Use of Relative Purity in the Processing and Application of Single-Walled Carbon Nanotubes

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Use of Relative Purity in the Processing and Application of Single-Walled Carbon Nanotubes

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R. Sen, *Nantero*, MA
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H. Hu, *ORNL*
S. Niyogi, *LANL*
J. Tang

V. Parpura
Y. Yan
N. Myung
R. Kawakami

NSF
DOD/DARPA/ DMEA

A Purity Standard for Single-Walled Carbon Nanotubes

Rapid, well defined, and quantitative

Widely available

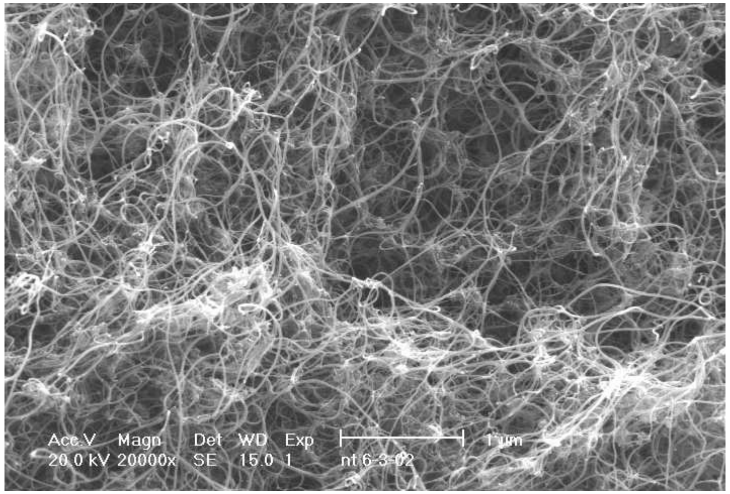
Applicable to bulk samples

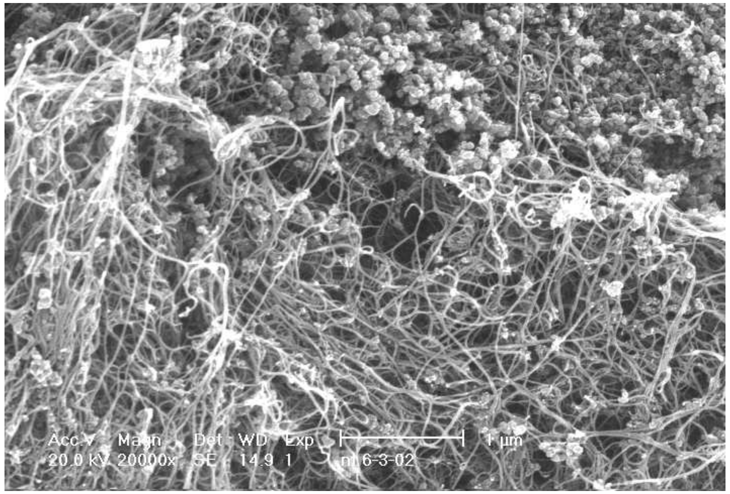
…but sensitive to nanostructure

Growing nanotech trade hit by questions over quality

Nature, December, 2004

SEM Images of As-Prepared SWNT Soot

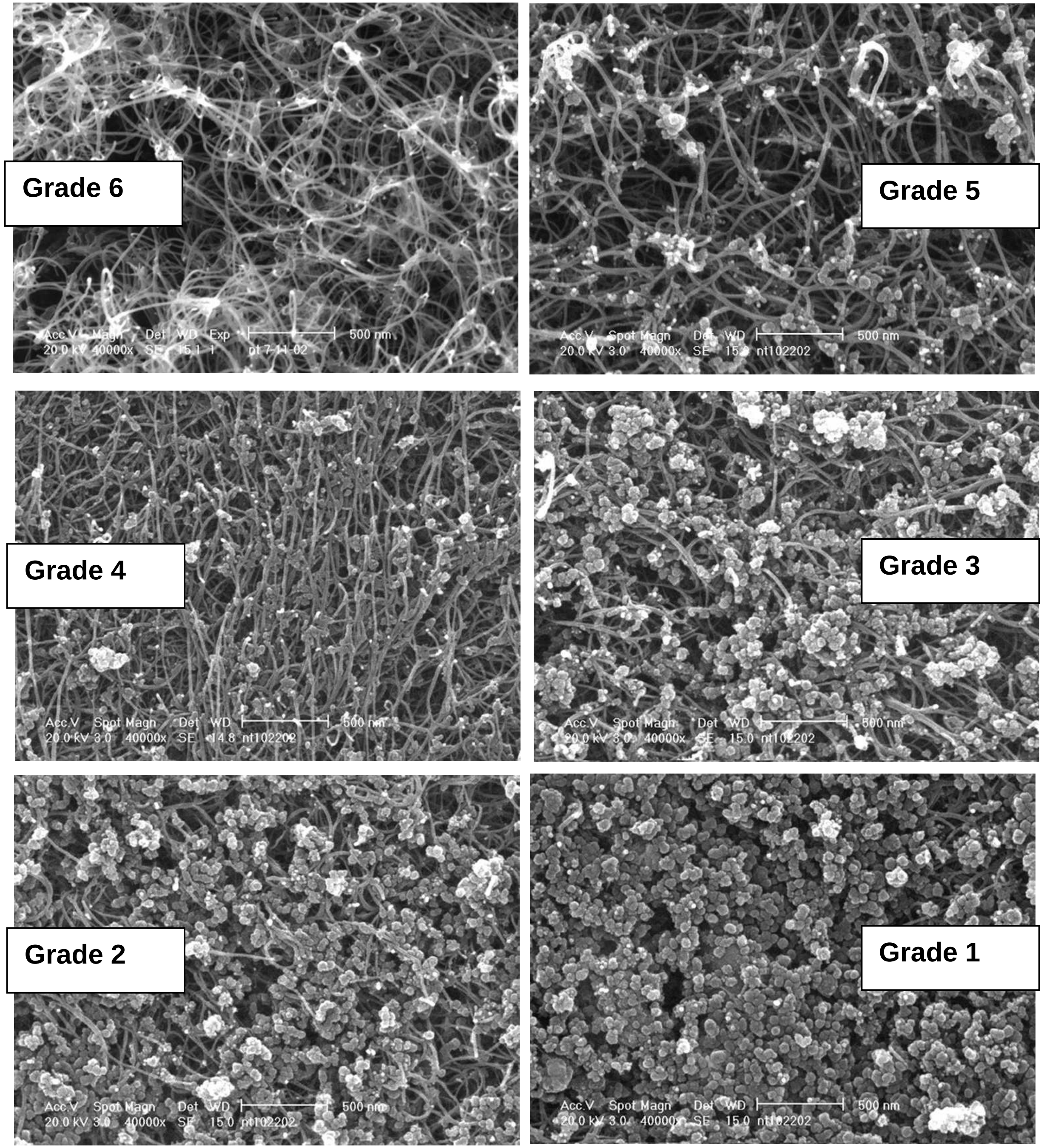




two regions of the same sample…

SEM: Less than 10^{-12} g of carbon nanotubes per frame
Bulk scale: 1-10 g (lab); 100 g - kg (industrial)

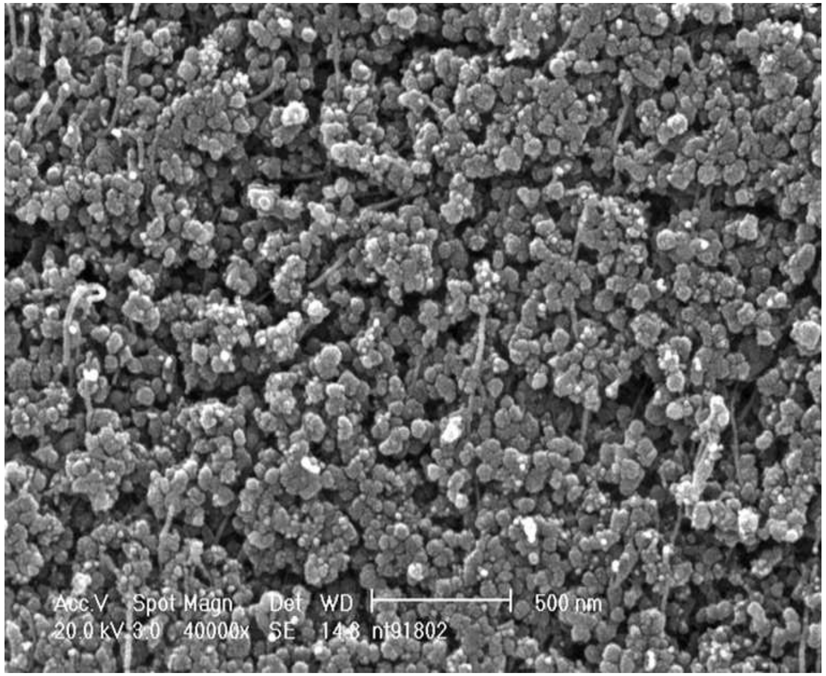
Itkis, M. E.; Perea, D.; Jung, R.; Niyogi, S.; Haddon, R. C.,
Comparison of Analytical Techniques for Purity Evaluation of Single-Walled Carbon Nanotubes.
J. Am. Chem. Soc. **2005,** 127, 3439-3448.



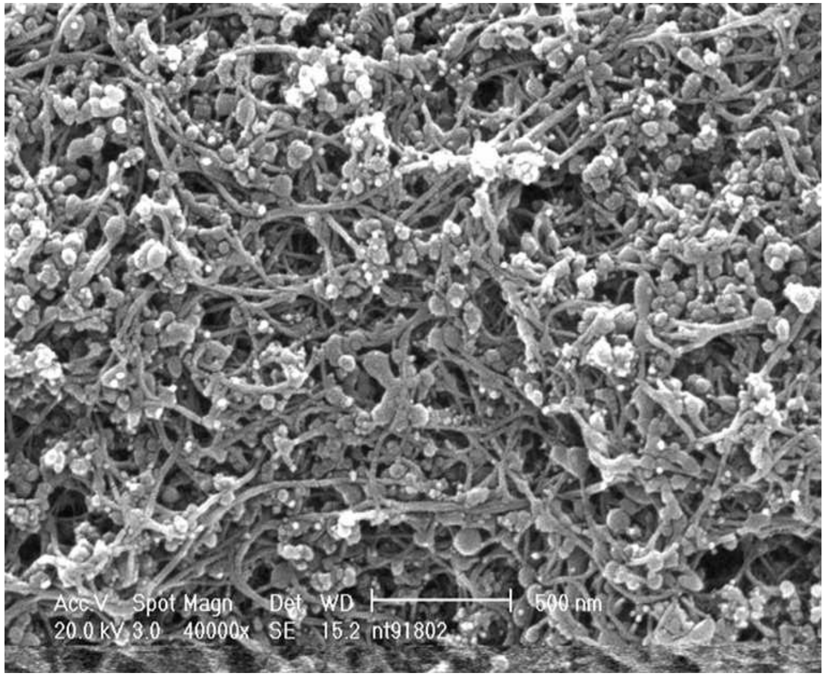
Reference SEM images for grading scheme of as-prepared SWNT soot unpublished, 1998-

Itkis, M. E.; Perea, D.; Jung, R.; Niyogi, S.; Haddon, R. C., Comparison of Analytical Techniques for Purity Evaluation of Single-Walled Carbon Nanotubes. *J. Am. Chem. Soc.* **2005,** 127, 3439-3448.

Effect of sample preparation on SEM images and SEM grading for as-prepared SWNT soot.

