

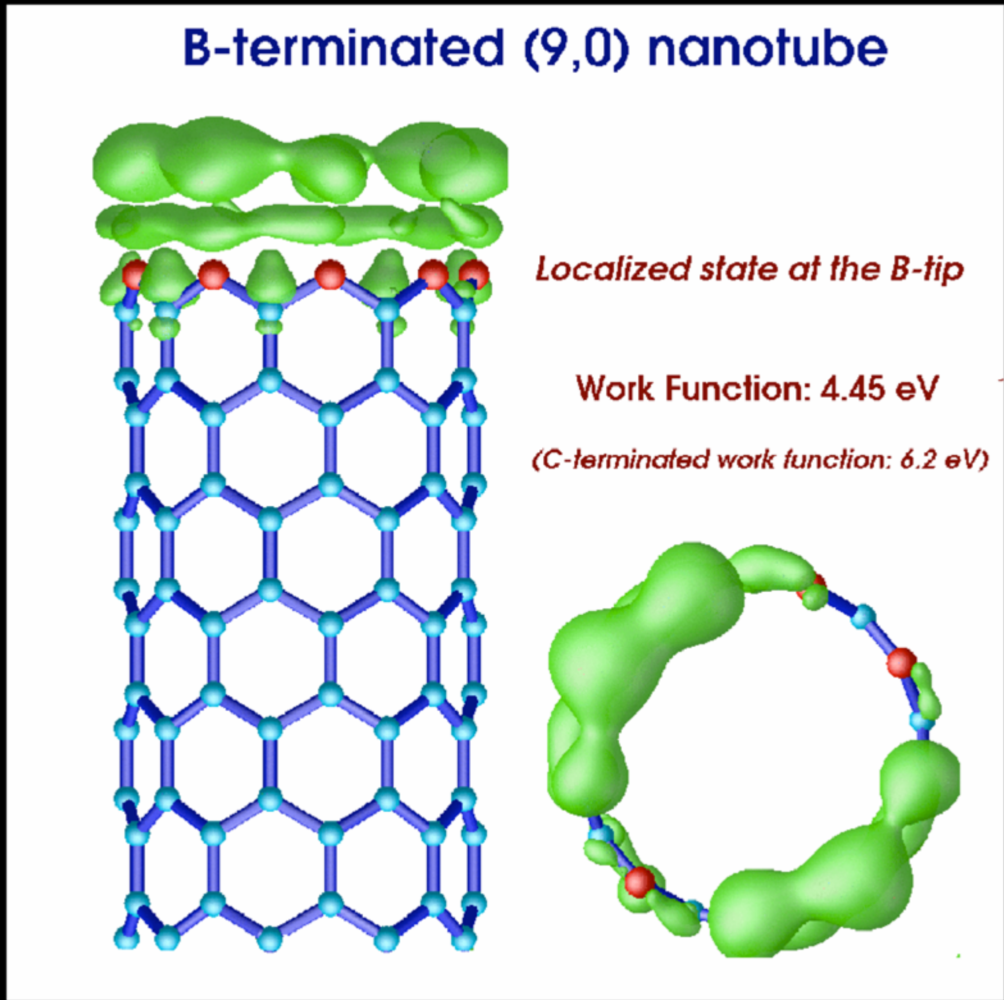


Enhanced Field Emission in B-doped Carbon Nanotubes



J.-C. Charlier, et al. Nanoletters 2, 1191 (2002)

Open B-doped Carbon Nanotubes



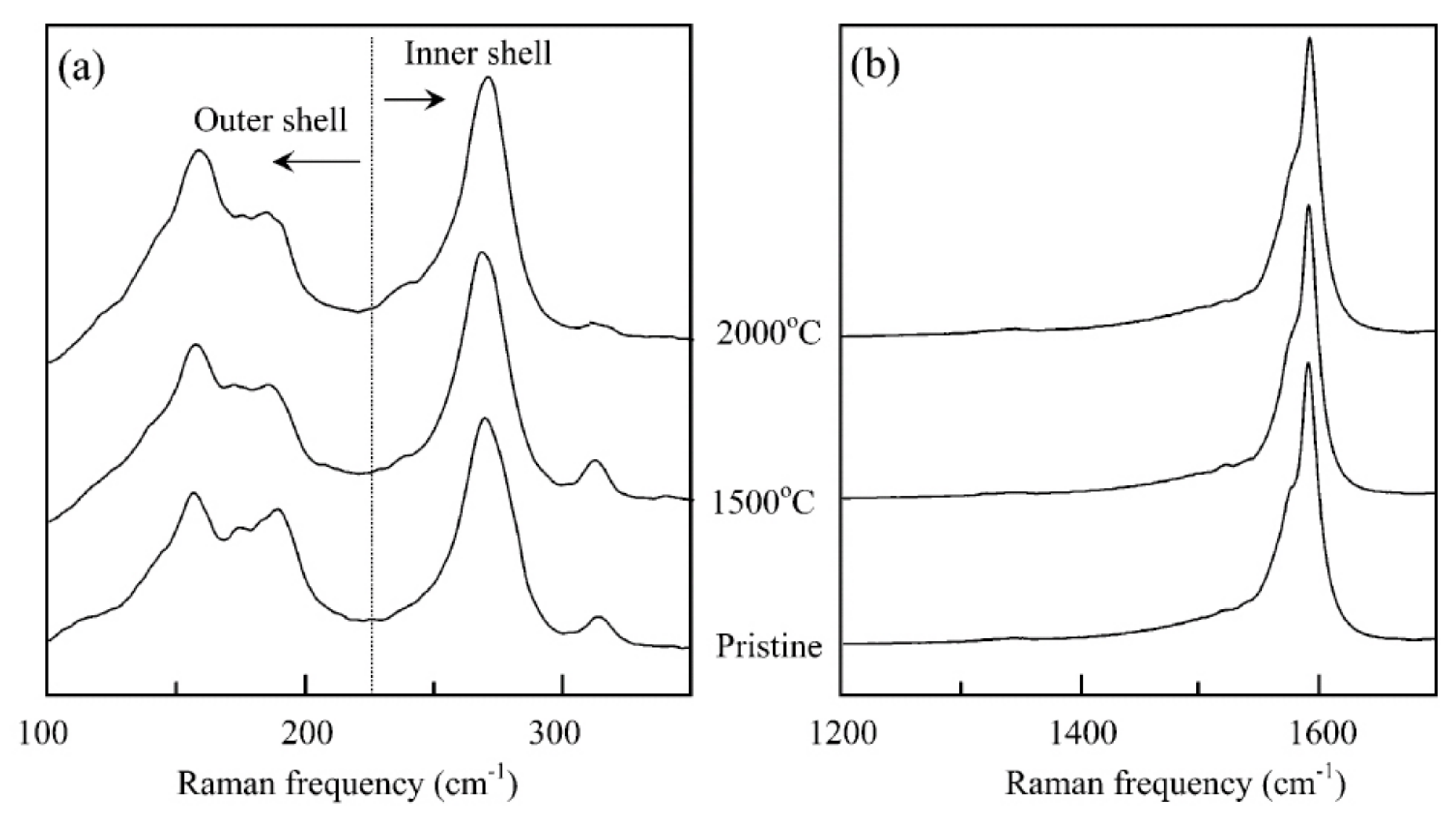
J.-C. Charlier, V. Menieur, et al. Nanoletters 2, 1191-1195 (2002)

Boron as Atomic Welder

Connecting DWNTs

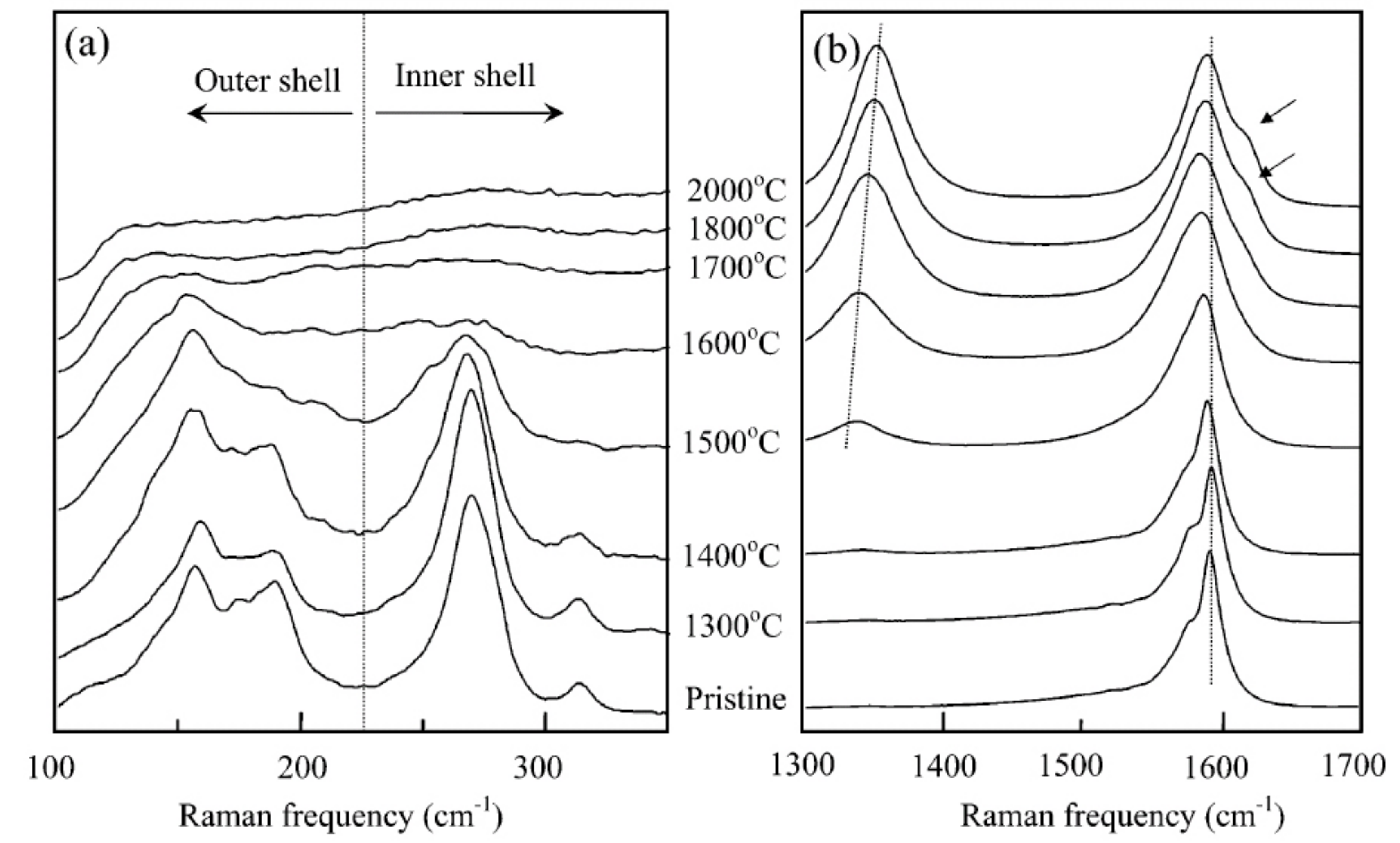
By Thermal Annealing

Connecting Nanotubes: No Boron addition



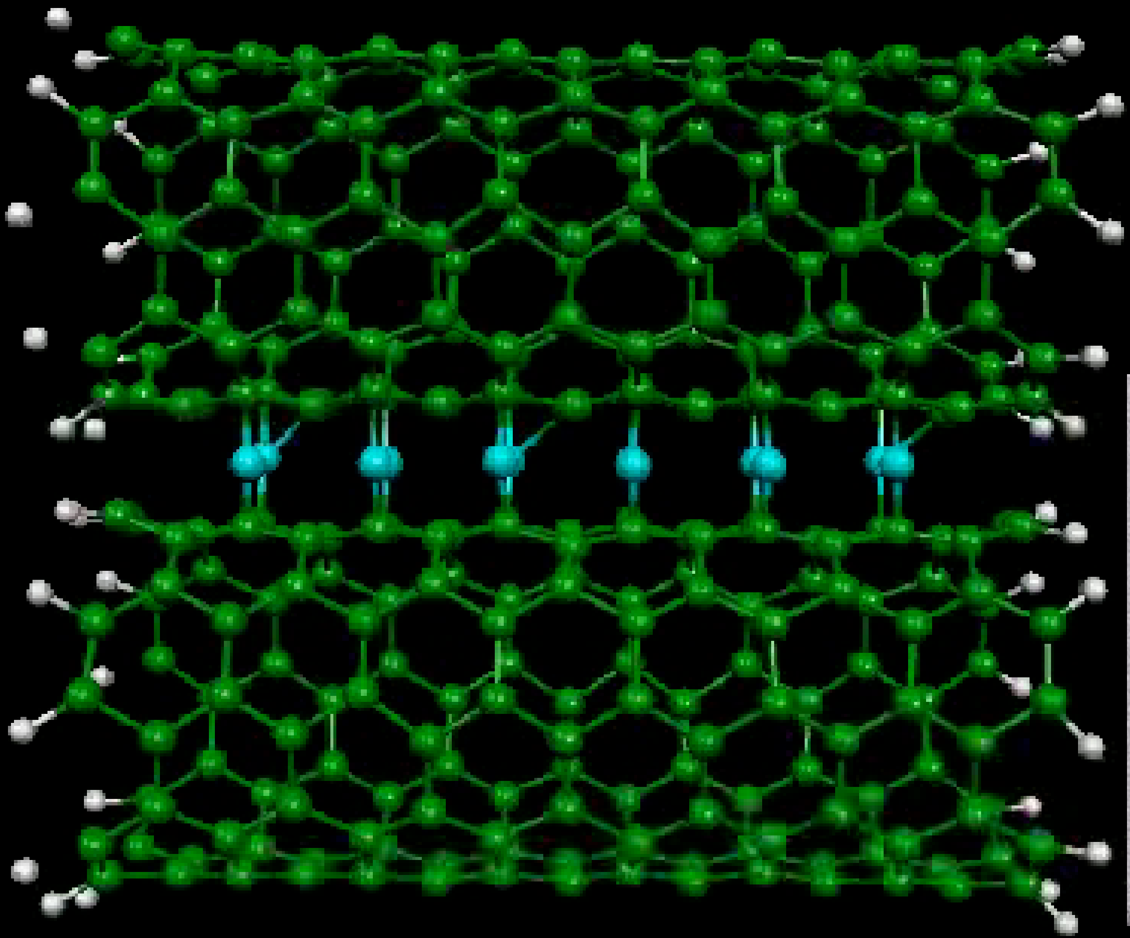
M. Endo, H. Muramatsu, T. Hayahsi, Y.A. Kim, G. Van Lier, J.-C. Charlier, H. Terrones, M. Terrones, M.S. Dresselhaus. Nano Letters 5, 1099 (2005)