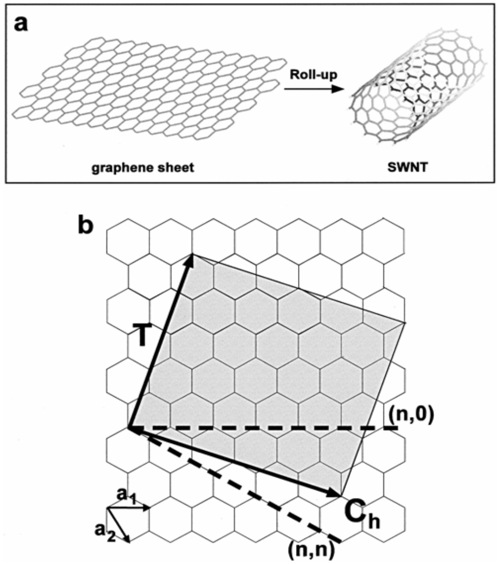


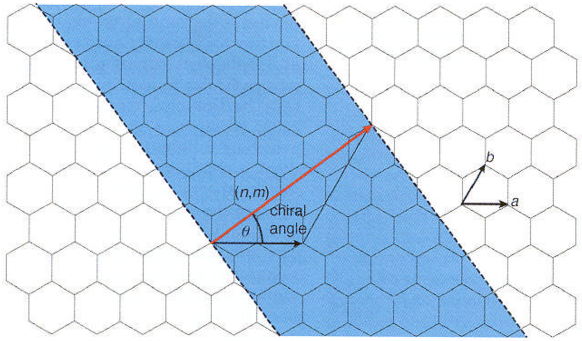
Unprocessed dry powder sample
SEM grade 1

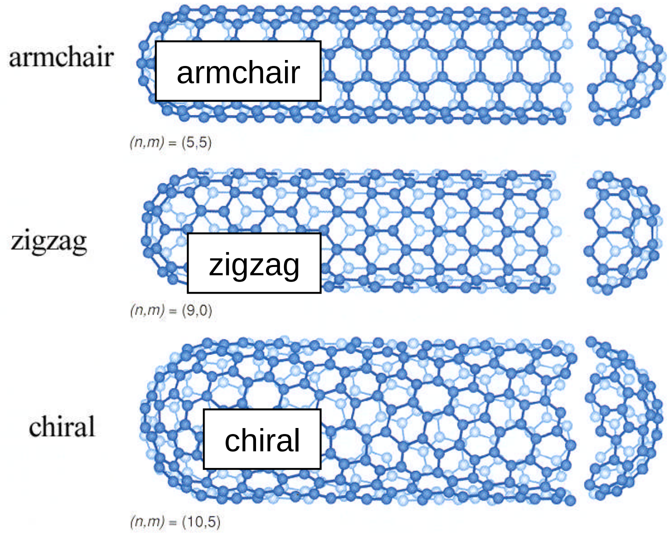


Sample mounted as DMF dispersion
SEM grade 2-3

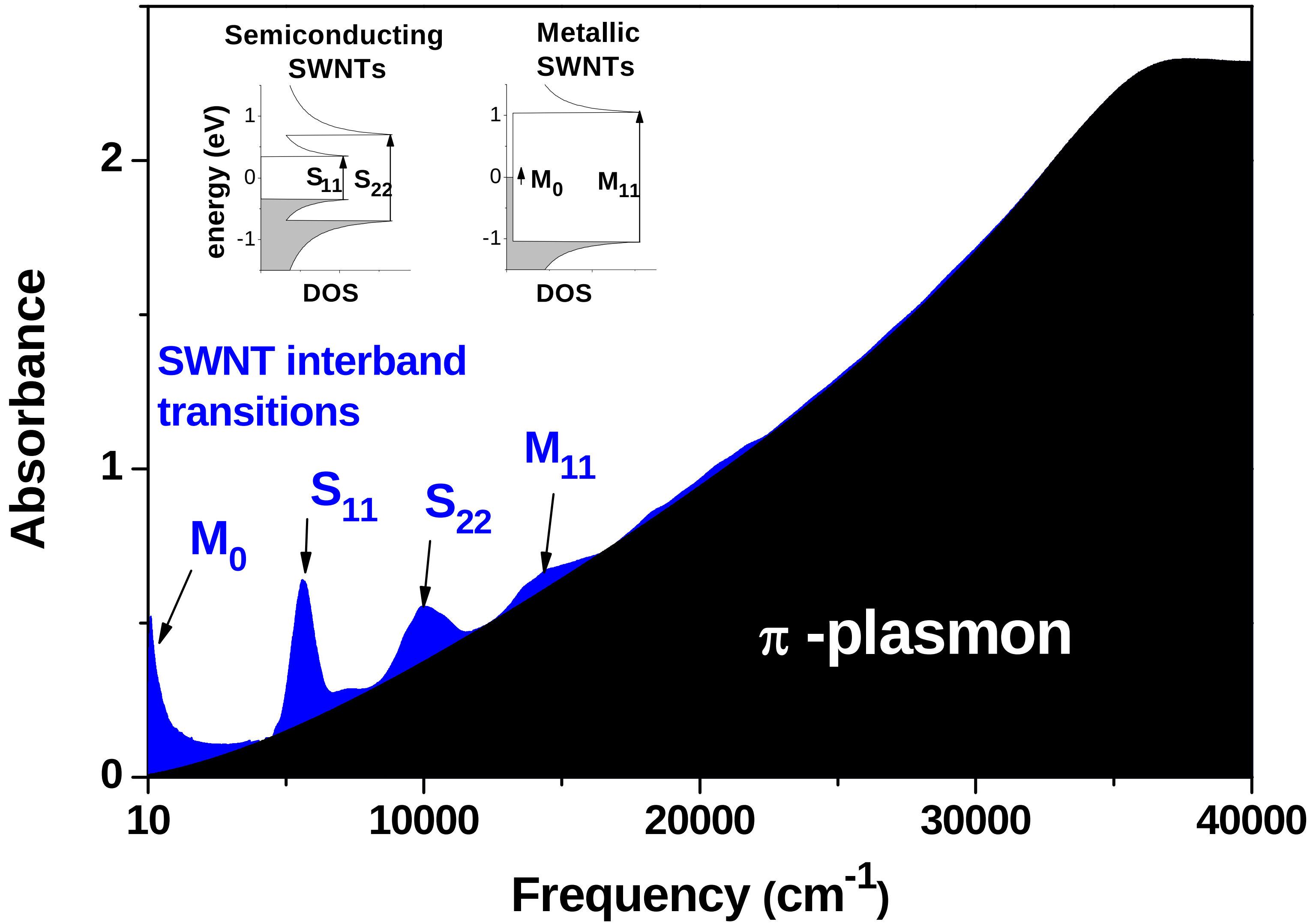
Topology of Single-Walled Carbon Nanotubes





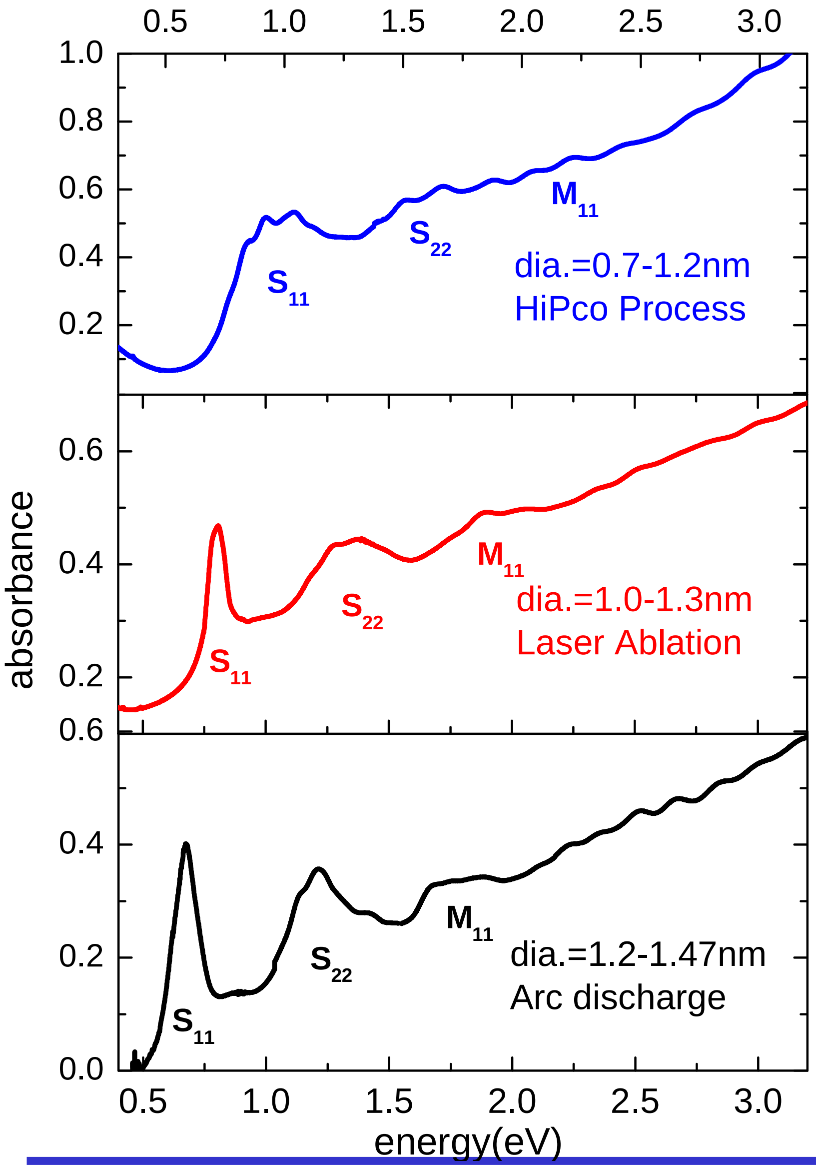


Density of States (DOS) and Optical Properties of SWNTs

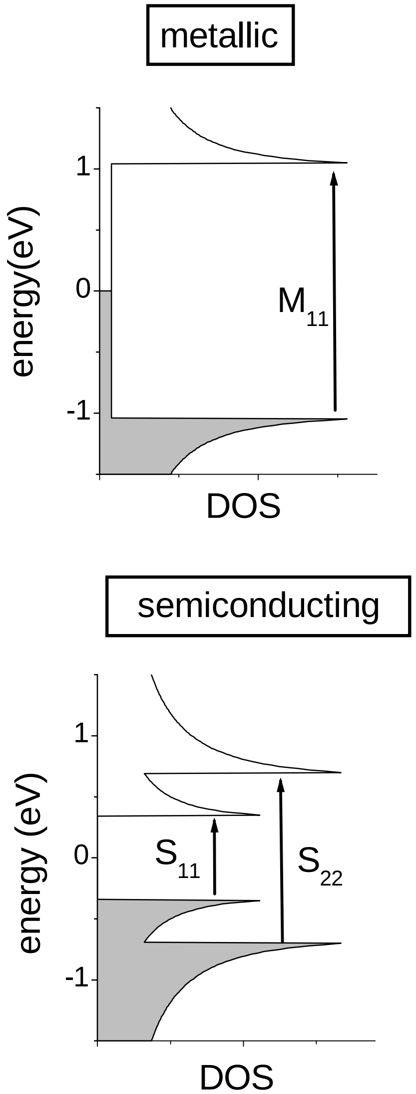


M. Itkis et al. *Nano Lett.* **2003**, *3*, 309.

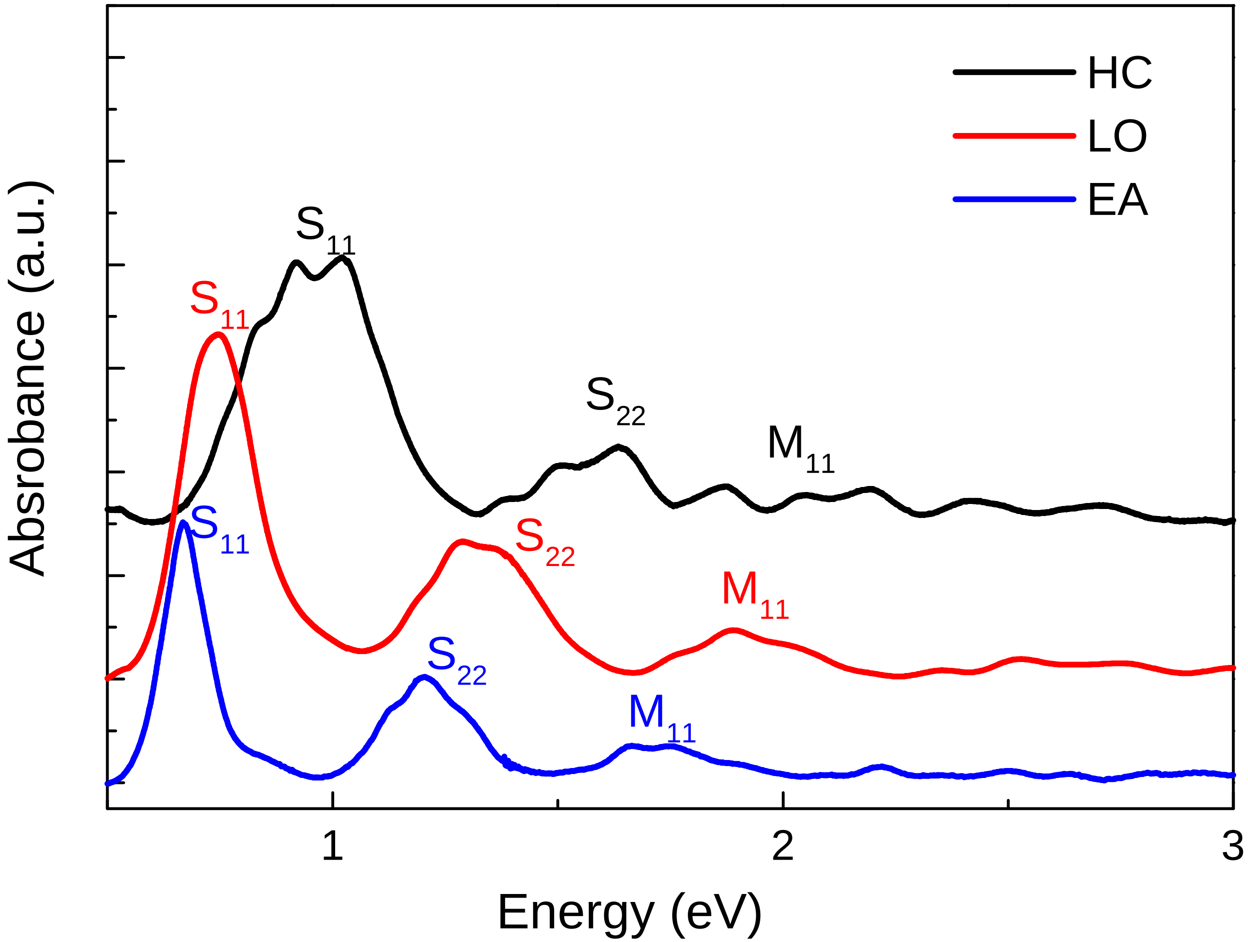
Near-IR transmission spectra of SWNT films