Connecting Nanotubes: Using B as an Atomic Welder

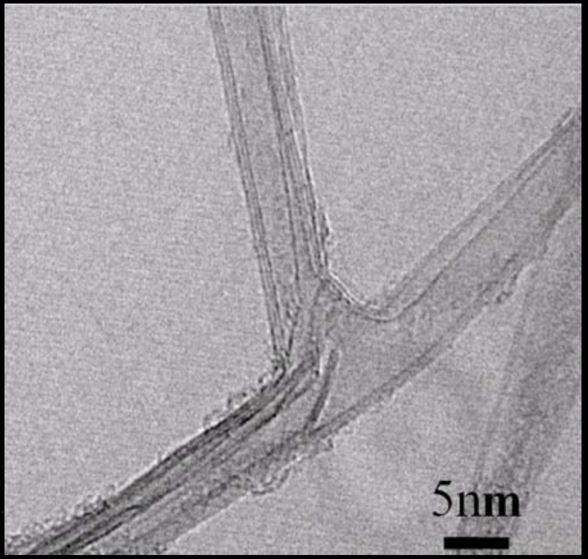


M. Endo, H. Muramatsu, T. Hayahsi, Y.A. Kim, G. Van Lier, J.-C. Charlier, H. Terrones, M. Terrones, M.S. Dresselhaus. Nano Letters 5, 1099 (2005)

Connecting Nanotubes: Using B as an Atomic Welder



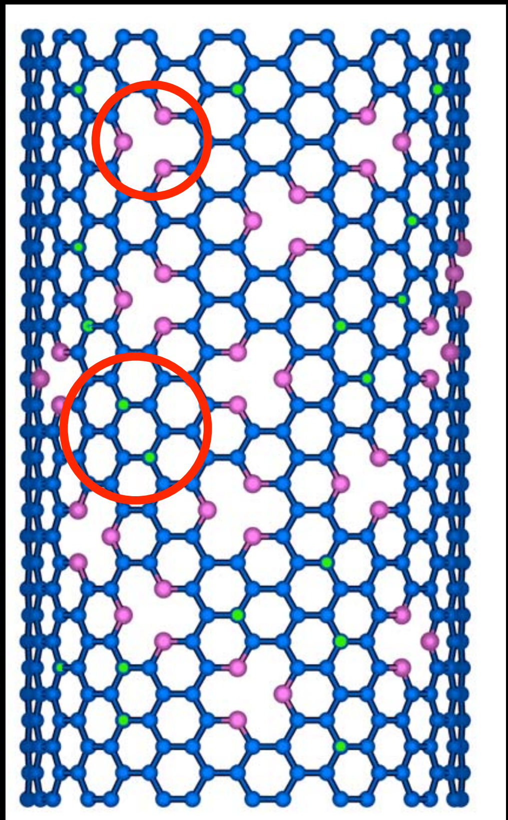
First Principles Molecular Dynamics Simulations 2500 ºC



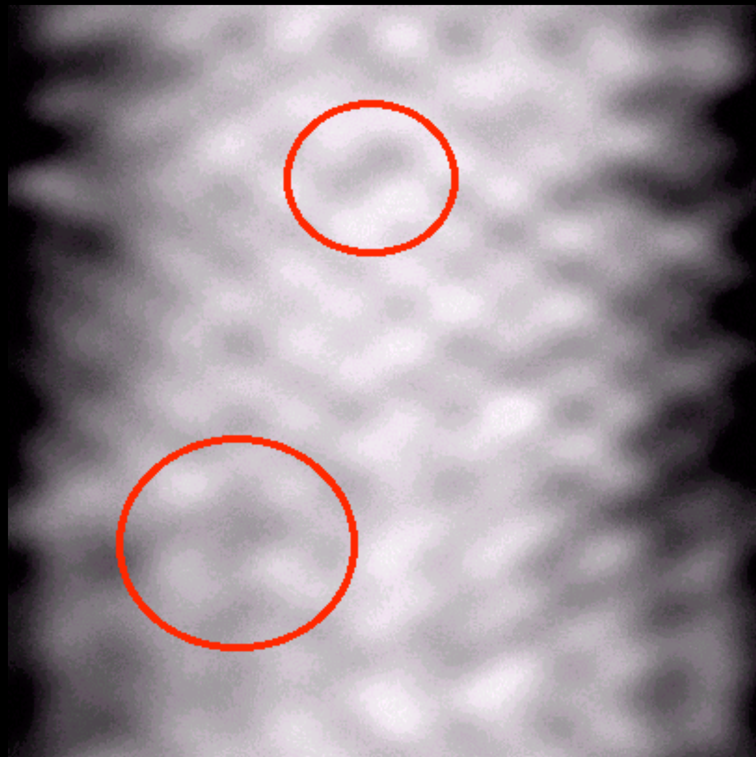
M. Endo, H. Muramatsu, T. Hayahsi, Y.A. Kim, G. Van Lier, J.-C. Charlier, H. Terrones, M. Terrones, M.S. Dresselhaus. Nano Letters 5, 1099 (2005)

Nitrogen Doped Carbon Nanotubes

Structure of MW-CN_x Nanotubes



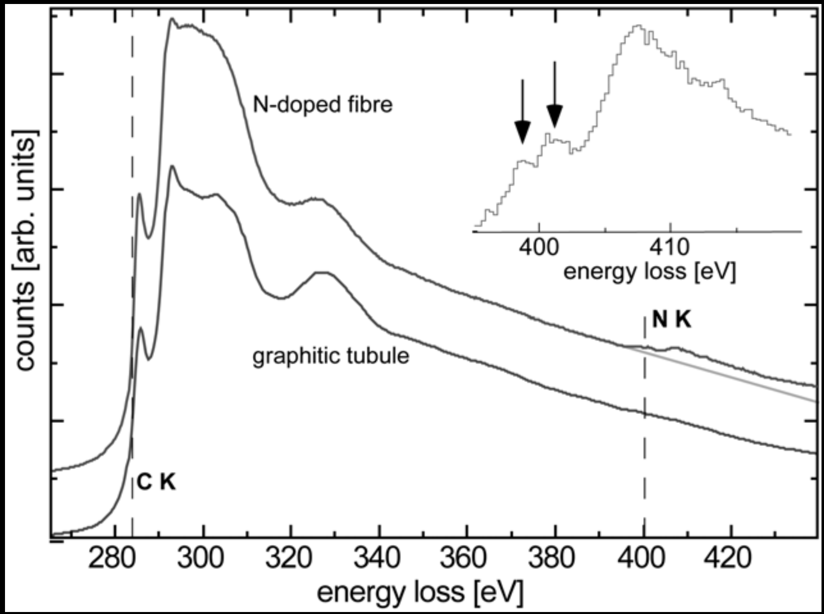
CN_x nanotube containing pyridine-like and highly coordinated N atoms replacing C atoms



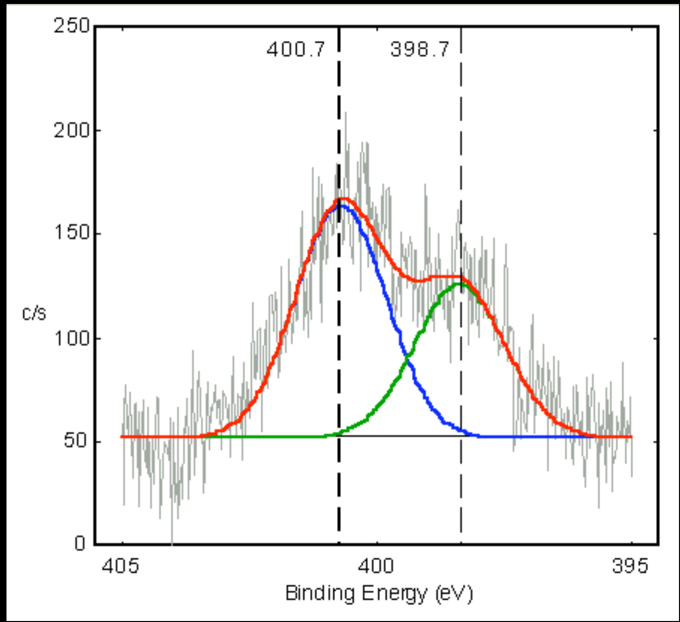
STM image of the surface of a 20 nm nanotube with distortions and holes (circled), possibly due to the presence of pyridine-like islands (holes)

R. Czerw, et al. Nanoletters 1, 457-460 (2001)

EELS and XPS spectra from CN_x nanotubes



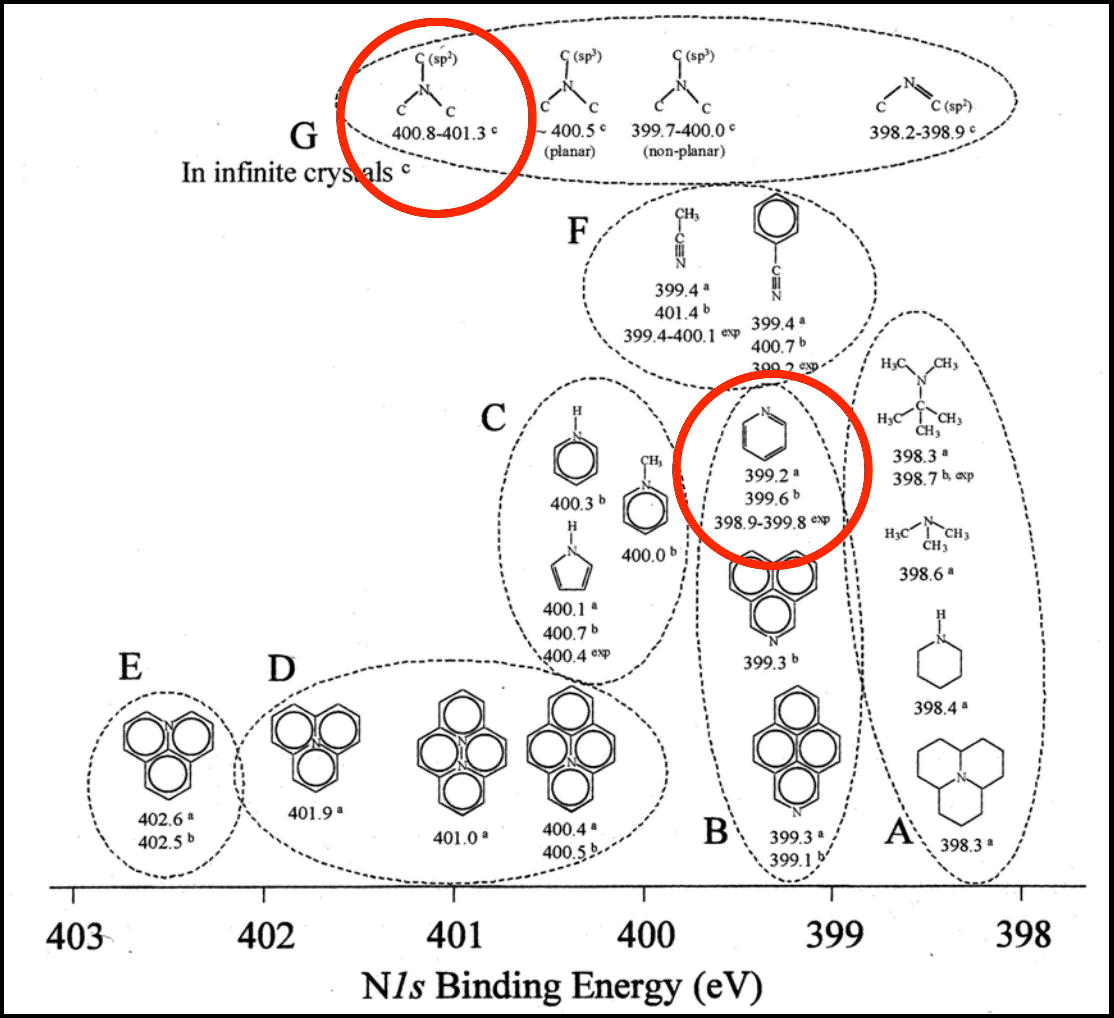
EELS spectra of a C_xN_y nanotube, showing C and N edges. Inset exhibits a splitting in the p of the N K-shell due to two different types of bonds*



N1s signal form the XPS spectrum of CN_x nanofibers revealing two peaks at ca. 398.7 eV and 400.9 eV

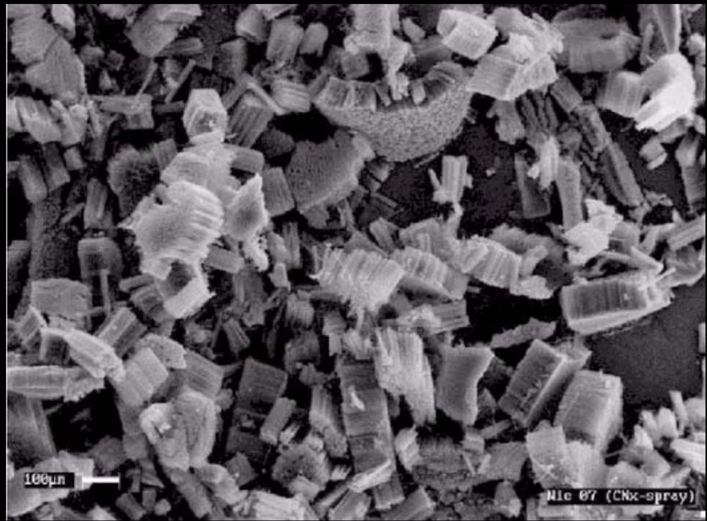
M. Terrones, et al, Applied Physics Letters 75, 3932-3934 (1999)
M. Terrones, et al. Advanced Materials 11, 655-658 (1999)

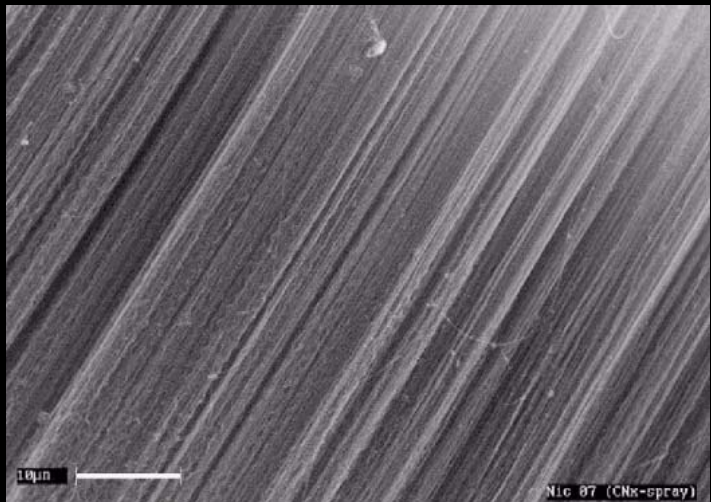
Calculated N1s binding energies for various CN_x structures