Schematic of electronic density of states



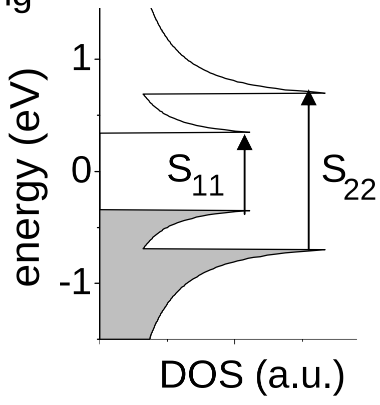
Interband electronic transitions of SWNTs produced by different methods



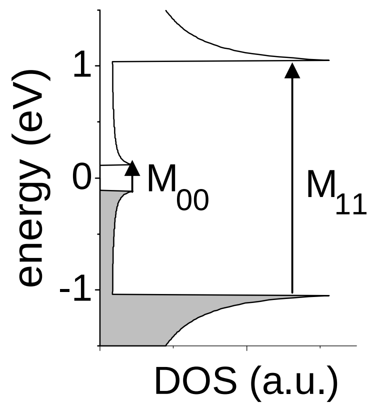
Hamon, M. A.; Itkis, M. E.; Niyogi, S.; Alvaraez, T.; Kuper, C.; Menon, M.; Haddon, R. C., Effect of Rehybridization on the Electronic Structure of Single-Walled Carbon Nanotubes. *J. Am. Chem. Soc.* **2001,** 123, 11292-11293.

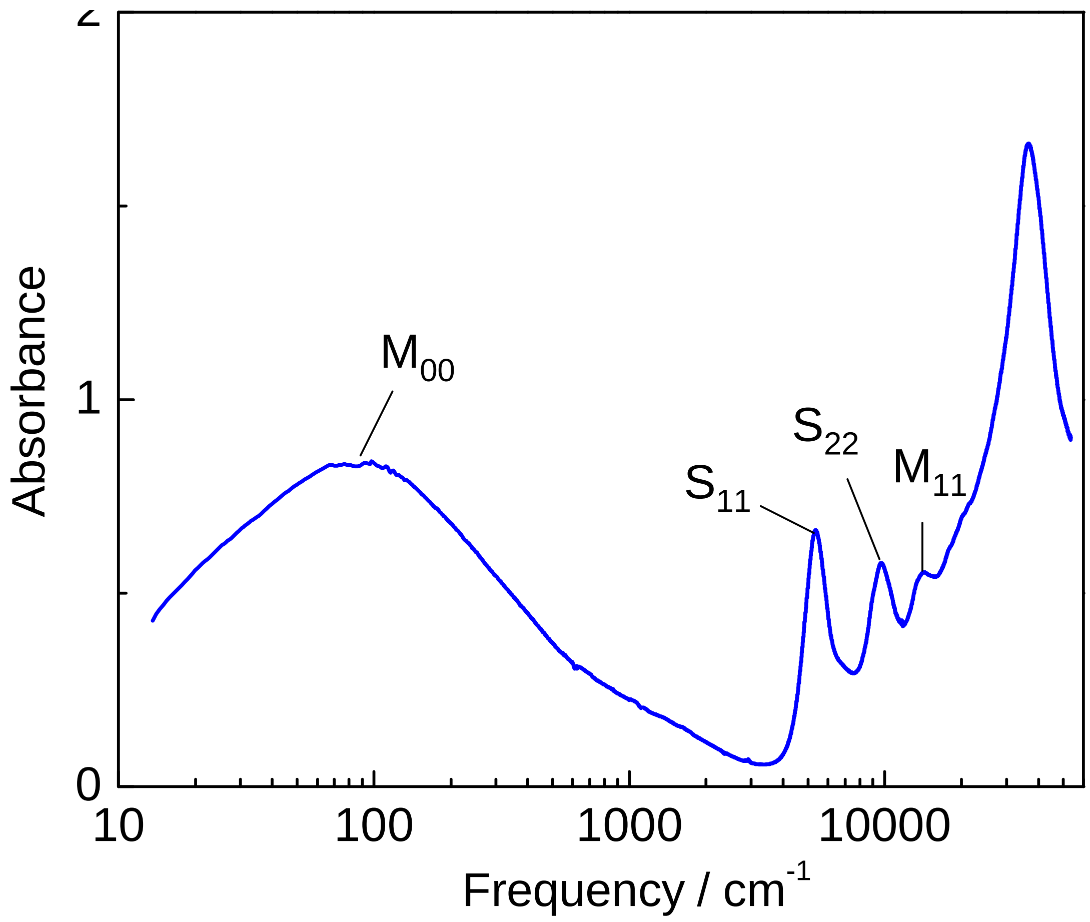
Optical excitations in SWNTs: Band Picture

Semiconducting SWNTs



Metallic SWNTs



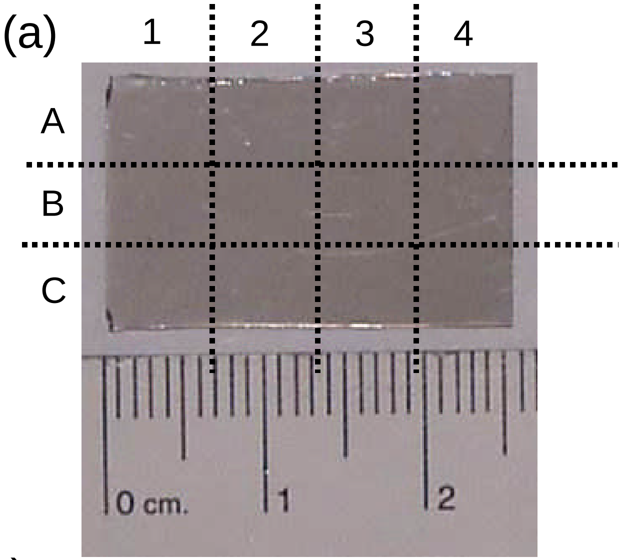


Itkis, M. E.; Niyogi, S.; Meng, M.; Hamon, M.; Hu, H.; Haddon, R. C., Spectroscopic Study of the Fermi Level Electronic Structure of Single Walled Carbon Nanotubes. *NanoLett.* **2002,** 2, 155-159.

Purification of As-Prepared (AP-) SWNTs

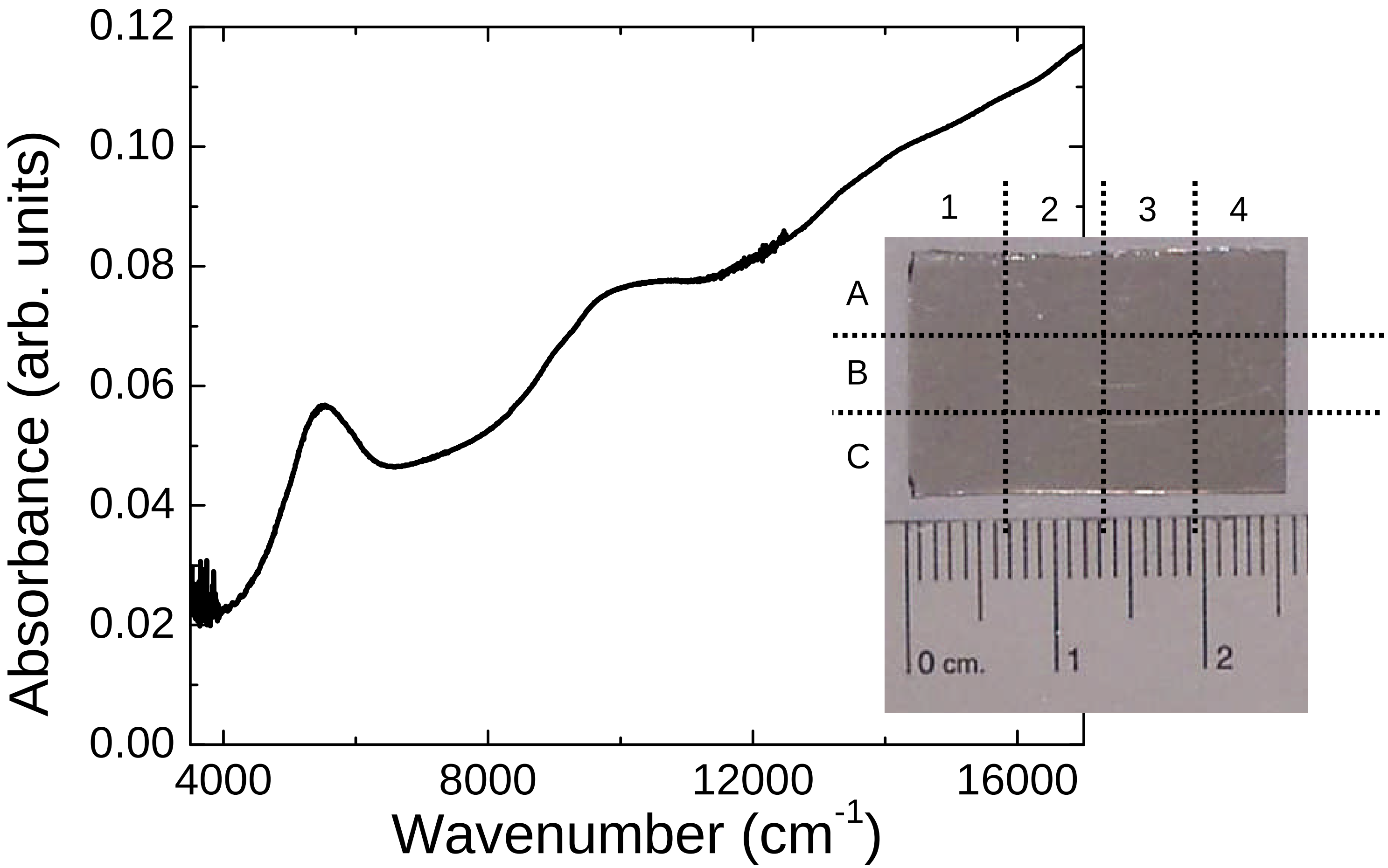
AP-SWNT films preheated in argon and then subjected to flowing oxygen at temperature

(a)



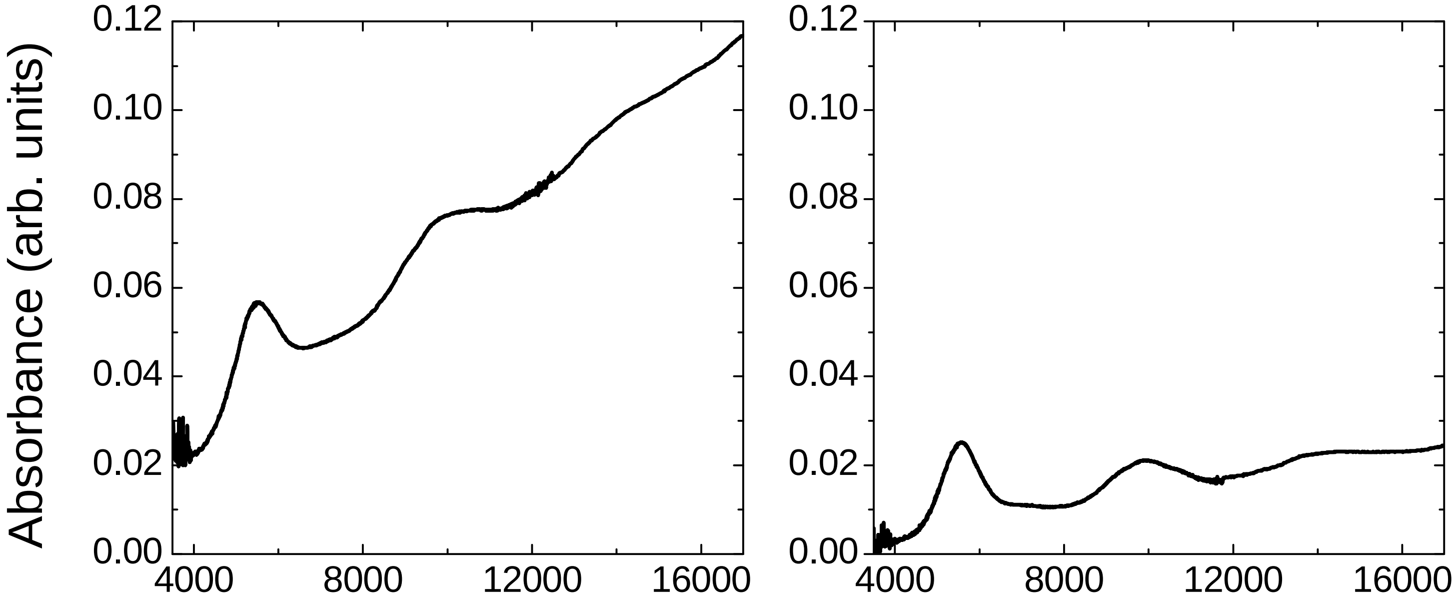
Sen, R.; Rickard, S. M.; Itkis, M. E.; Haddon, R. C.,
Controlled Purification of Single-Walled Carbon Nanotube Films by Use of Selective Oxidation and Near-IR Spectroscopy. *Chem. Mater.* **2003,** 15, 4273-4279

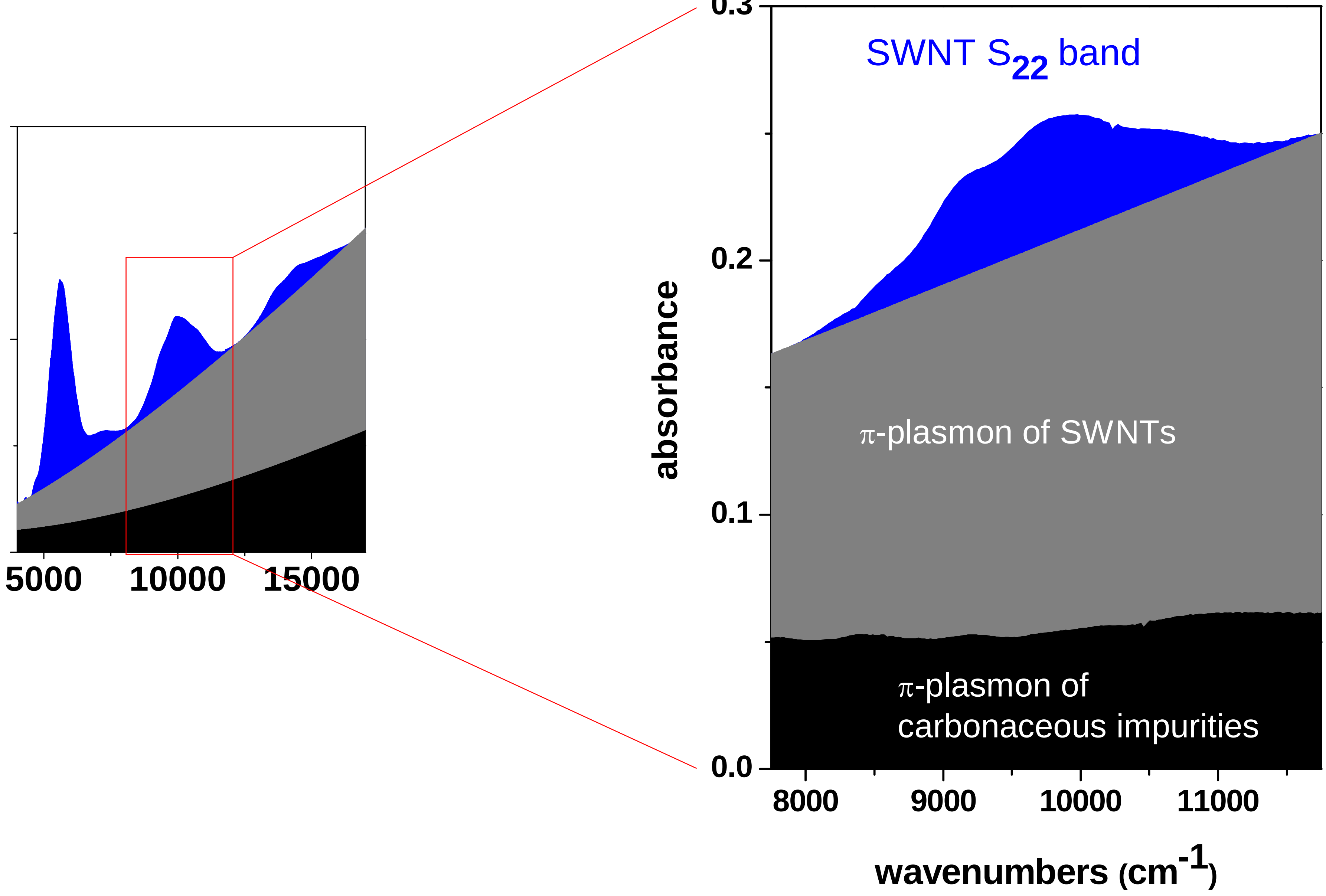
NIR Spectrum of As-Prepared (AP-) SWNT Film



NIR spectra of as-prepared (AP-) SWNT film

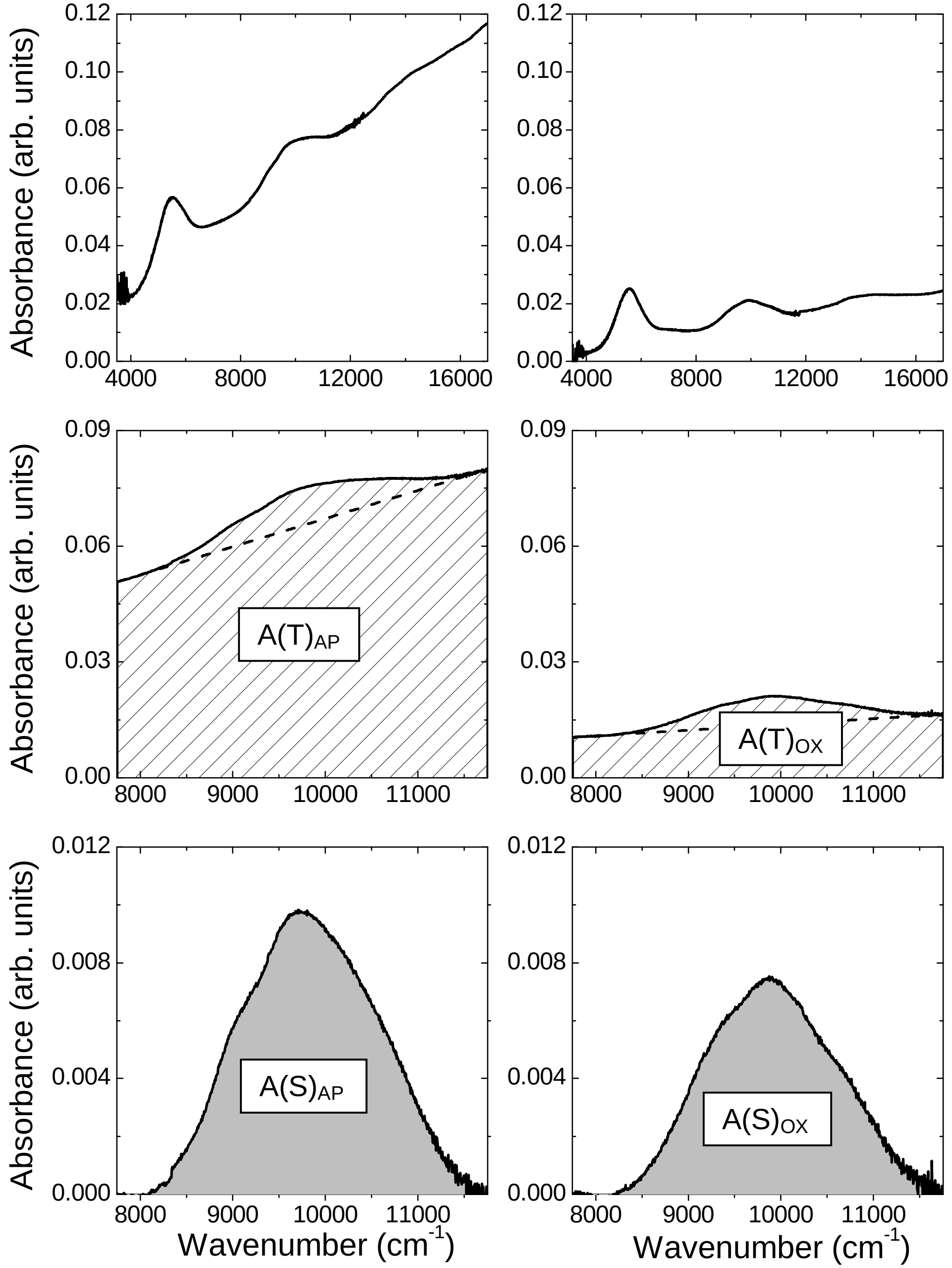
NIR Spectra of AP-SWNT film after heating at 292^{o}C in flowing oxygen for 4h





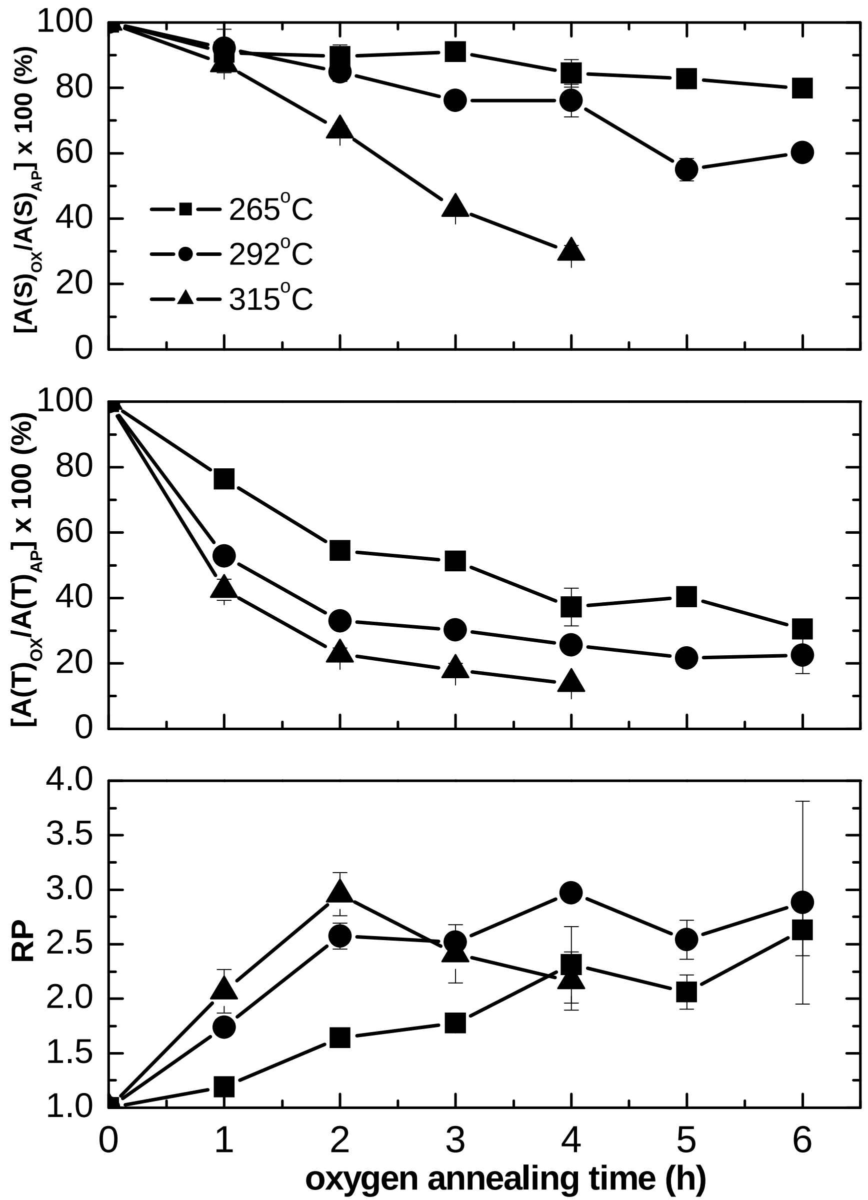
5000
10000
15000
0.3
0.2
0.1
0.0
SWNT S22 band
π-plasmon of SWNTs
π-plasmon of
carbonaceous impurities
absorbance
8000
9000
10000
11000
wavenumbers (cm-1)

NIR spectra of as-prepared
(AP-) SWNT film



NIR spectra of the film after heating at 292^{o}C in flowing oxygen for 4h

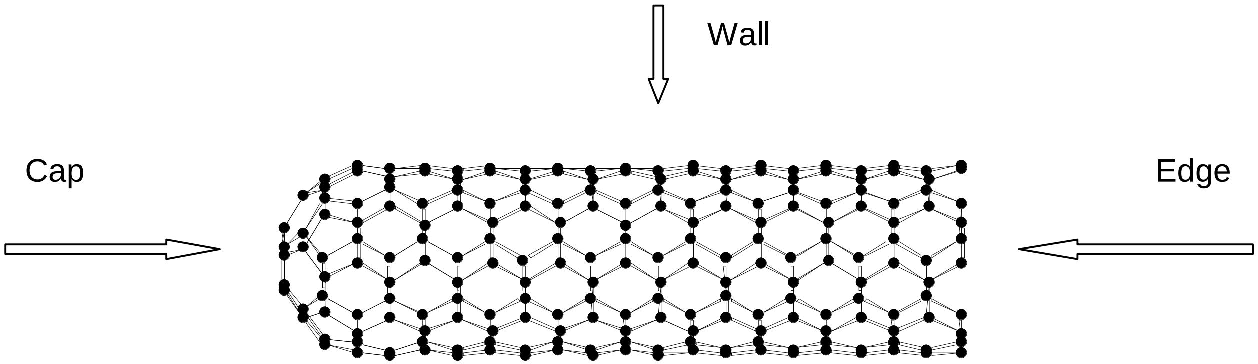
Evolution of NIR spectra of an as-prepared (AP-) SWNT film as a function of oxygen treatment



Sensitive to nanostructure and the presence of defects?