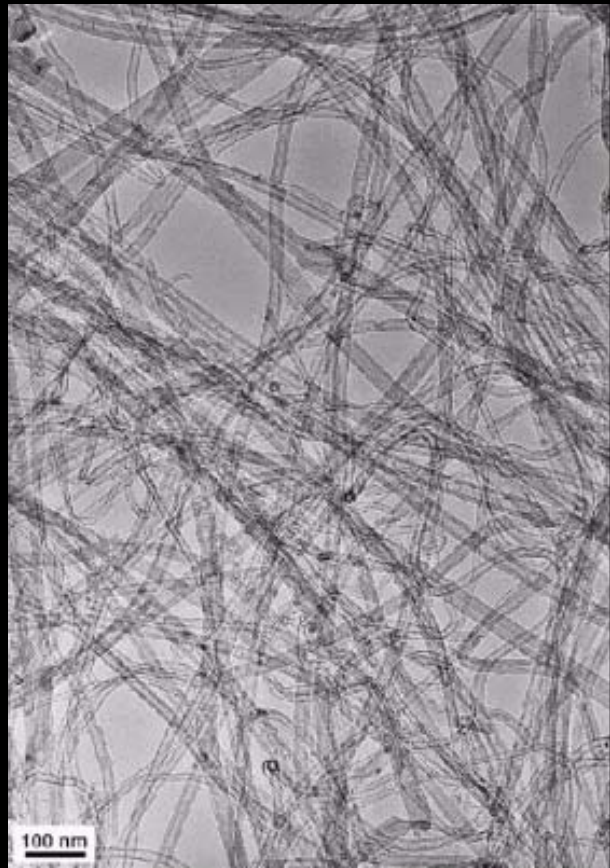


N. Hellgren, PhD. Thesis 1999 (Sweden)

Production of MW-CNx Nanotubes







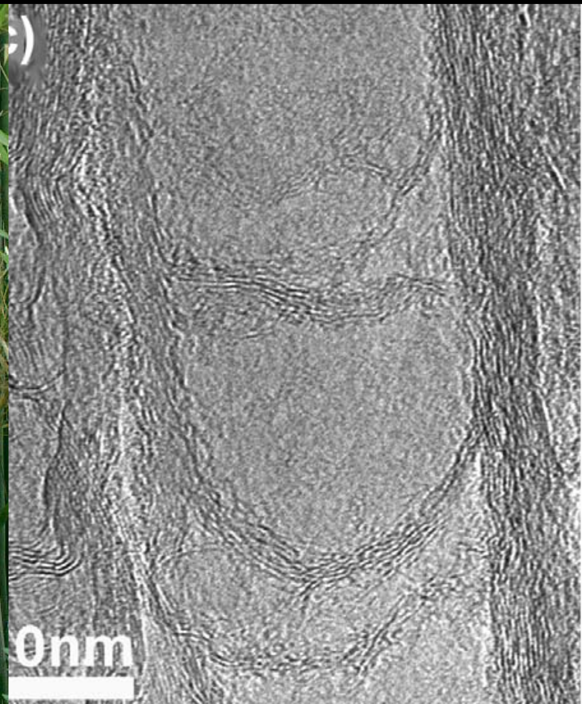
Aligned Nanotubes

N. Grobert, et al. Chemical Communications 5, 471-472 (2001)
M. Mayne, et al. Chemical Physics Letters 338, 101-107 (2001)
M. Terrones, et al. Nature 388, 52-55 (1997)

N-doped MWNTs: Bamboo-shape

Bundle of Aligned Nanotubes

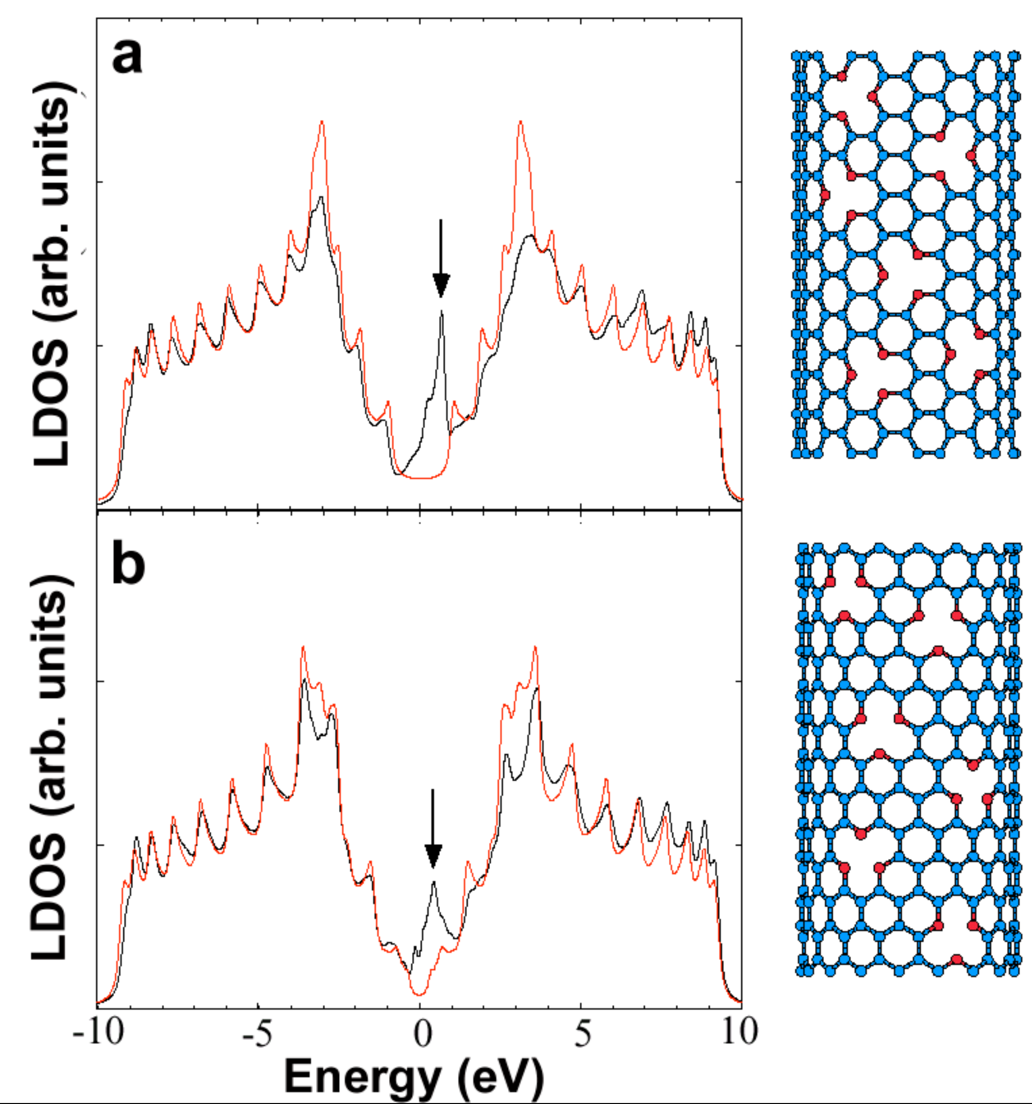
Bundle of Bamboo Trees



HRTEM image of an individual N-doped carbon nanotube

M. Terrones, et al, Applied Physics Letters 75, 3932-3934 (1999)

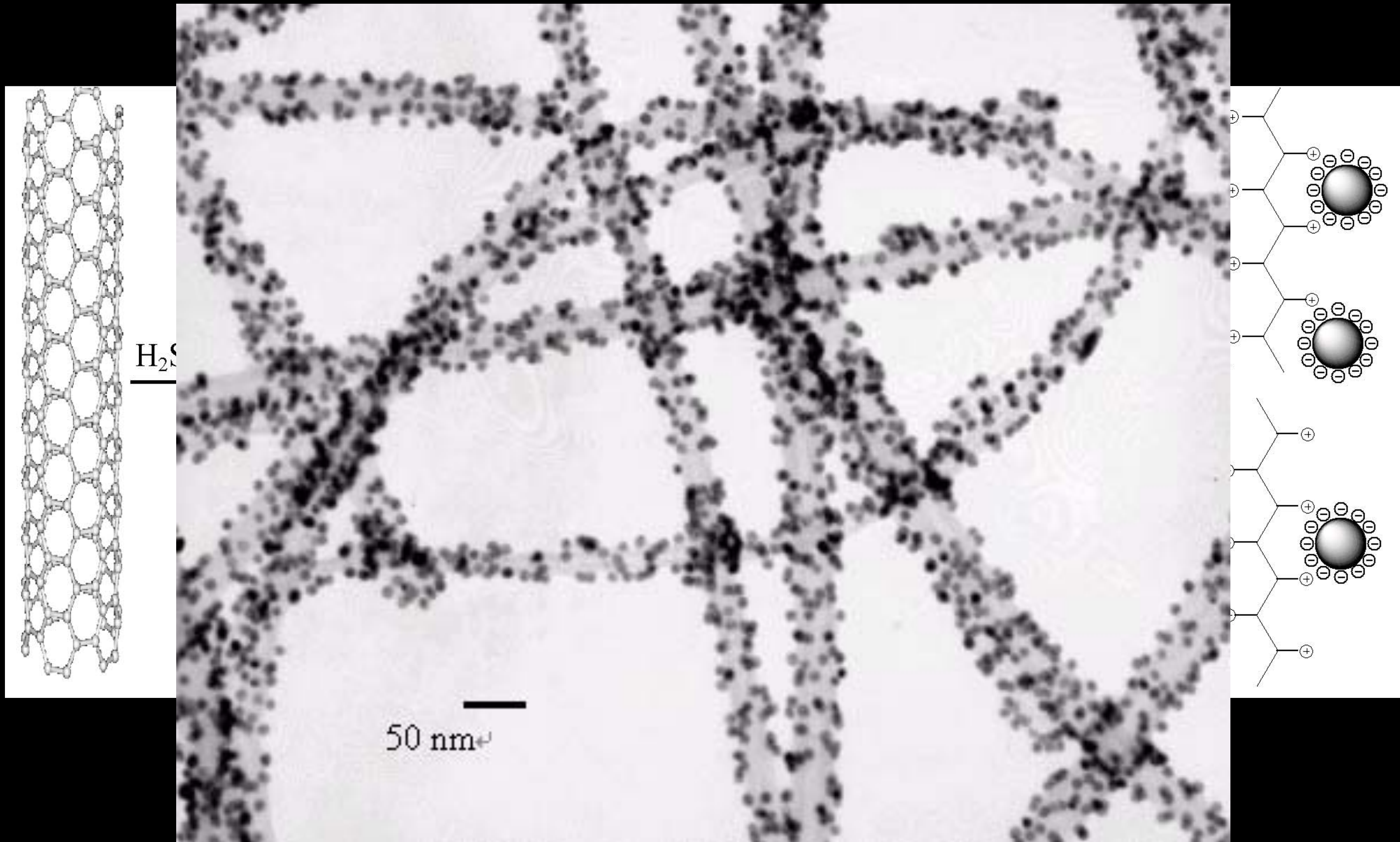
DOS of a CN_x nanotube



Theoretical LDOS associated with a Pyridine-like structure with N-doping carbon nanotubes displaying (a) armchair (10,10) and (b) zigzag (17,0) configurations. In both cases, N atoms were placed randomly (N: red spheres – C: blue spheres; right hand images).

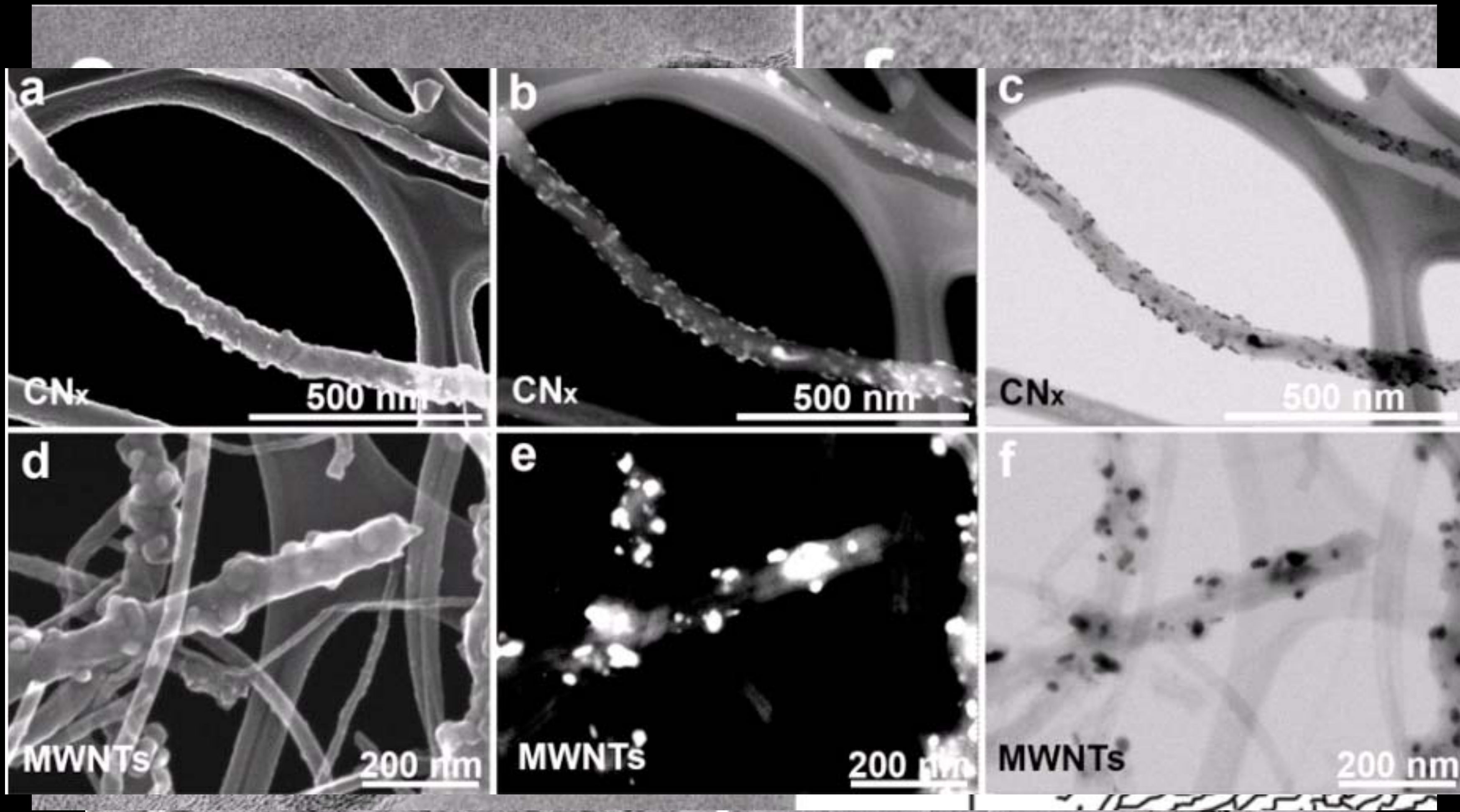
R. Czerw, et al. Nanoletters 1, 457-460 (2001)

Applications of CN_x Nanotubes



K. Jiang, et al. Nanoletters 3, 275 (2003)

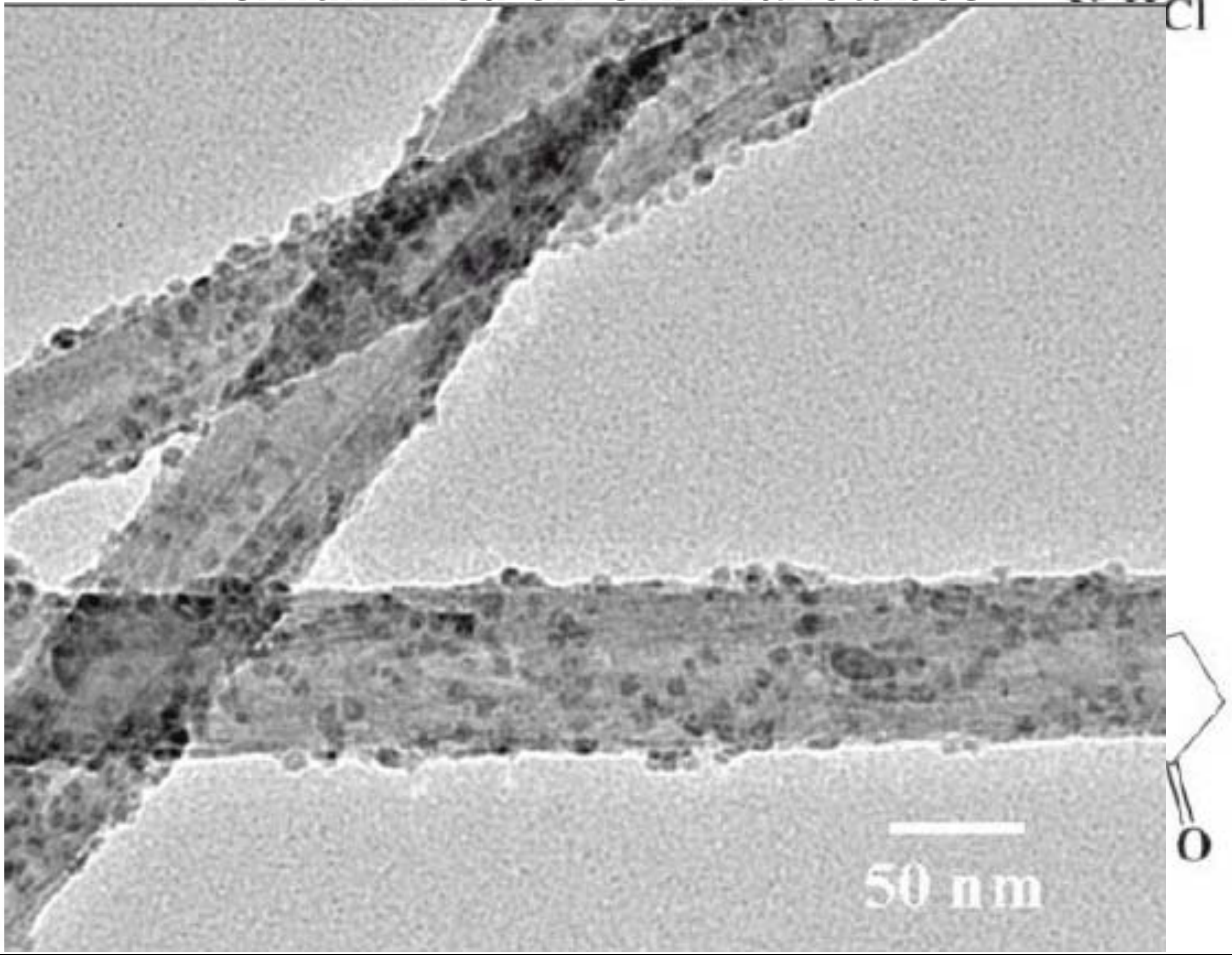
Anchorage of Ag particles on CNx NTs



A. Zamudio, et al. Small 2 (2005) 346-350

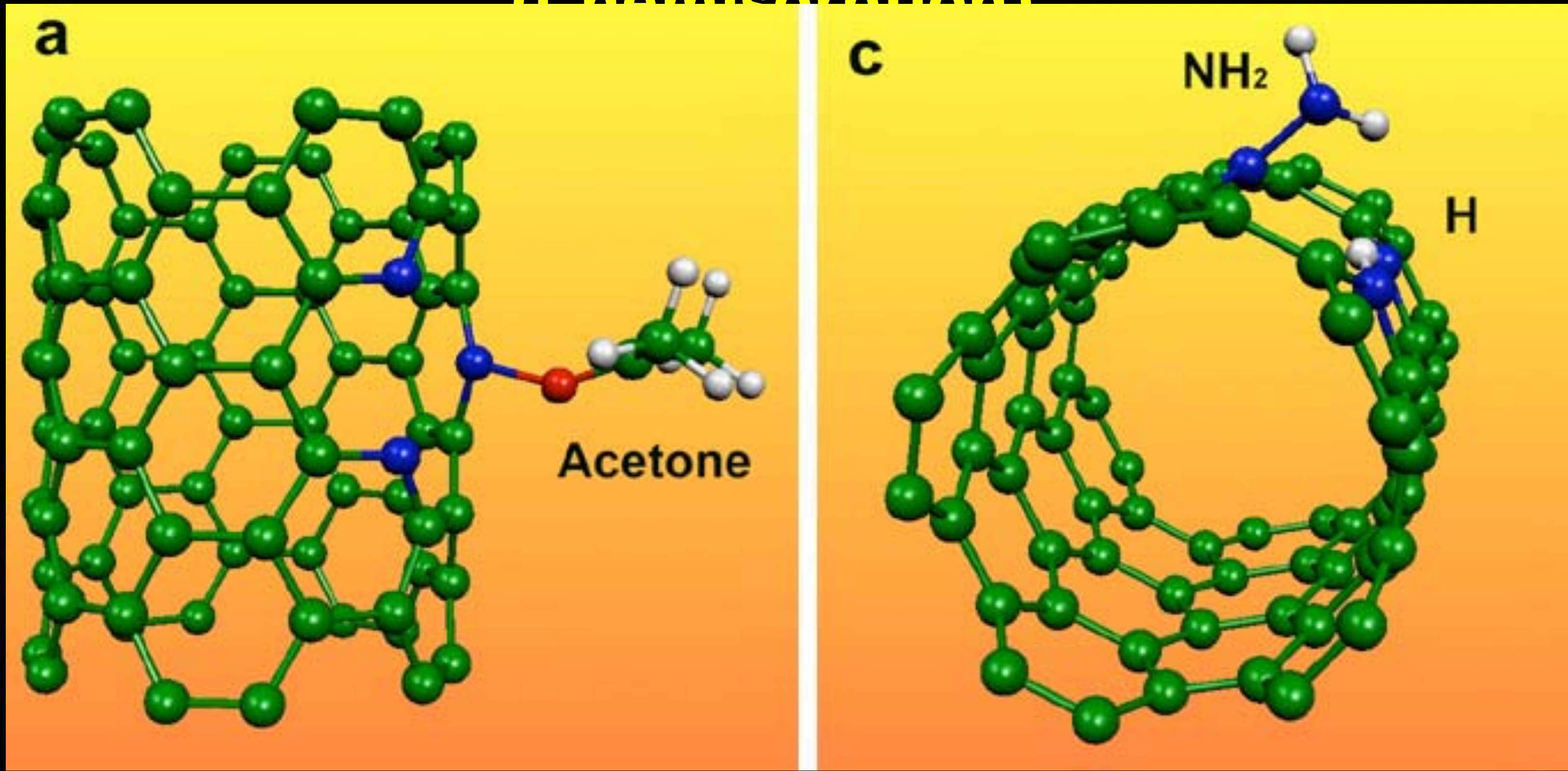
CNx NTs as protein immobilizers

Ferritin fixed on CNx Nanotubes



K. Jiang, L.S. Schadler, R.W. Siegel, X.Zhang, H. Zhang, M. Terrones
J. Mater. Chem. 14, 37 (2004)

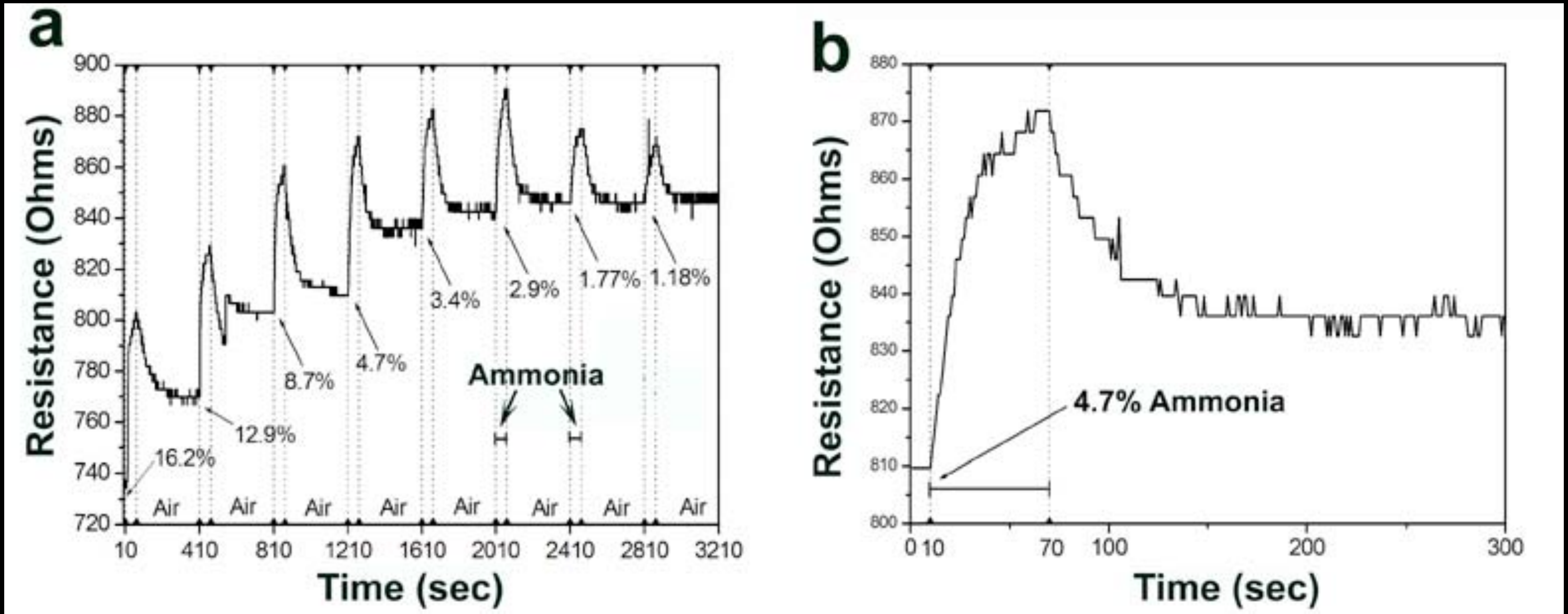
Ab-initio calculations confirm the high reactivity of pyridinic sites to various molecules (Chemisorption)



Molecular Models showing the reactivity of pyridine-like sites

F. Villalpando-Paez, A.H. Romero, E. Munoz-Sandoval, L.M. Martinez, H. Terrones and M. Terrones, Chemical Physics Letters, in press (2004)

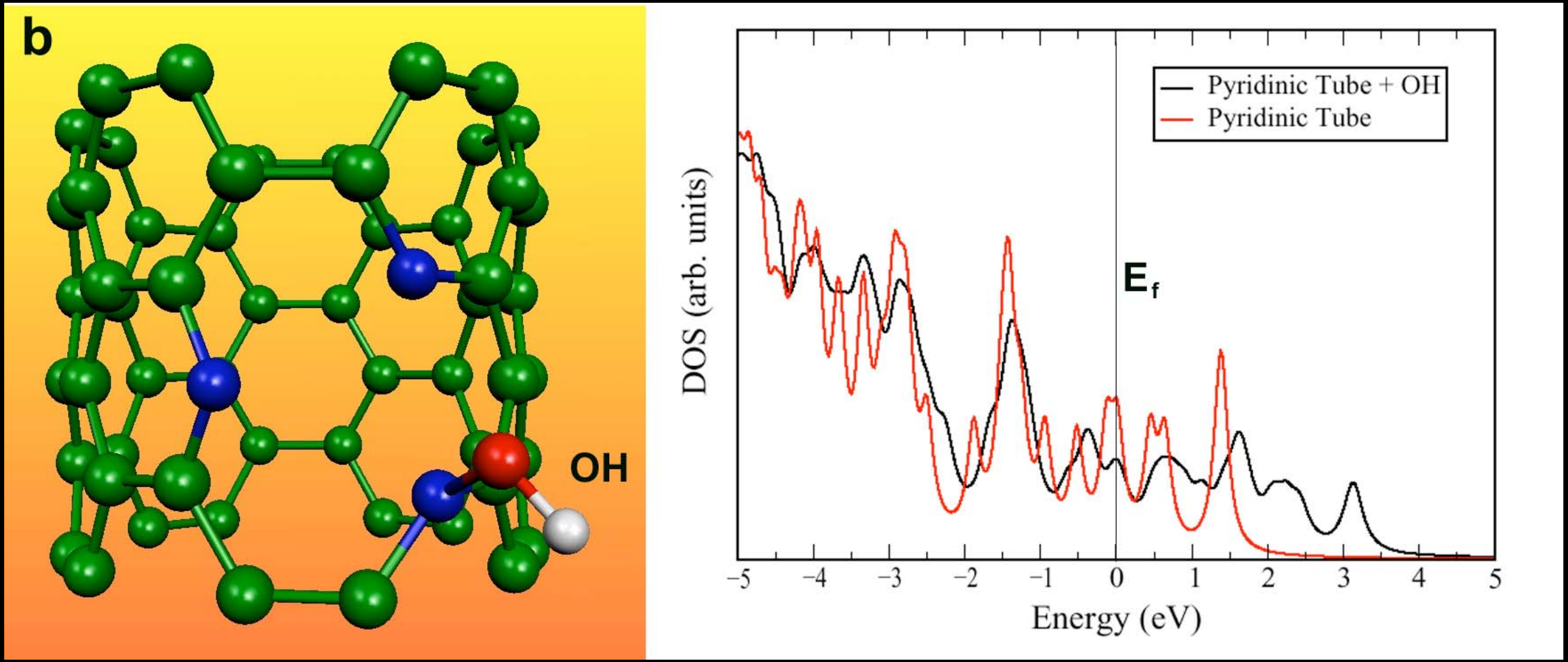
CN_x NT Sensors also exhibit fast responses For toxic and reactive gases



Plots indicating the response for Ammonia using different concentrations

F. Villalpando-Paez, A.H. Romero, E. Munoz-Sandoval, L.M. Martinez, H. Terrones and M. Terrones, Chemical Physics Letters, in press (2004)

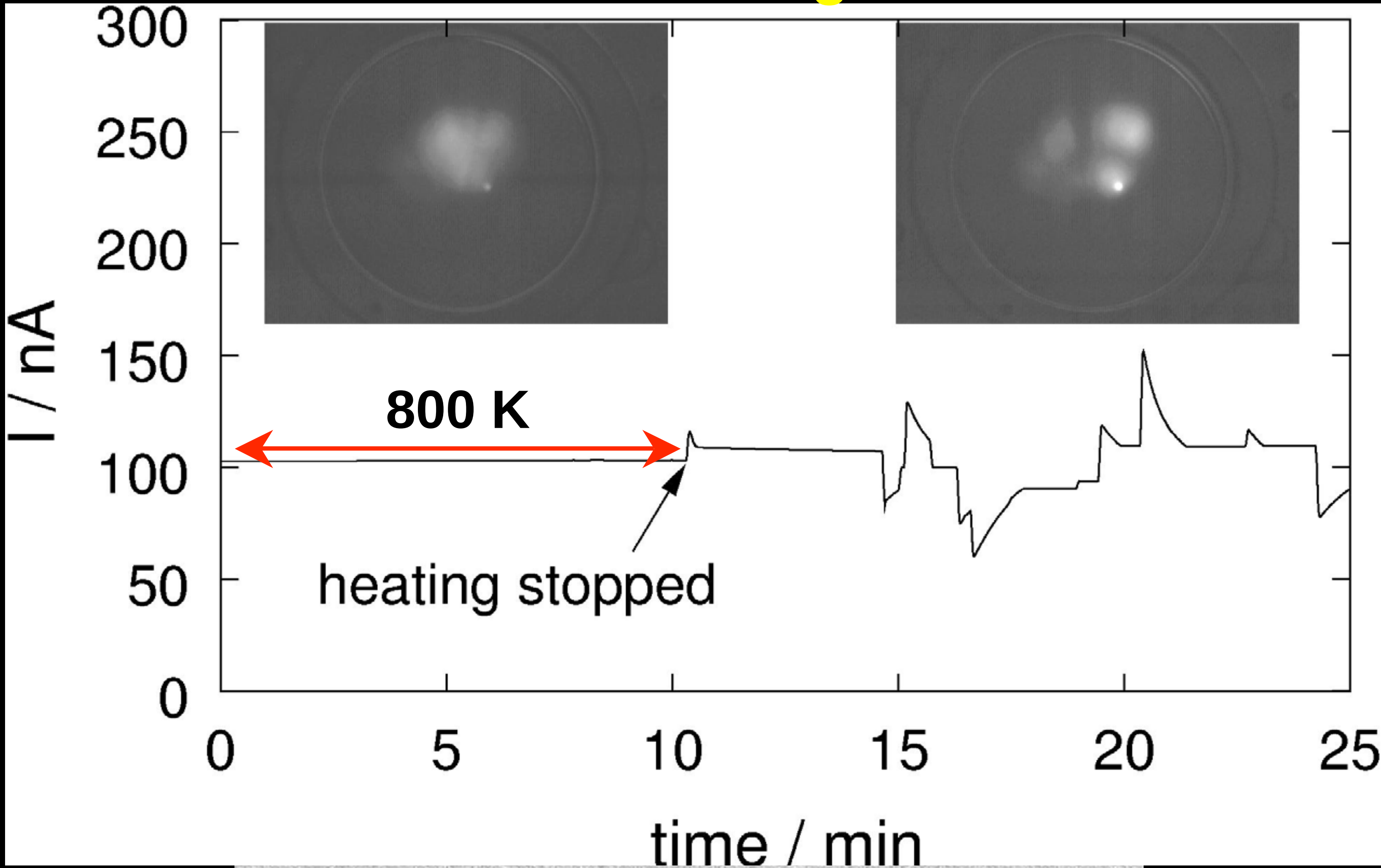
Due to the reactivity of the pyridine-like sites with molecules, the electronic properties change