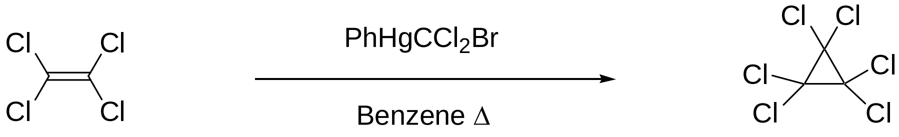
Nanotube Chemistry

COVALENT WALL CHEMISTRY

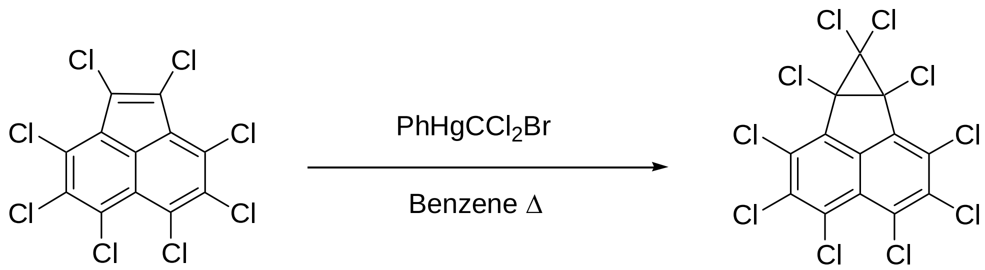


Y. Chen, R. C. Haddon, S. Fang, A. M. Rao, P. C. Eklund, W. H. Lee, E. C. Dickey, E. A. Grulke, J. C. Pendergrass, A. Chavan, B. E. Haley, R. E. Smalley, Chemical Attachment of Organic Functional Groups to Single-Walled Carbon Nanotube Material, *J. Mater. Res.* **1998**, *13,* 2423.

Dichlorocarbene Addition Chemistry



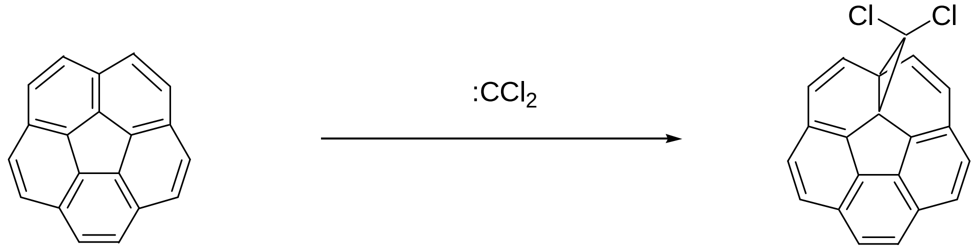
Seyferth, D., *Acc. Chem. Res.,* **1972**, *5*, 65. 83%



Haddon, R. C.; Chichester, S. V.; Stein, S. M.; Marshall, J. H.; Mujsce, A. M., *J. Org. Chem.* **1987**, *52*, 711.

$$C_{60} \xrightarrow[\text{Benzene } \Delta]{PhHgCBr_3} C_{61}Br_2$$

Osterodt, J.; Vogtle, F., *J. C. S. Chem. Commun.* **1996**, 547.

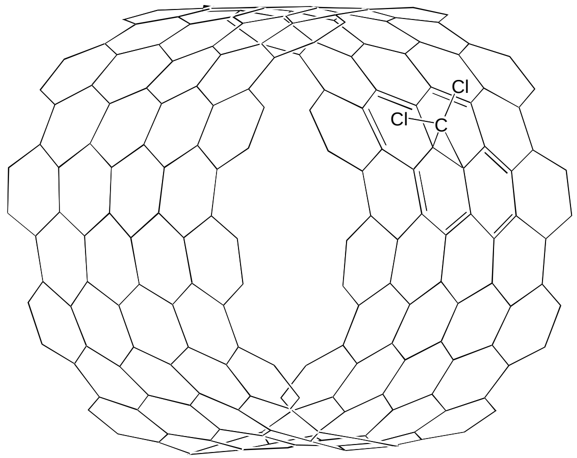


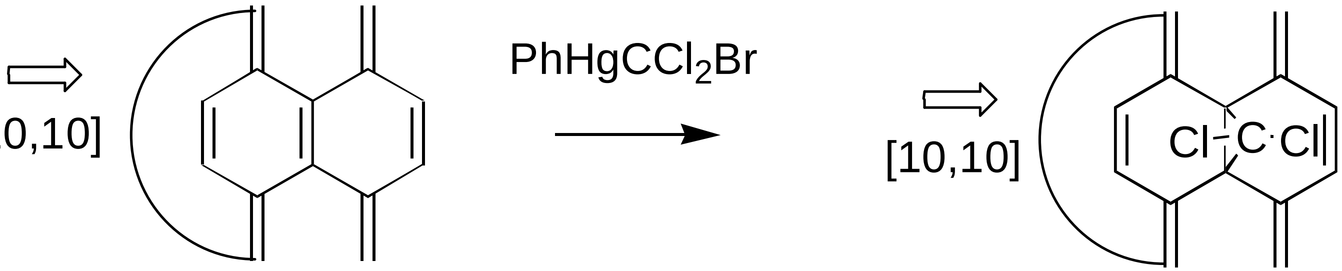
Scott, L. T.; Preda, D. V., *C&EN.* **1998**, 46 (April 13th).