Molecular Models showing the reactivity of pyridine-like sites and the corresponding DOS, shwing that the OH molecules decrease the number of states at the Ef, thus producing lower conductances along the tube

F. Villalpando-Paez, A.H. Romero, E. Munoz-Sandoval, L.M. Martinez, H. Terrones and M. Terrones, Chemical Physics Letters, in press (2004)

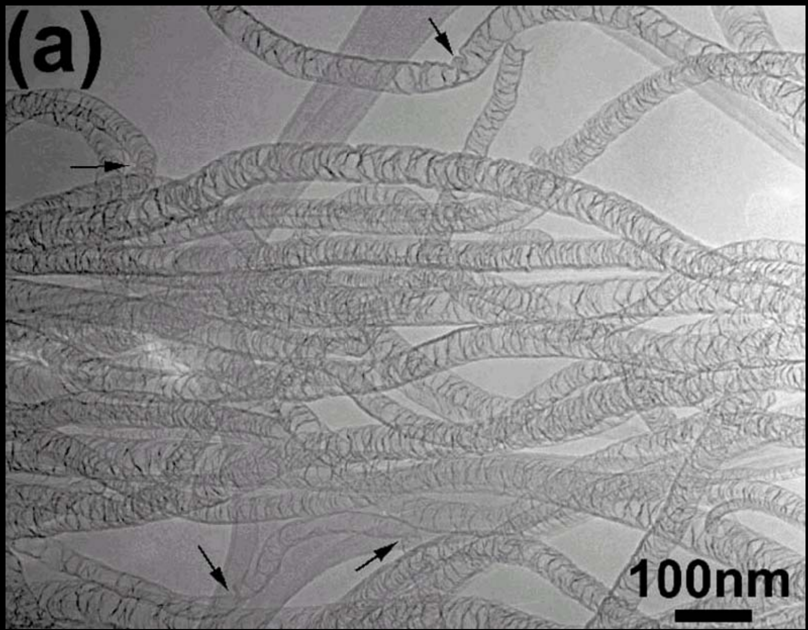
Field Emission from a single CN_x Nanotube



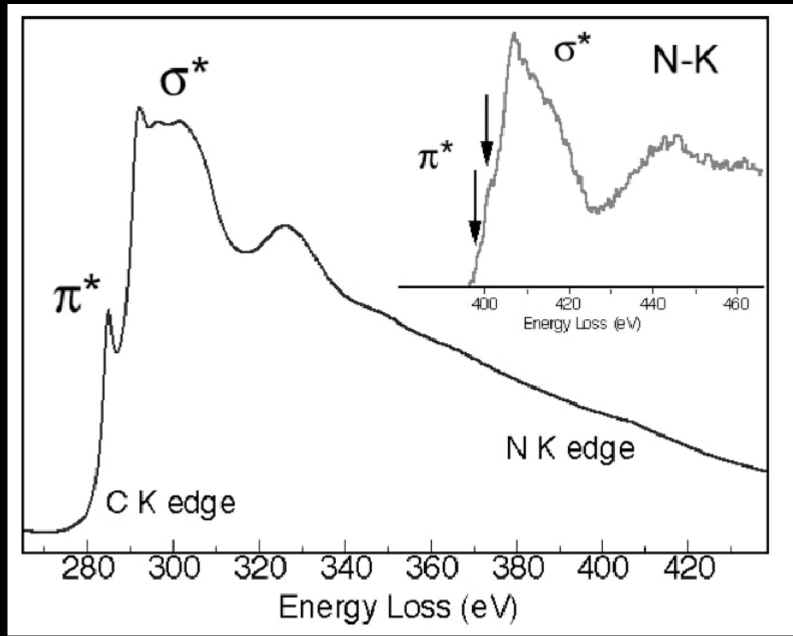
Maya Doytcheva, Niels de Jonge, Monja Kaiser, Marisol Reyes-Reyes, Mauricio Terrones Chemical Physics Letters 396, 126 (2004)

Epoxy Composites using CN_x Nanotubes

CNx Nanotubes Composites: Medium concentration of pyrydene sites (2-5%)



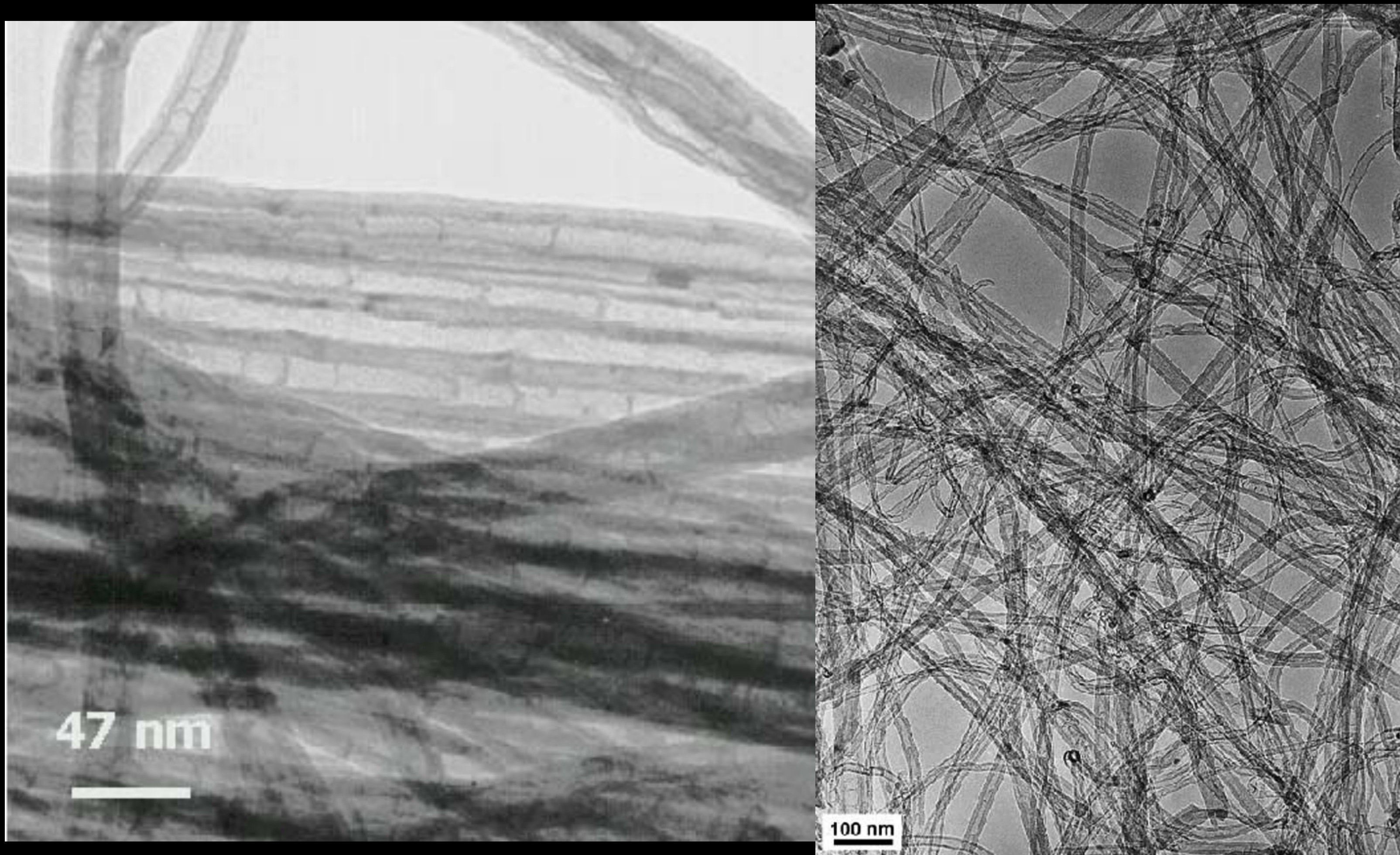
TEM image showing the mechanical stability of CN_x nanotubes



EL spectra of CN_x nanotubes containing less proportion of pyrydene-liked sites

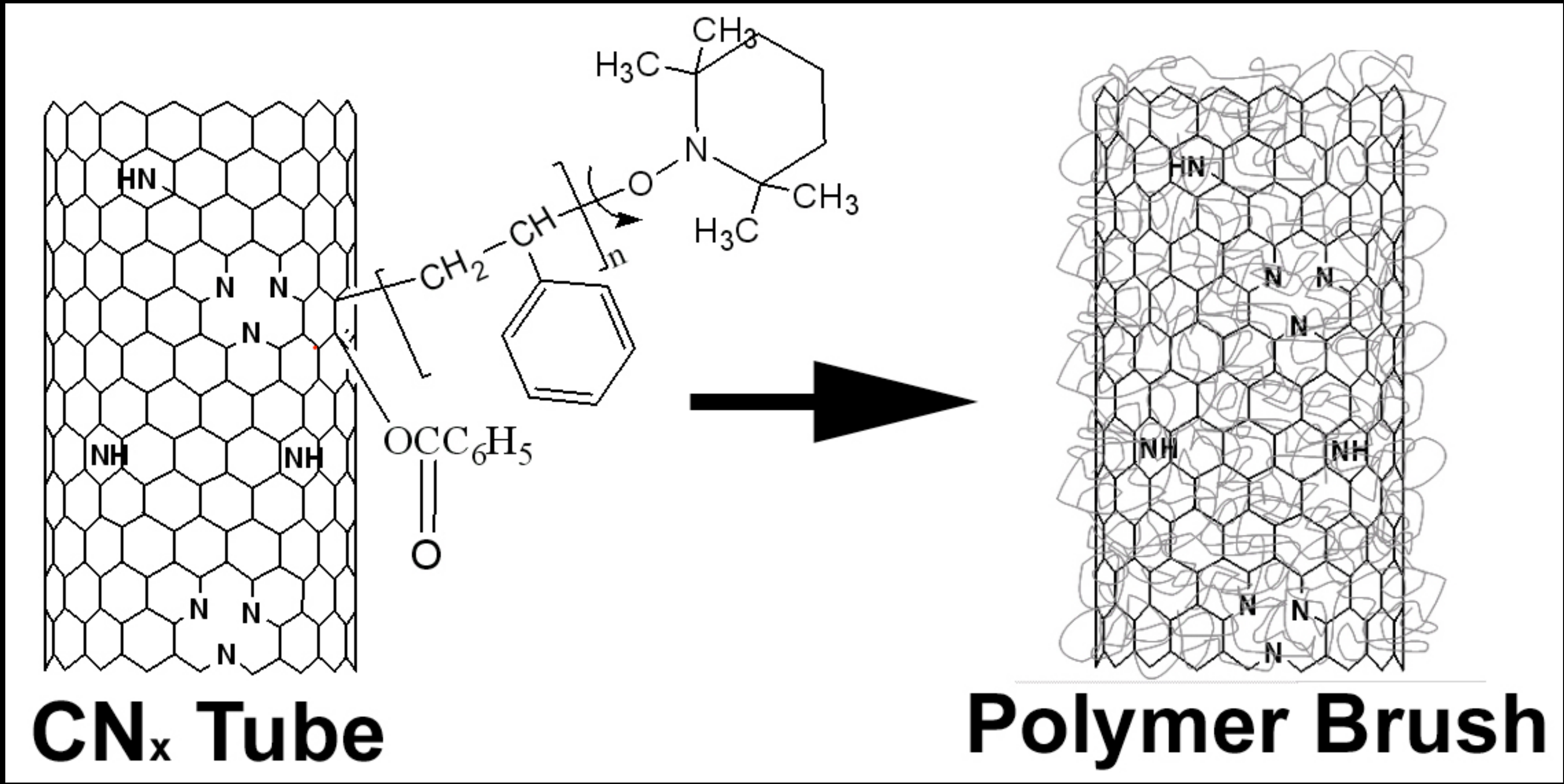
TEM image shows a medium degree of corrugation of CN_x nanotubes

CNx Nanotubes Composites: Low concentration of pyrydene sites (<2%)



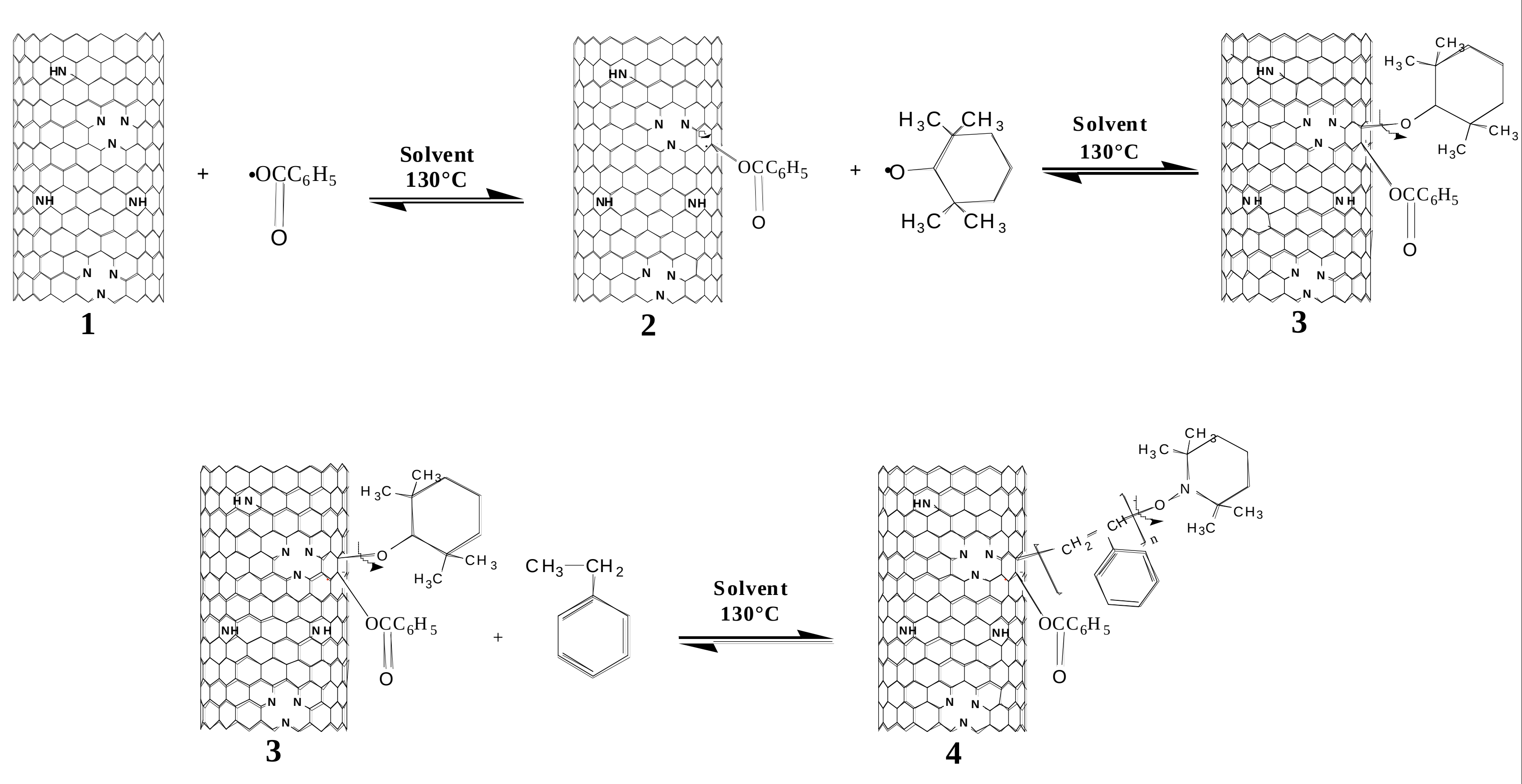
TEM images showing low degree of corrugation of CN_x nanotubes

Polystyrene covalently grafted to CNx Nanotubes via Nitroxide Mediated Radical Polymerization



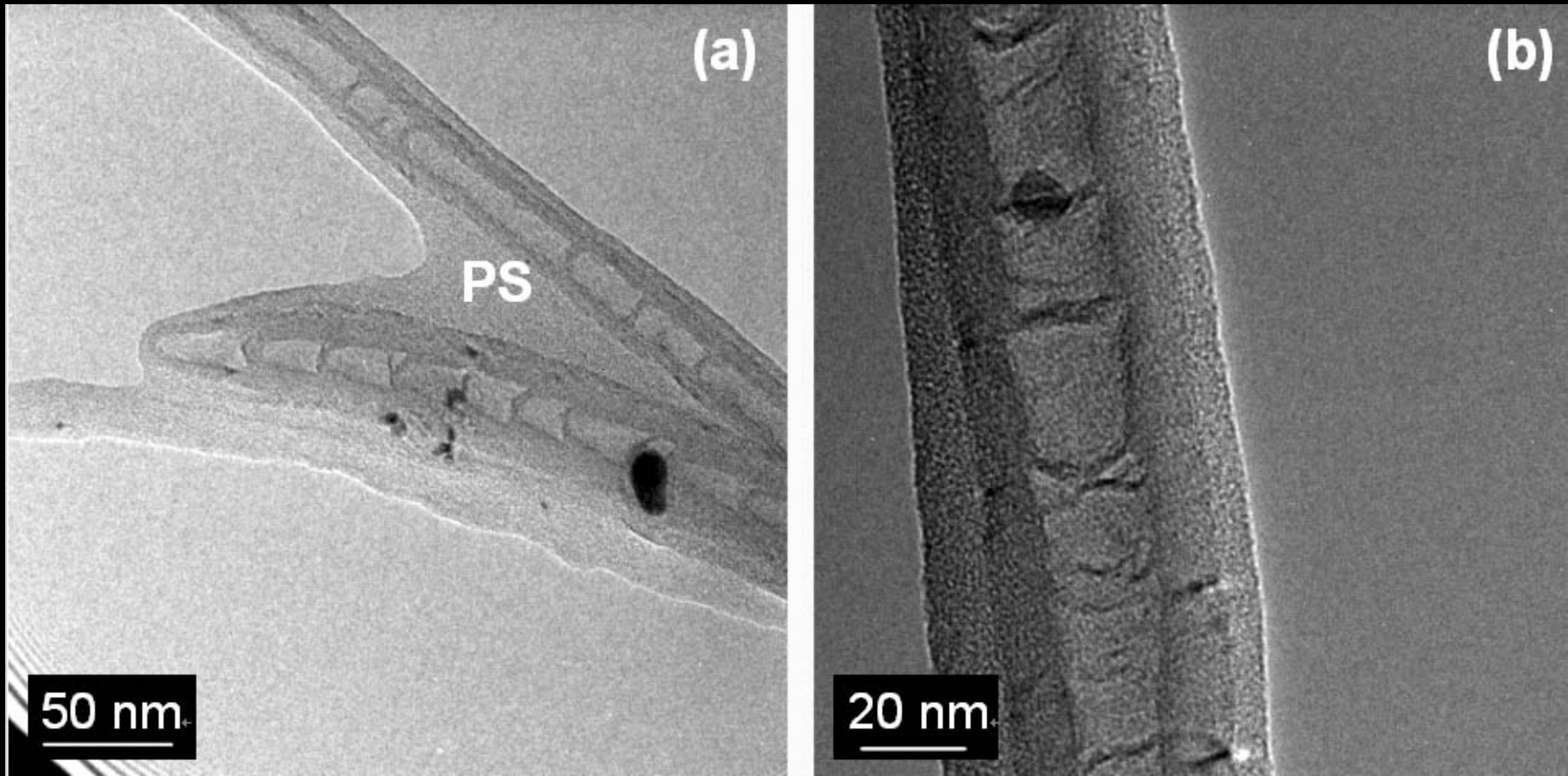
M. Dehonor, K. Masenelli-Varlot, A. González-Montiel, C. Gauthier, J.Y. Cavaillé, H. Terrones and M. Terrones. Chem. Commun., 5349-5351 (2005)

Polystyrene covalently grafted to CNx Nanotubes via NMRP



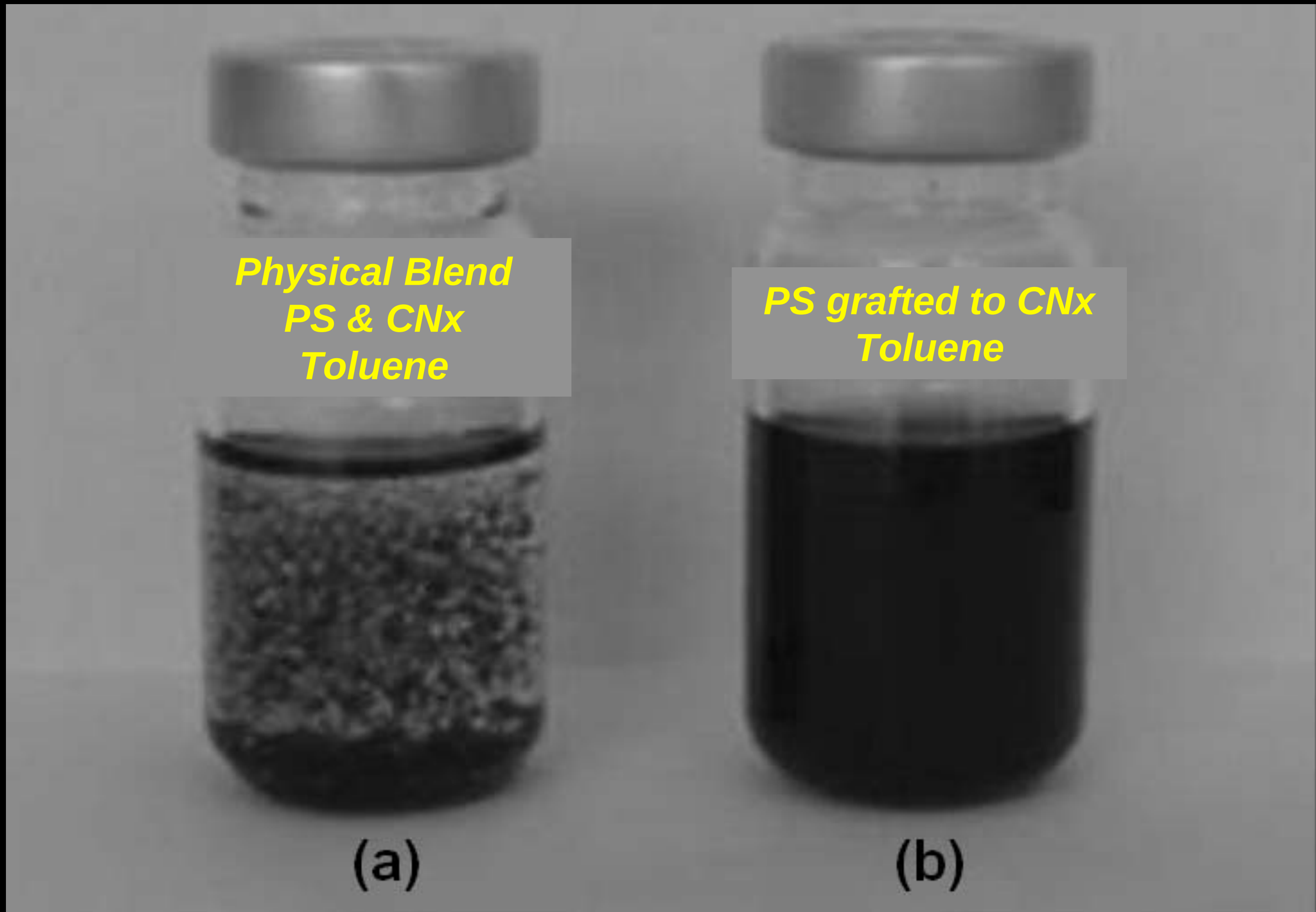
M. Dehonor, K. Masenelli-Varlot, A. González-Montiel, C. Gauthier, J.Y. Cavaillé, H. Terrones and M. Terrones. Chem. Commun., 5349-5351 (2005)

Polystyrene covalently grafted to CN_x Nanotubes: No acid treatment required!



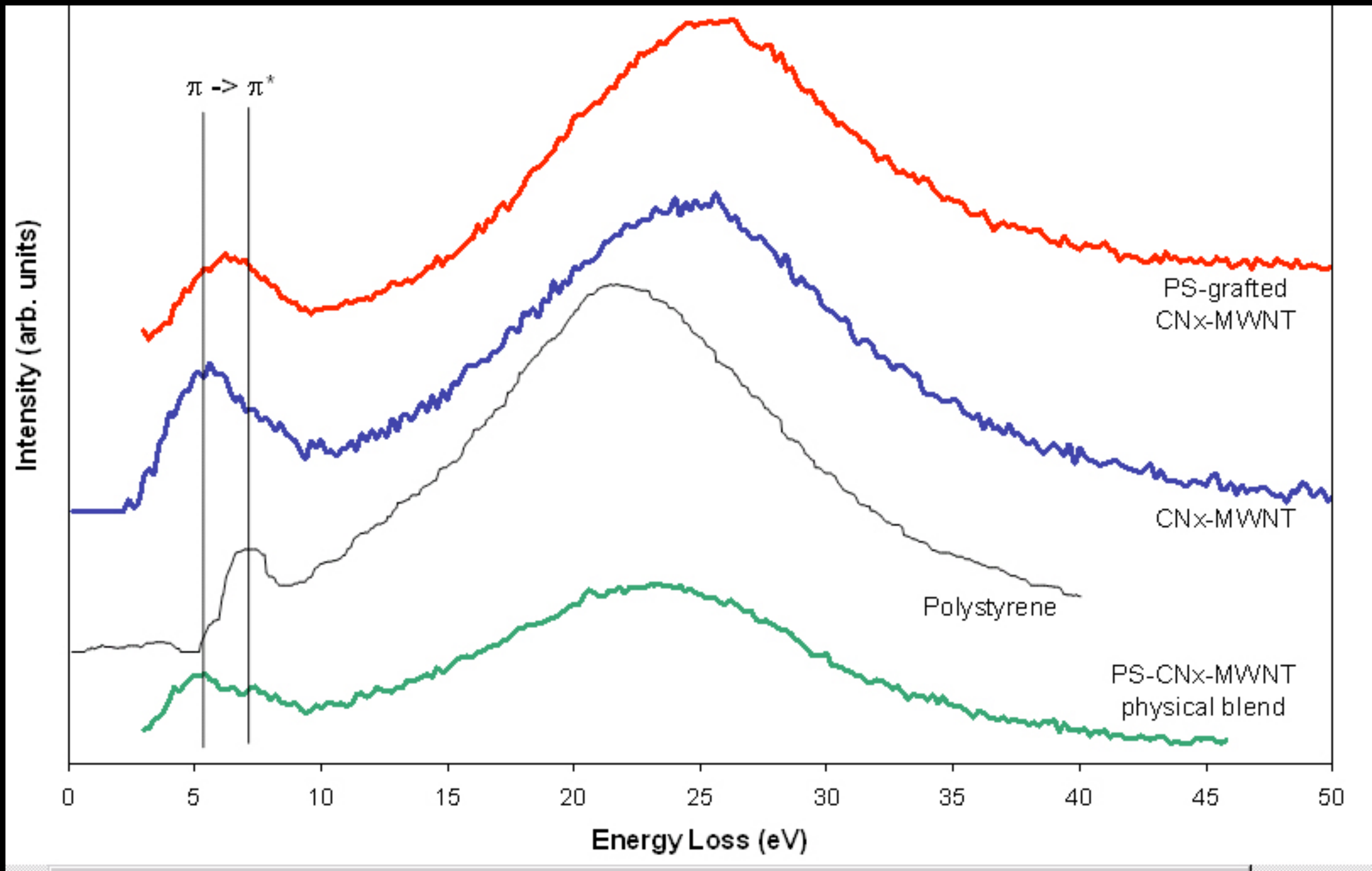
M. Dehonor, K. Masenelli-Varlot, A. González-Montiel, C. Gauthier, J.Y. Cavaillé, H. Terrones and M. Terrones. Chem. Commun, 5349-5351 (2005)