Wall Chemistry

Reaction of SWNT with Dichlorocarbene

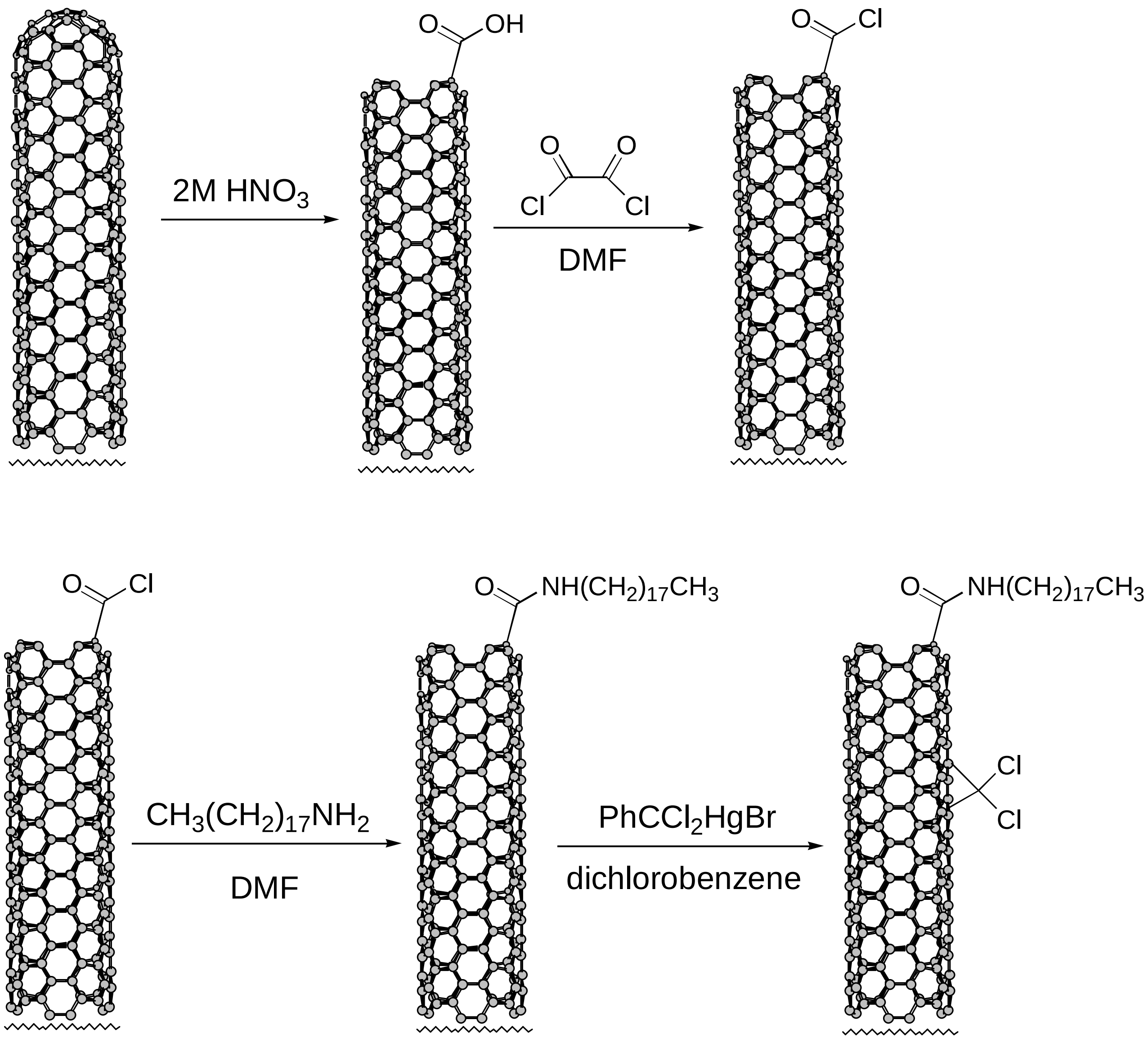
SWNT + $PhHgCCl_2Br \rightarrow$

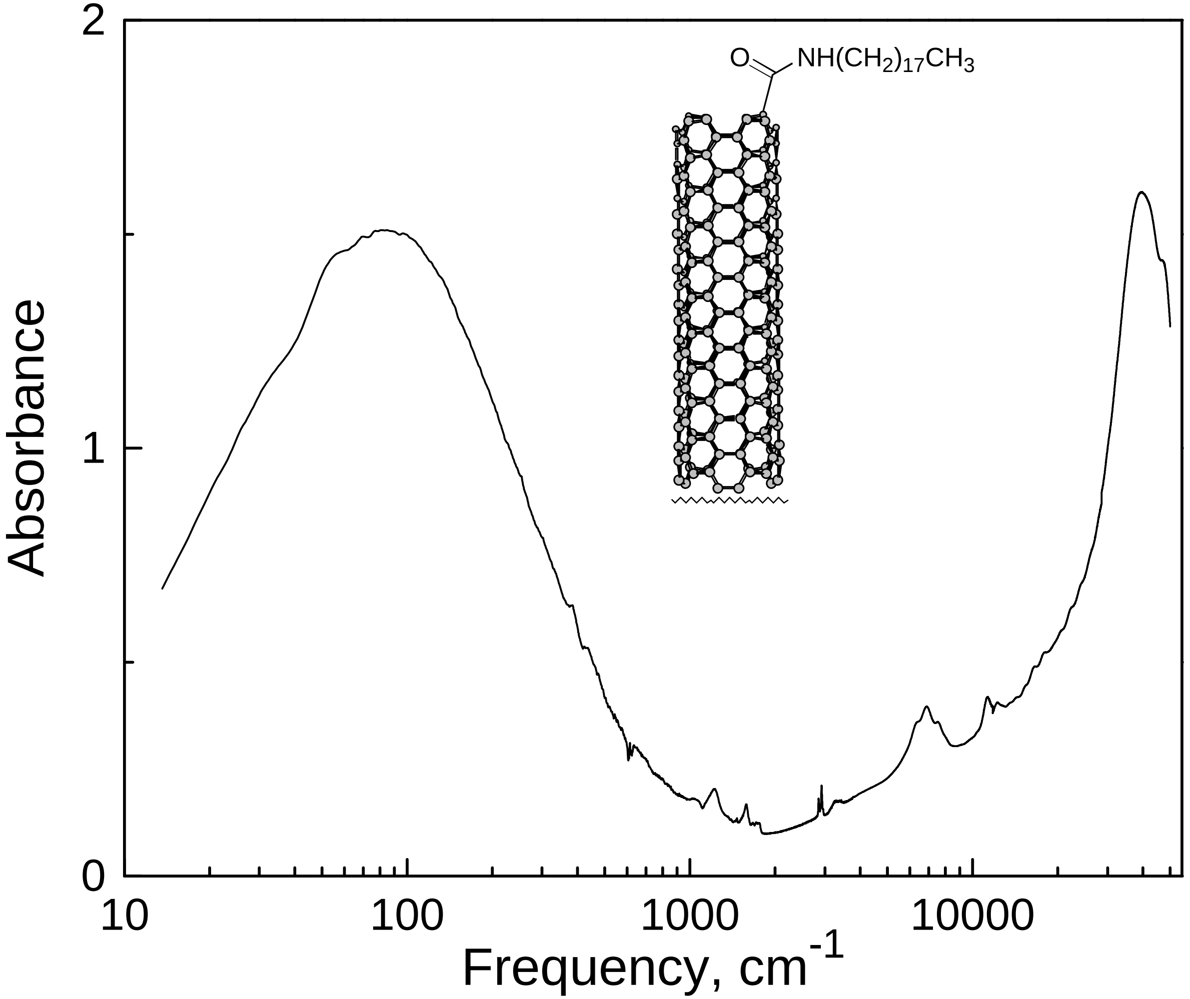




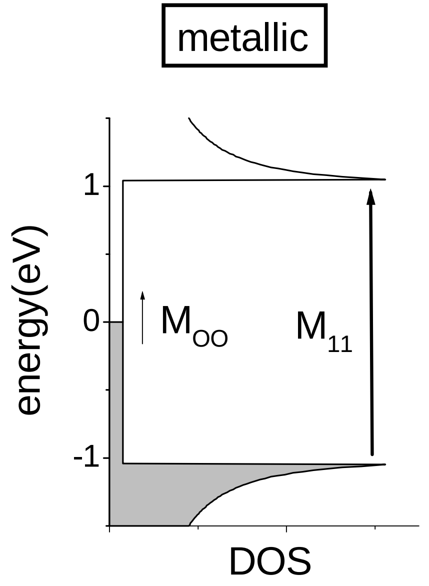
Chen, Y.; Haddon, R. C.; Fang, S.; Rao, A. M.; Eklund, P. C.; Lee, W. H.; Dickey, E. C.; Grulke, E. A.; Pendergrass, J. C.; Chavan, A.; Haley, B. E.; Smalley, R. E. *J. Mater. Res.* **1998**, *13*, 2423-2431.
Chen, J.; Hamon, M. A.; Hu, H.; Chen, Y.; Rao, A. M.; Eklund, P. C.; Haddon, R. C. *Science* **1998**, *282*, 95-98.
Hu, H.; Zhao, B.; Hamon, M. A.; Kamaras, K.; Itkis, M. E.; Haddon, R. C. *J. Am. Chem. Soc.* **2003**, *125*, 14893-14900.
Kamaras, K.; Itkis, M. E.; Hu, H.; Zhao, B.; Haddon, R. C. *Science* **2003**, *301*, 1501.

Side-Wall Functionalization of Soluble-SWNTs

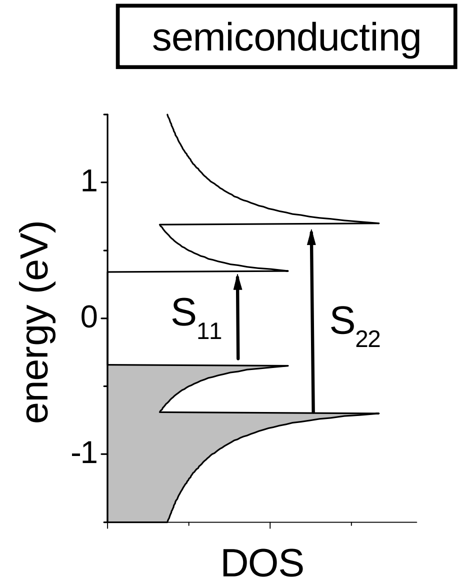




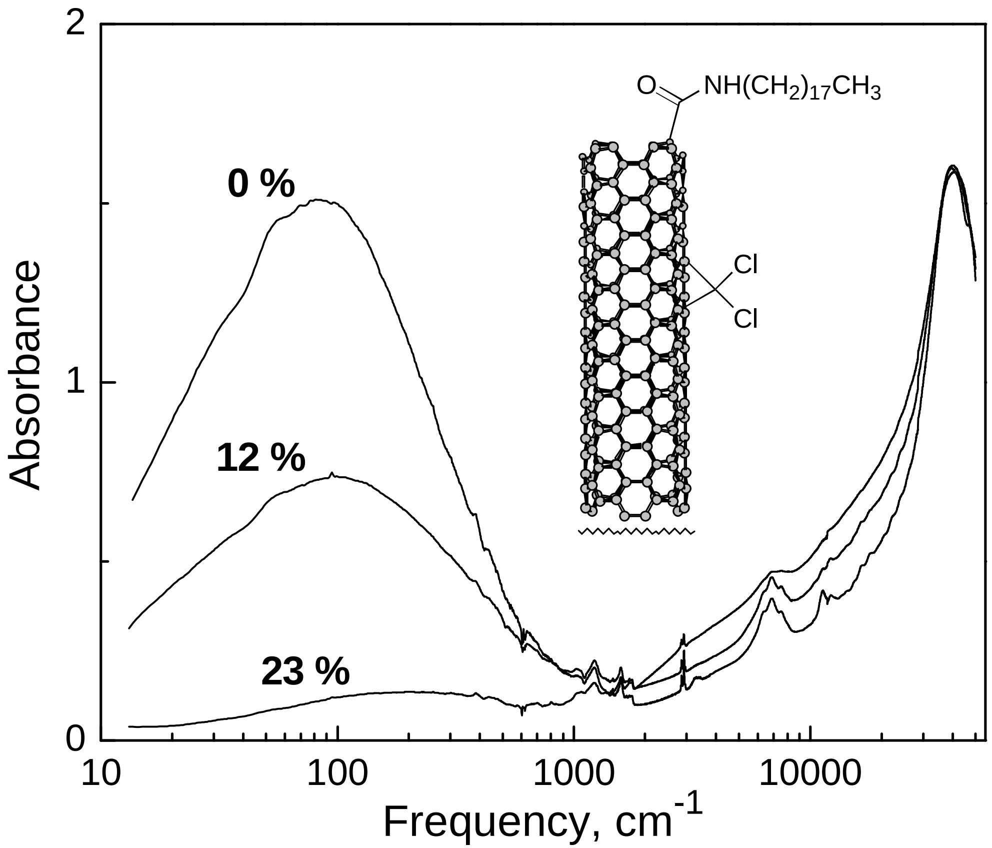
O
NH(CH2)17CH3
2
1
0
Absorbance
10
100
1000
10000
Frequency, cm-1



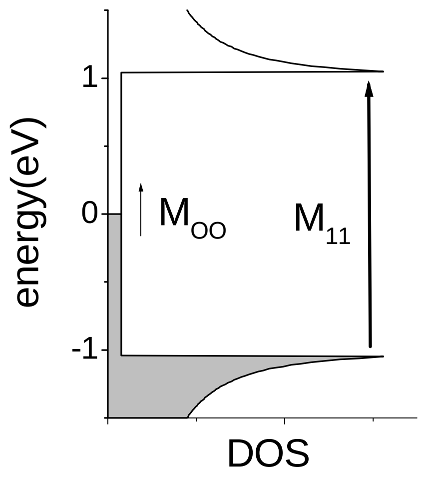
metallic
energy(eV)
1
0
-1
MOO
M11
DOS



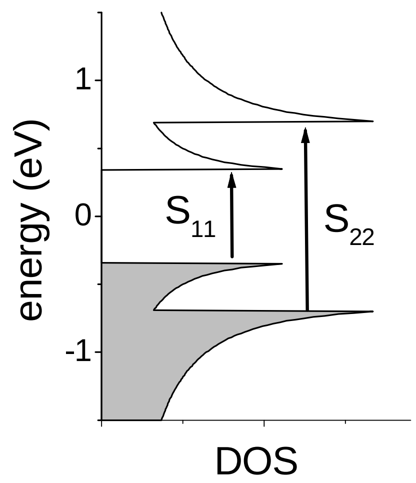
semiconducting
energy (eV)
1
0
-1
S11
S22
DOS