Polystyrene covalently grafted to CNx Nanotubes



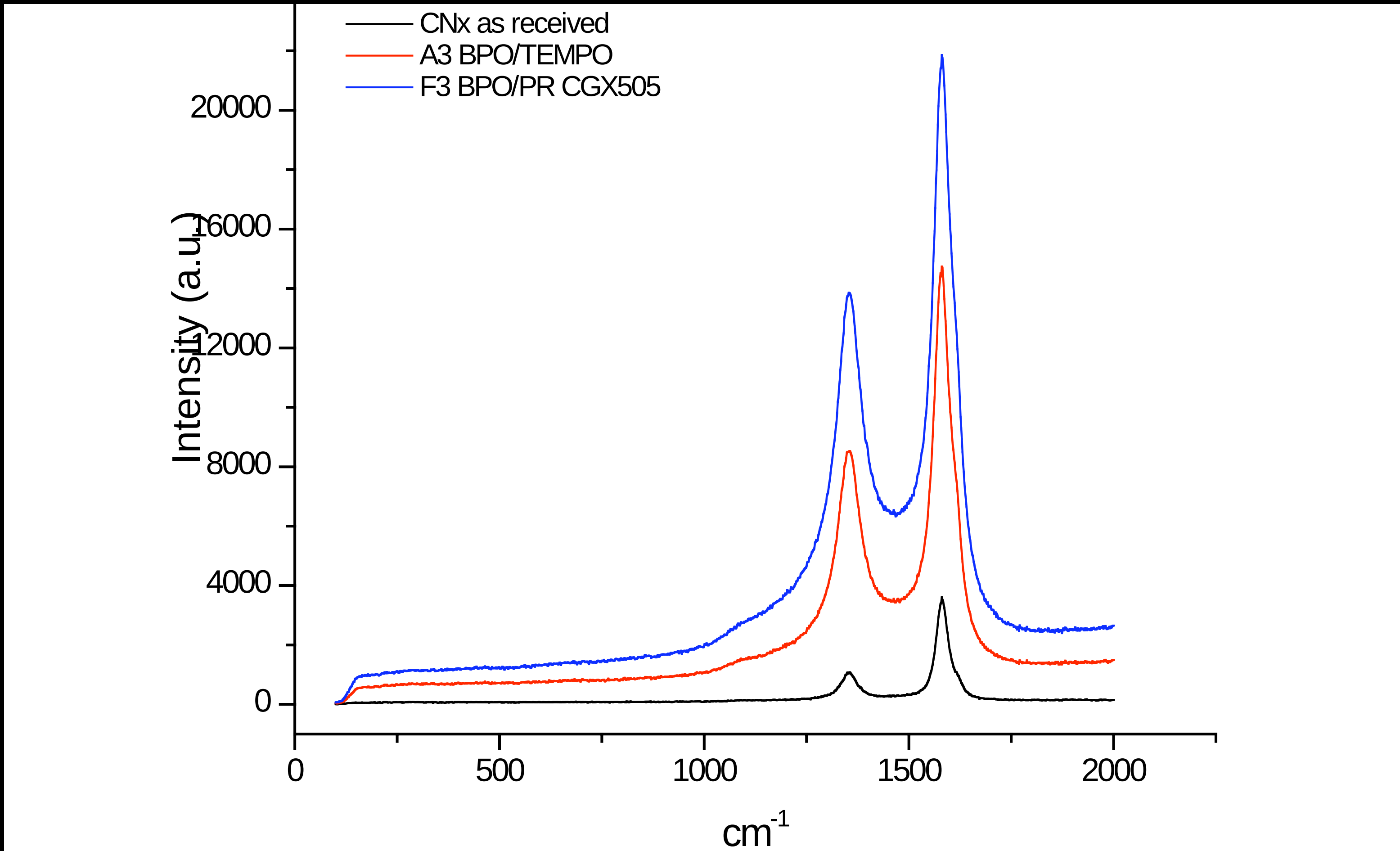
M. Dehonor, K. Masenelli-Varlot, A. González-Montiel, C. Gauthier, J.Y. Cavaillé, H. Terrones and M. Terrones. Chem. Commun 5349-5351 (2005)

Polystyrene covalently grafted to CNx Nanotubes



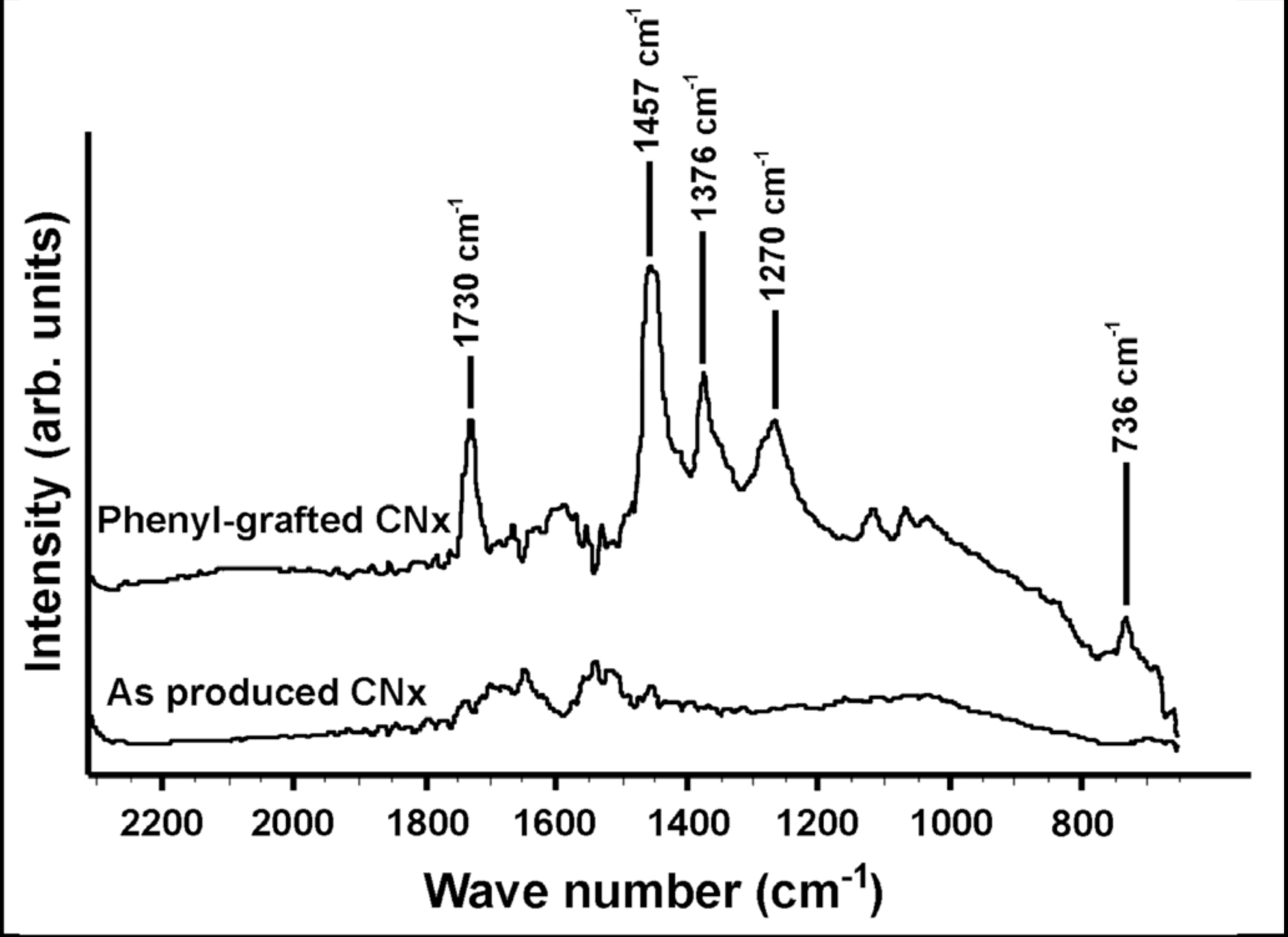
M. Dehonor, K. Masenelli-Varlot, A. González-Montiel, C. Gauthier, J.Y. Cavaillé, H. Terrones and M. Terrones. Chem. Commun , 5349-5351 (2005)

Raman Spectra: PS covalently grafted to CNx Nanotubes

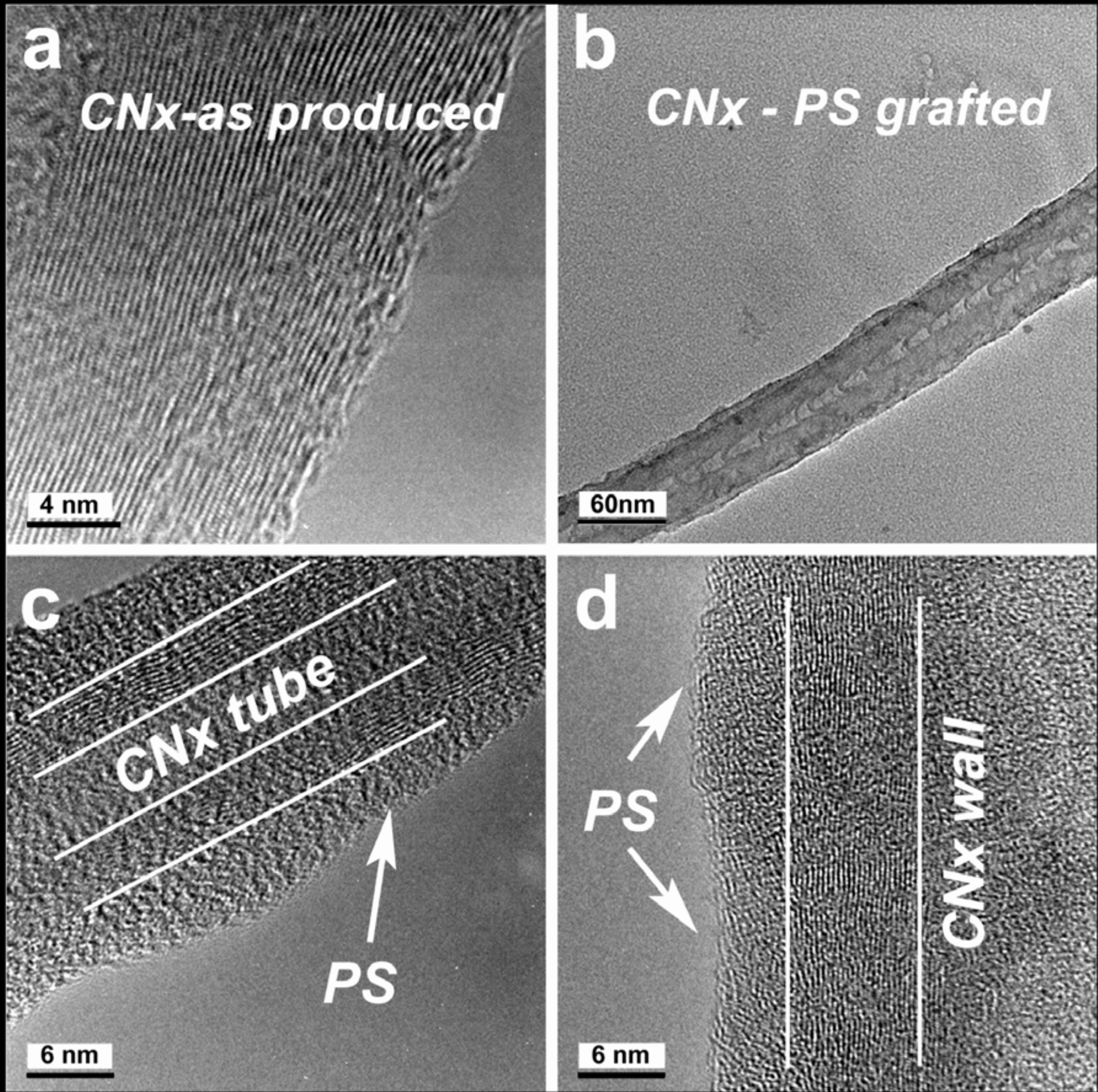


M. Dehonor, K. Masenelli-Varlot, A. González-Montiel, C. Gauthier, J.Y. Cavaillé, H. Terrones and M. Terrones. Chem. Commun., 5349-5351 (2005)

Efficient coating of PS on CNx Nanotubes via atomic transfer radical polymerization (ATRP)



B. Fragneaud, K. Masenelli-Varlot, A. González-Montiel, M. Terrones, J.Y. Cavaillé, Chem. Phys. Lett. 419 (2006) 567-573



Efficient coating of PS on CNx Nanotubes via ATRP

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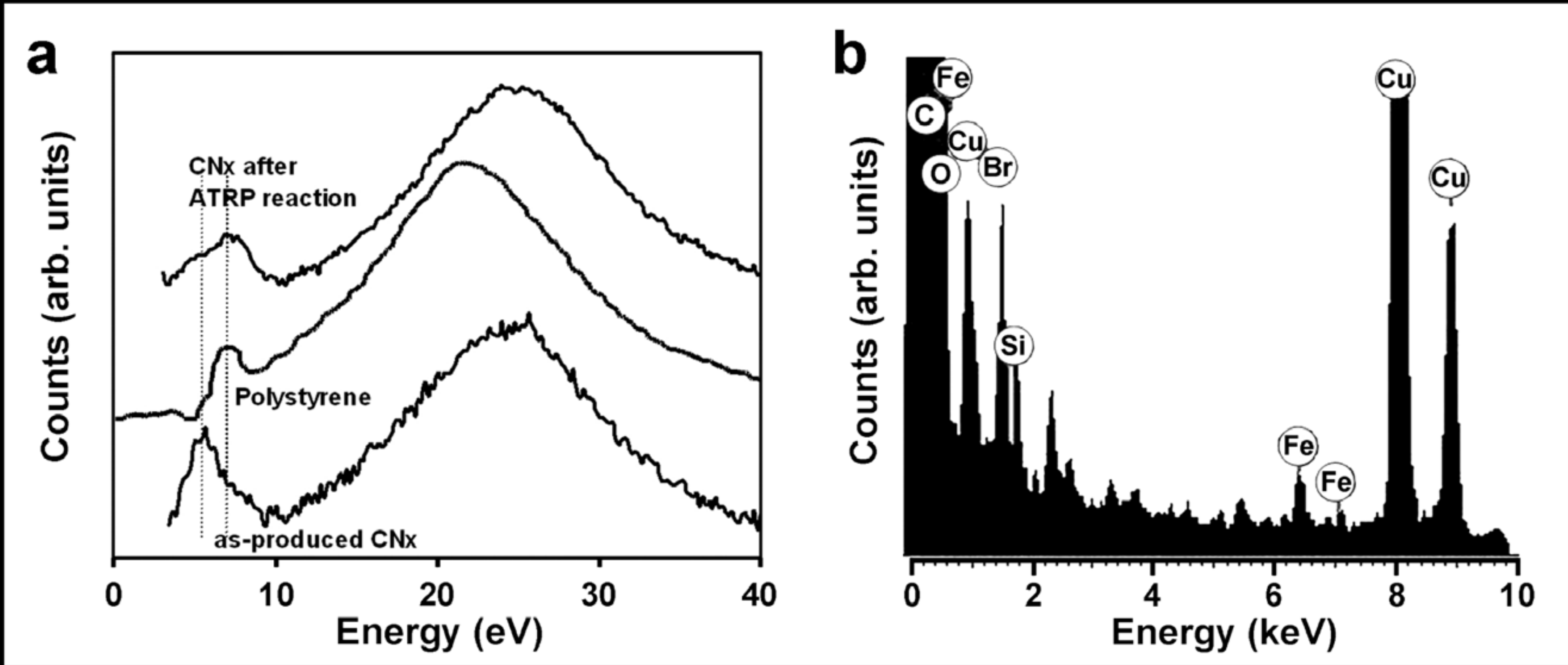

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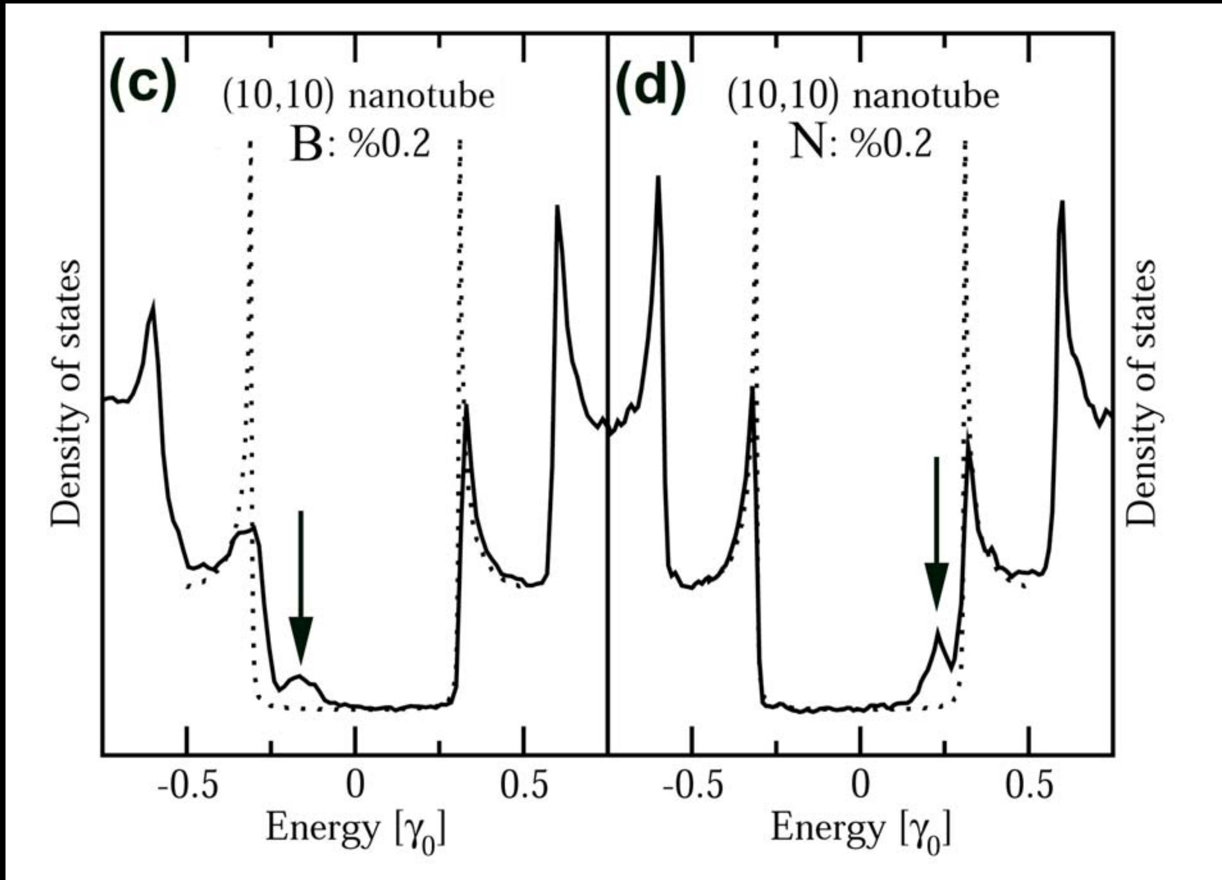
Challenges for Producing N-doped SWNTs

- Doping at very low levels (< 0.5 %)
- USE SWNTs and MWNTs
- Characterize efficiently such low doping levels
- Develop quantifications with Raman
- Perform Mechanical Tests
- Perform Transport Tests
- Thermal Conductivity Tests
- Produce Composites using Doped NTs
- Exploit New Chemical Properties
- Dope DWNTs with B and N
- Simulations for Raman Modes of Doped SWNTs

Why?

Electronic Properties with LOW doping levels

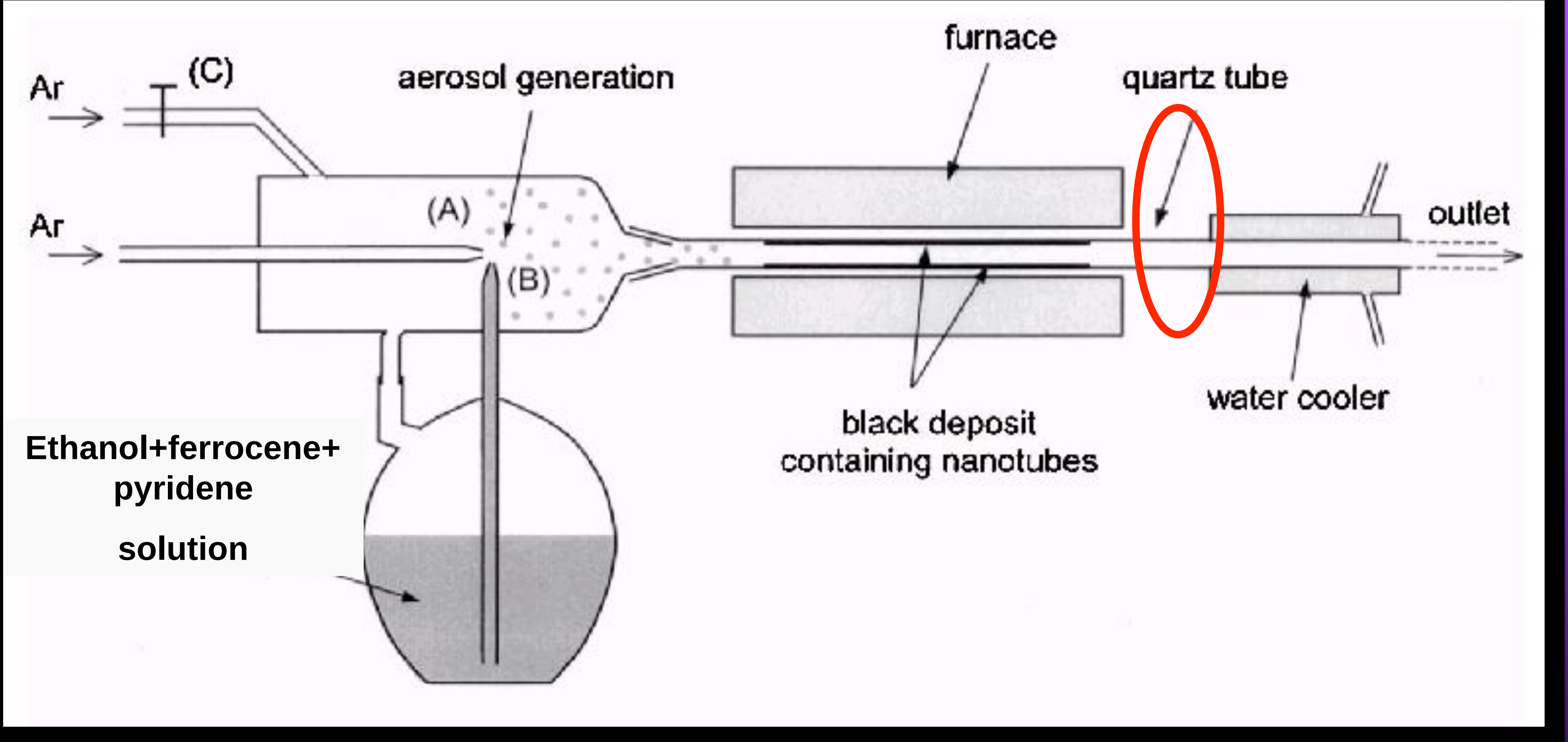


B-doped carbon nanotube (B = 0.2 at.%, solid line) exhibiting a clear peak in the valence band

N-doped carbon nanotube (N = 0.2 at.%, solid line), in which a sharp and localized peak arises in the CB

S. Latil, et al. Phys. Rev. Lett (2004), in press; M. Terrones, et al. Materials Today Magazine (2004), 7, 30-45.

Growth of Long Strands of N-SWNTs



F. Lupo, J.A. Rodríguez-Manzo, A. Zamudio, A.L. Elías, Y.A. Kim, T. Hayashi, M. Muramatsu, H. Terrones, M. Endo, M. Rühle and Mauricio Terrones
Chemical Physics Letters 410, 384 (2005)

Formation of a SWCNTs web at IPICYT

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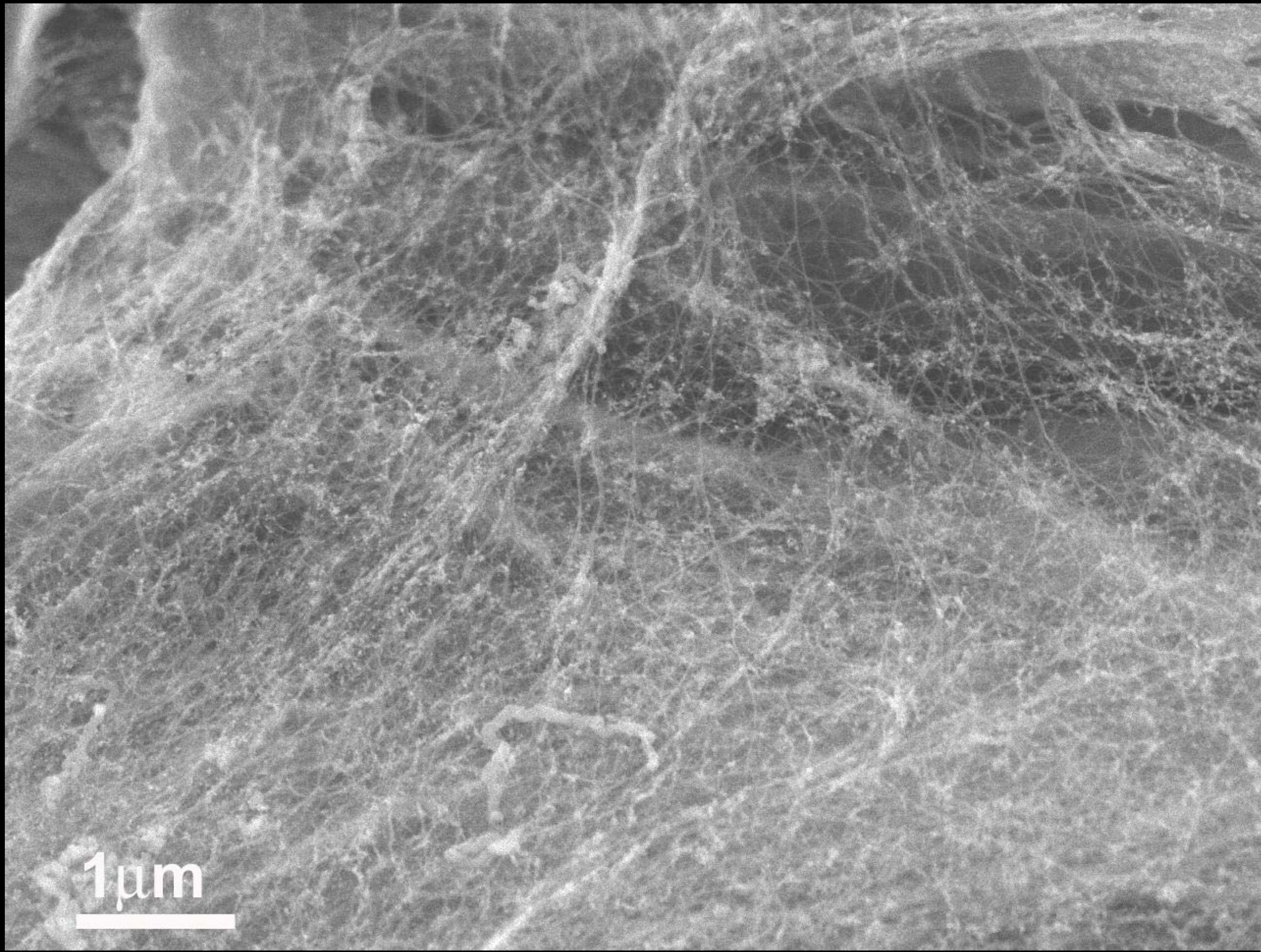
SEM: Outside the oven, 1.25%$FeCp_2$ wt, 950 ºC



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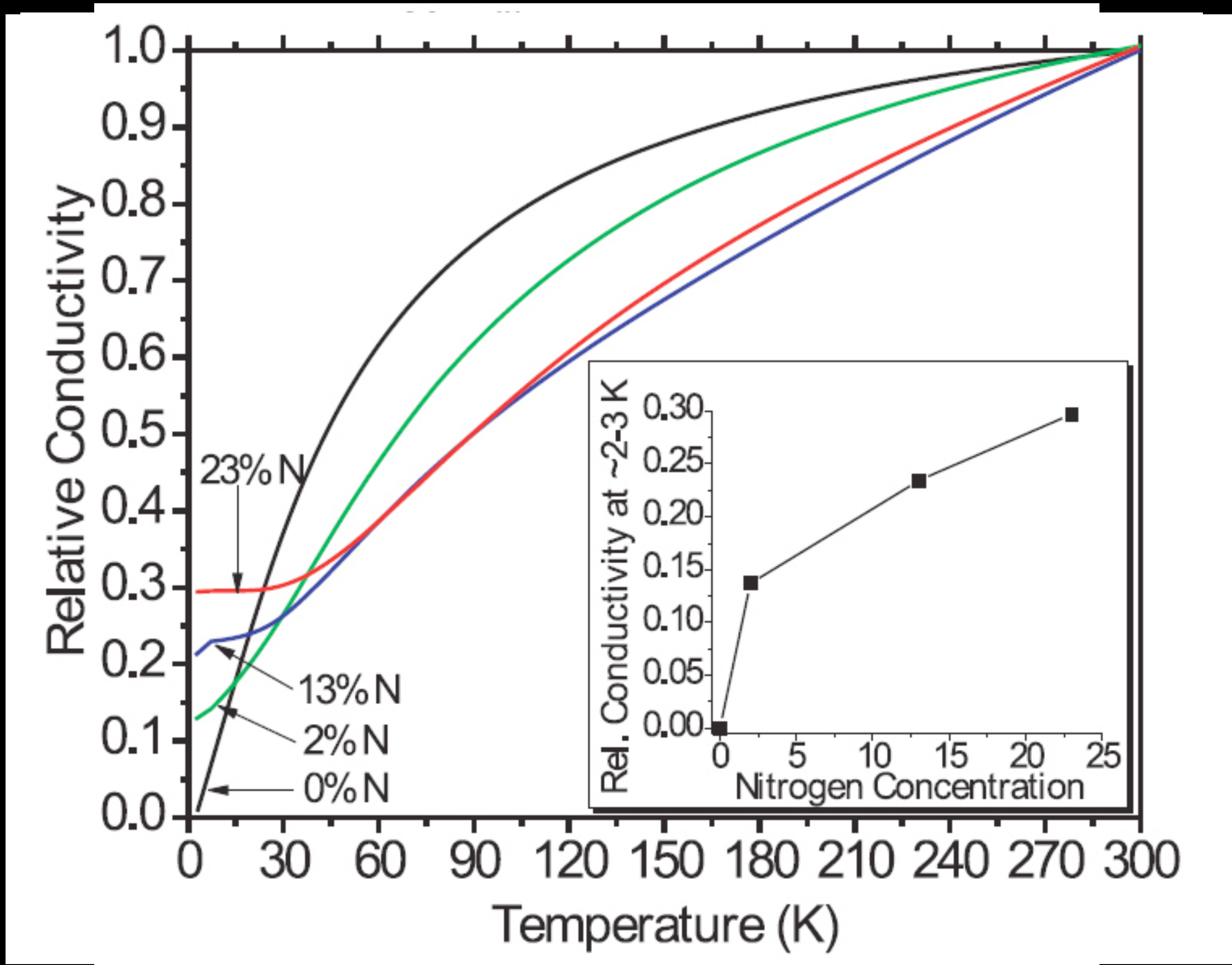
Production of N-doped SWNTs



Villalpando, F., et al. To be published

TGA of N-doped SWNTs