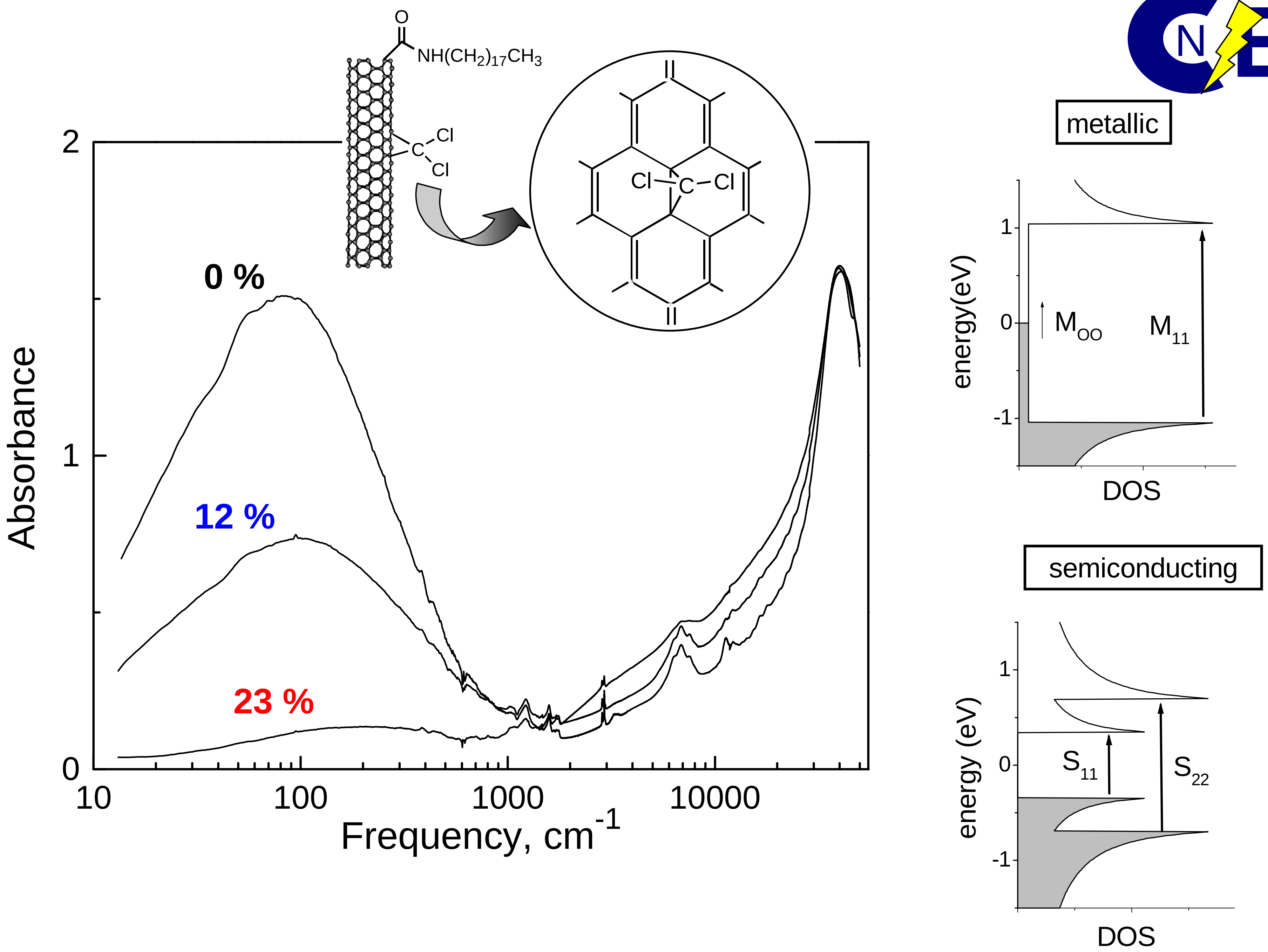


metallic



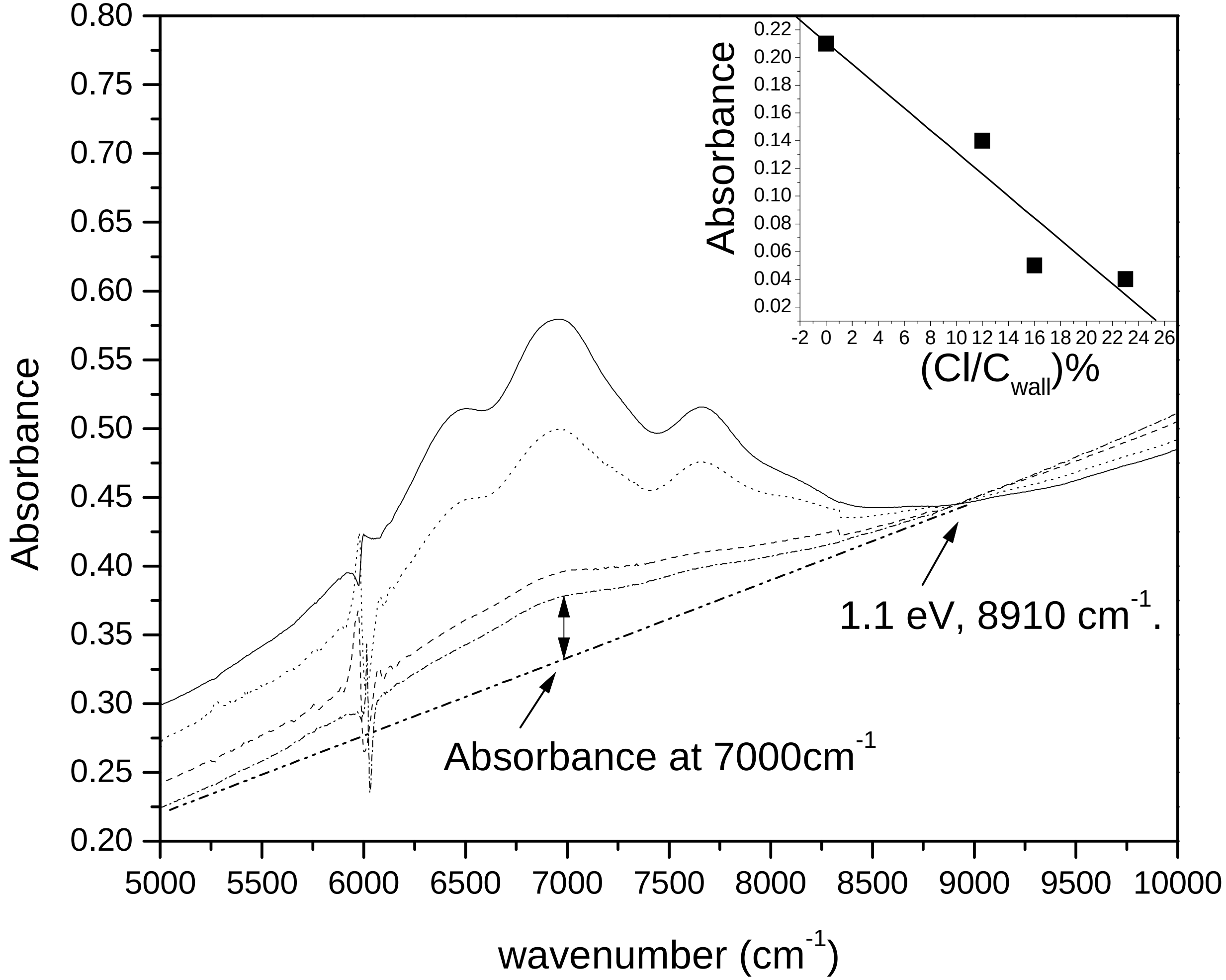
semiconducting





NH(CH2)17CH3
O
Cl
C
Cl
Cl
C
Cl
0 %
12 %
23 %
Absorbance
2
1
0
10
100
1000
10000
Frequency, cm-1
metallic
energy(eV)
M11
MOO
DOS
semiconducting
energy (eV)
S11
S22
DOS

Near-IR Spectra of SWNTs versus Degree of Functionalization



Near IR Purity Standard for Single-Walled Carbon Nanotubes

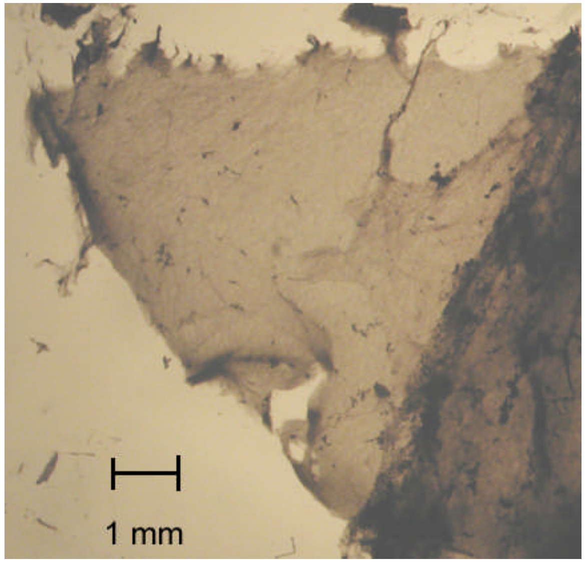
Rapid, well defined, and quantitative

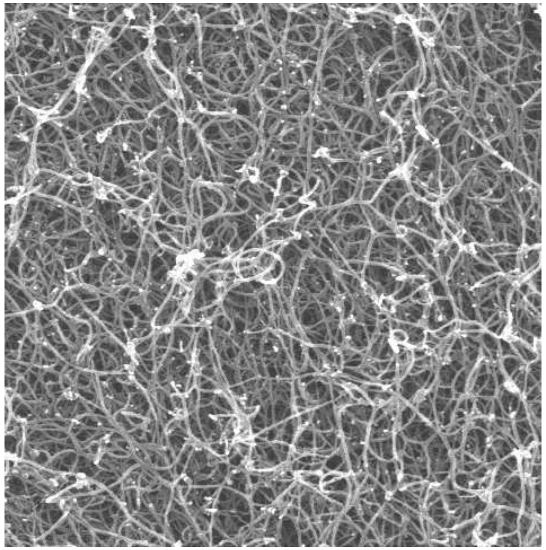
Widely available

Applicable to bulk samples

…but sensitive to nanostructure

As-Prepared SWNT Soot

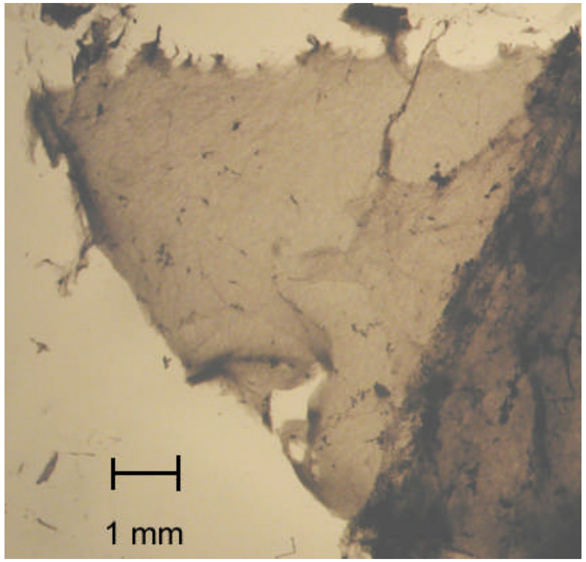


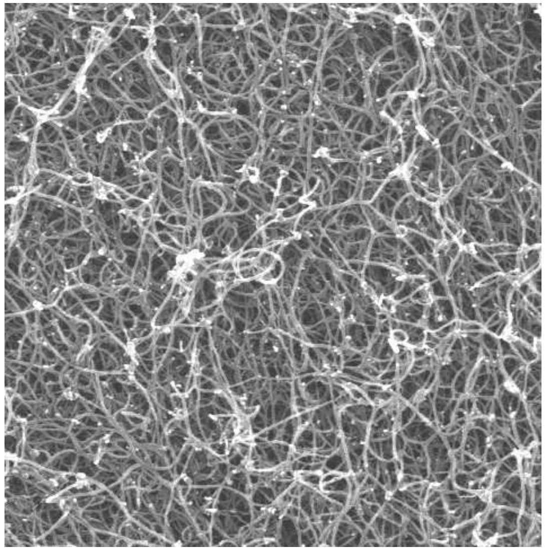


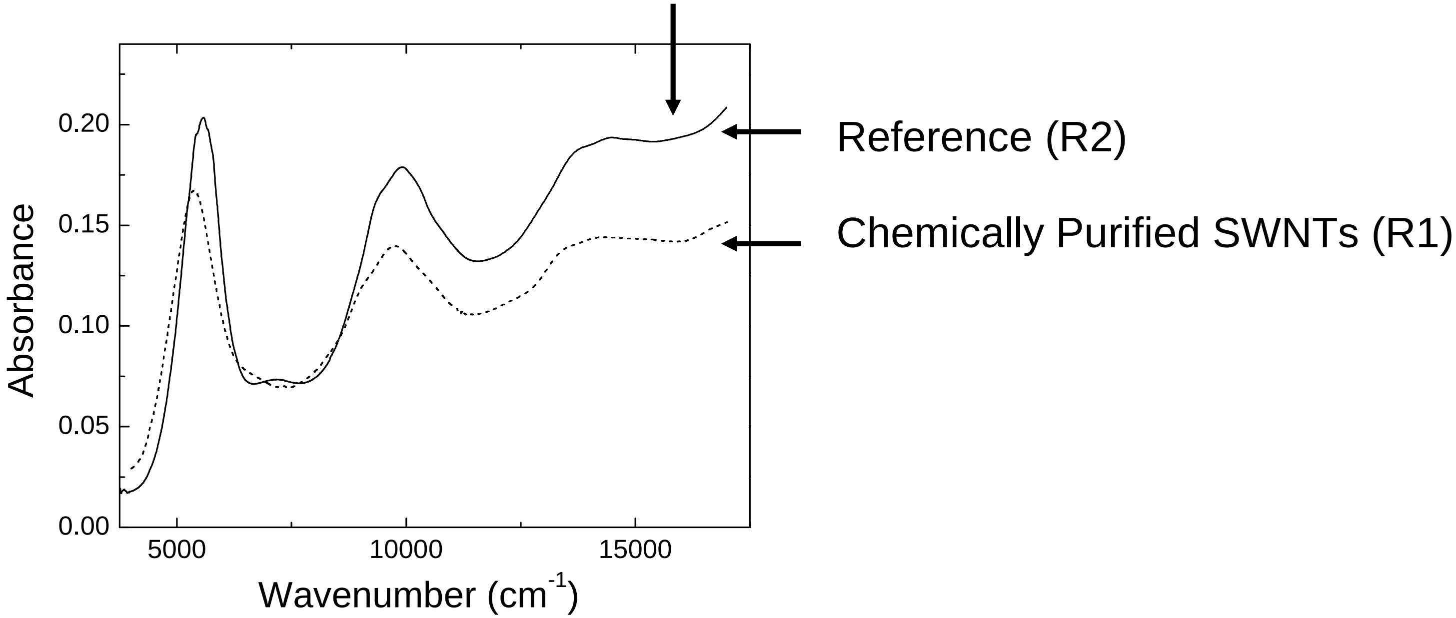
Web growth

M. E. Itkis *et al*. *Nano Lett* **3**, 309 (2003).

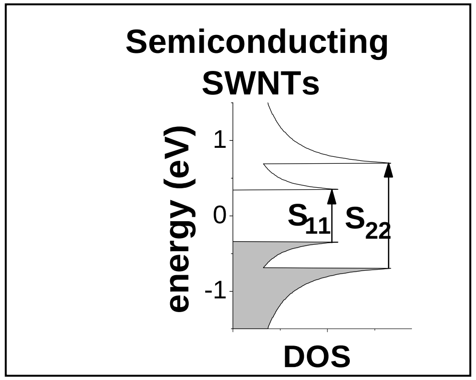
As-Prepared SWNT Soot – Seeded Web Growth

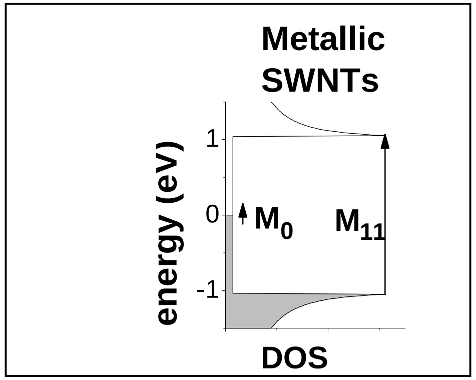


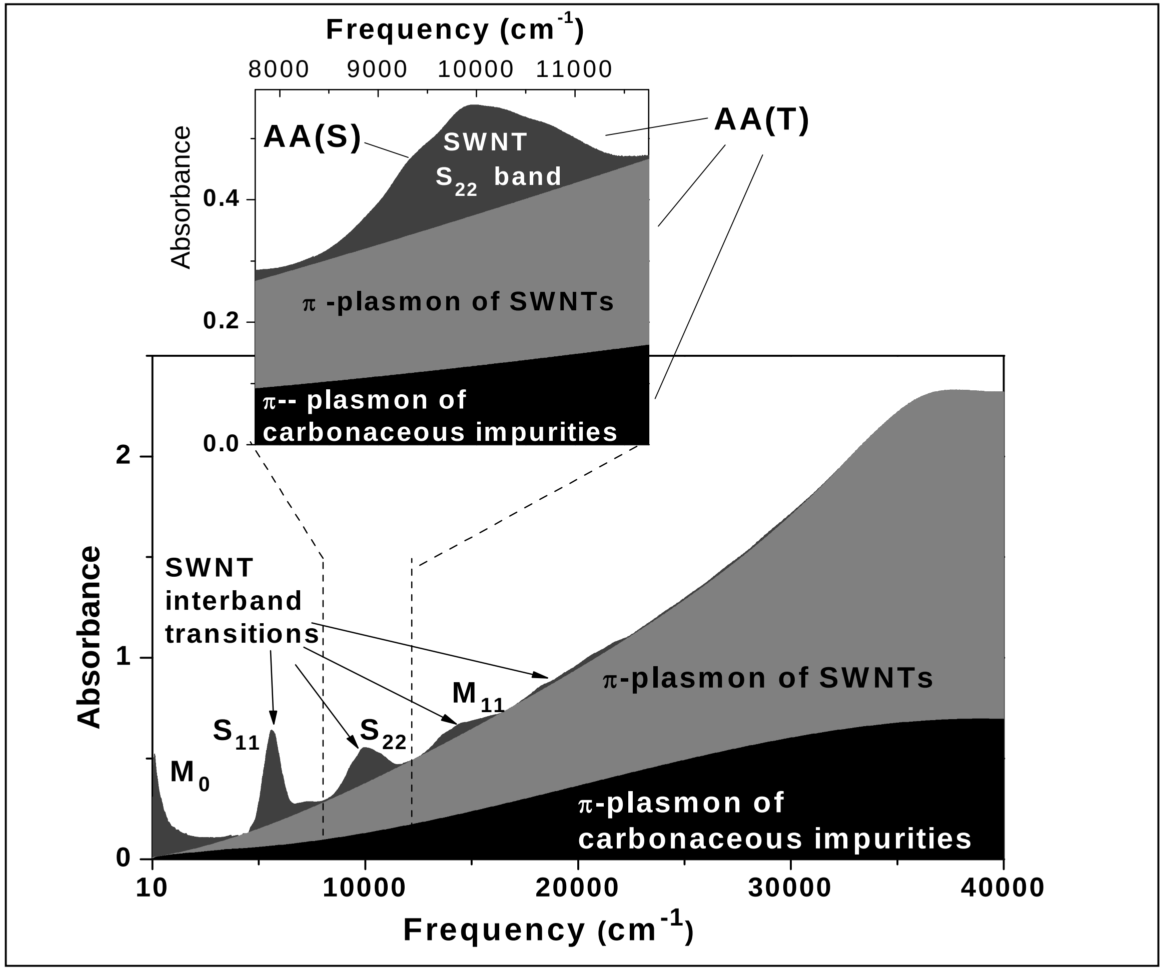




Purity evaluation





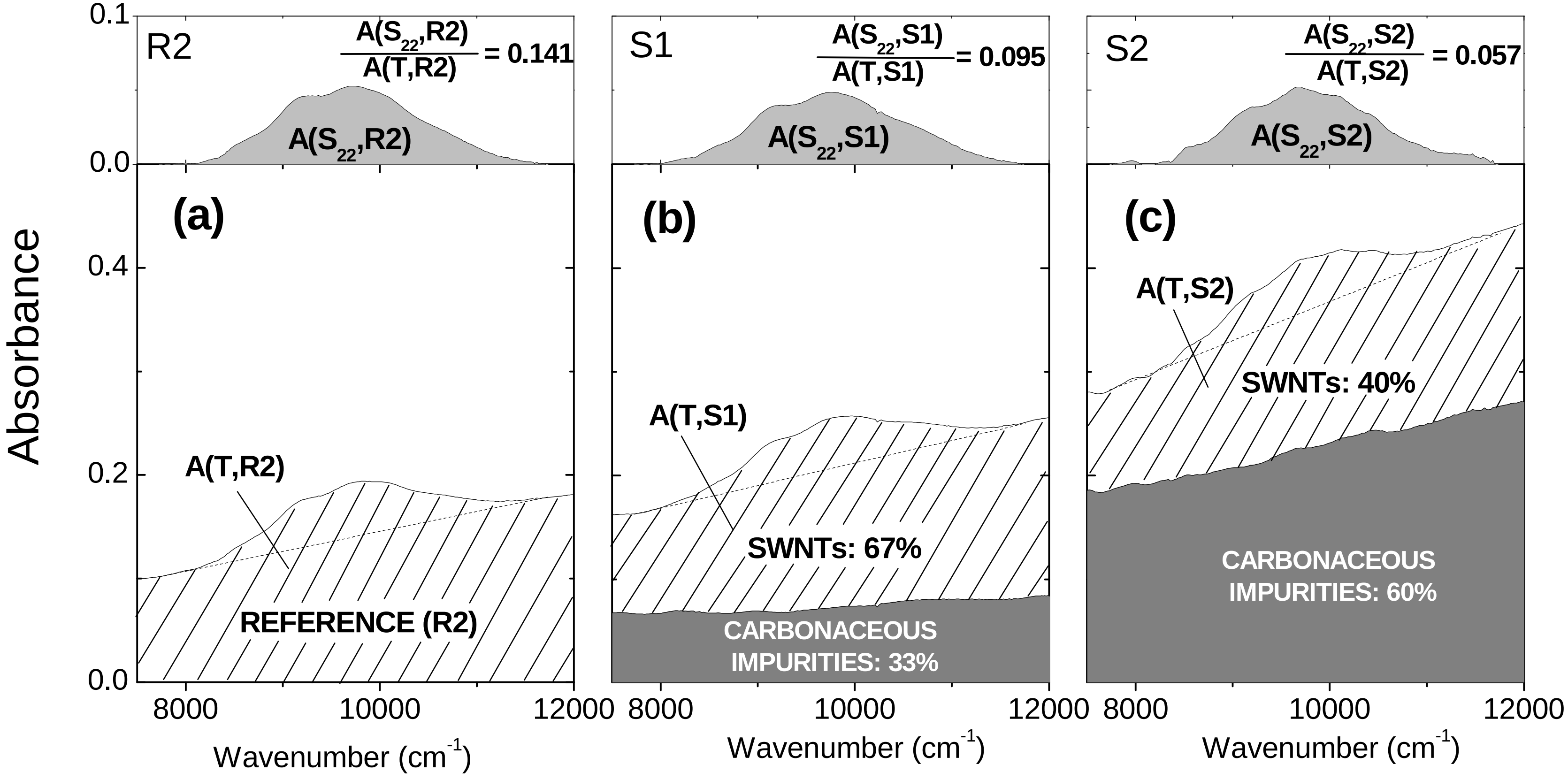


Solution phase near-IR spectroscopy provides relative purity (RP) of SWNTs against reference standard

Itkis M. et al Nanoletters, 2003, 3, 309; Haddon R. et al MRS Bulletin 2004, 29, 276.

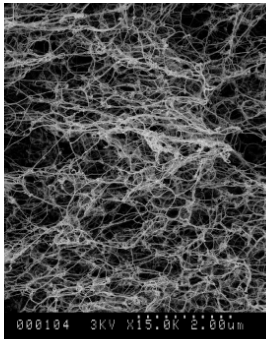
NIST http://www.msel.nist.gov/Nanotube2/Carbon_Nanotubes_Guide.htm

Purity Evaluation of As-Prepared SWNT Soot



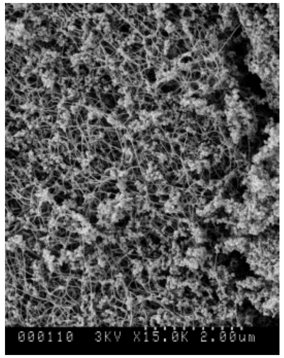
M. E. Itkis, *et al. Nano Lett* **3**, 309 (2003).

Chemistry of Single-Walled Carbon Nanotubes (SWNTs)



Analytical techniques

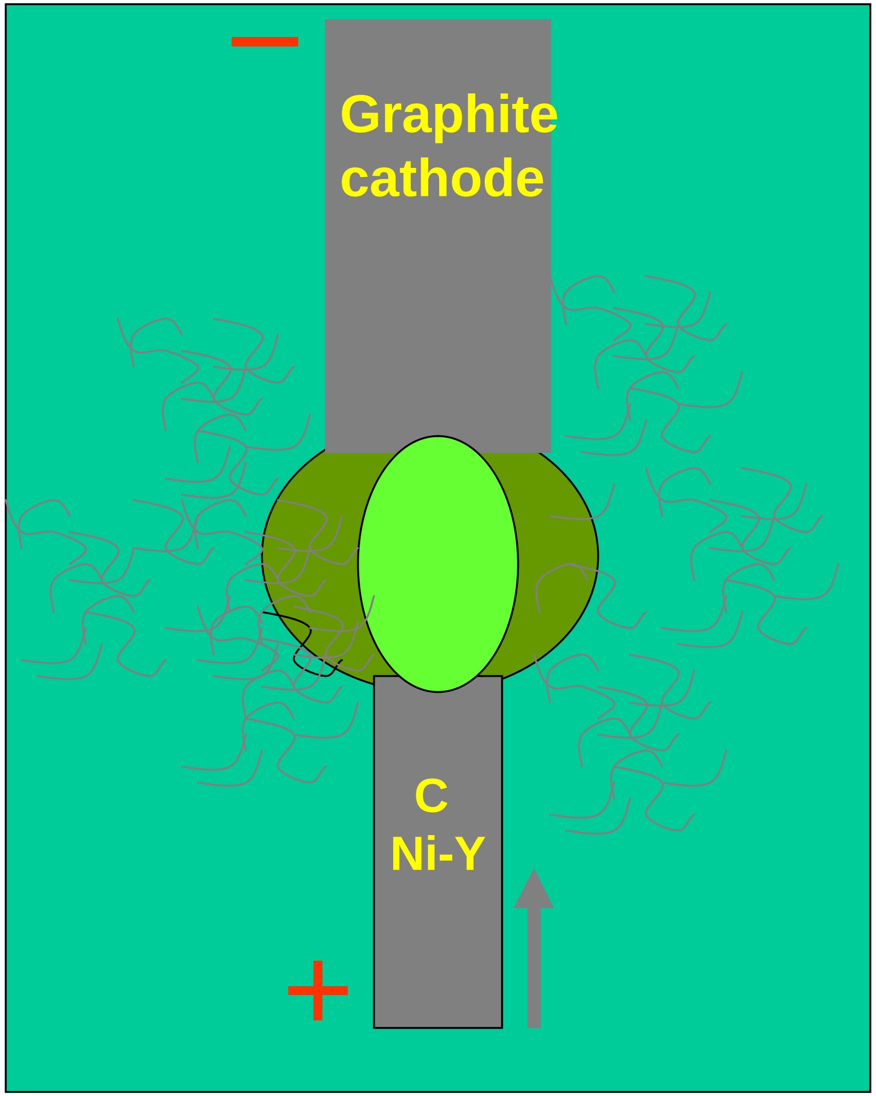
Measure of purity



Quality Control in the Carbon Nanotube Industry (2003)

Source	Advertised Purity (%)	NIR Purity (%)
Carbon Solutions Inc.	30-50	40
Aldrich Chemical	50-70	30
Alfa Aesar	10-20	15

Electric Arc Discharge Synthesis of SWNTs



Iijima and Ichihashi, *Nature* **1993,** 363, 603-605.

Bethune *et al* *Nature* **1993,** 363, 605-607.

Rate: 10-30g/hour

Problem – byproducts:
Carbonaceous impurities,
metallic nanoparticles

Parameters:

- Buffer gas – type, pressure
- Electrode composition
- Arc current/voltage
- Chamber geometry
- Temperature field

Metal Catalysts

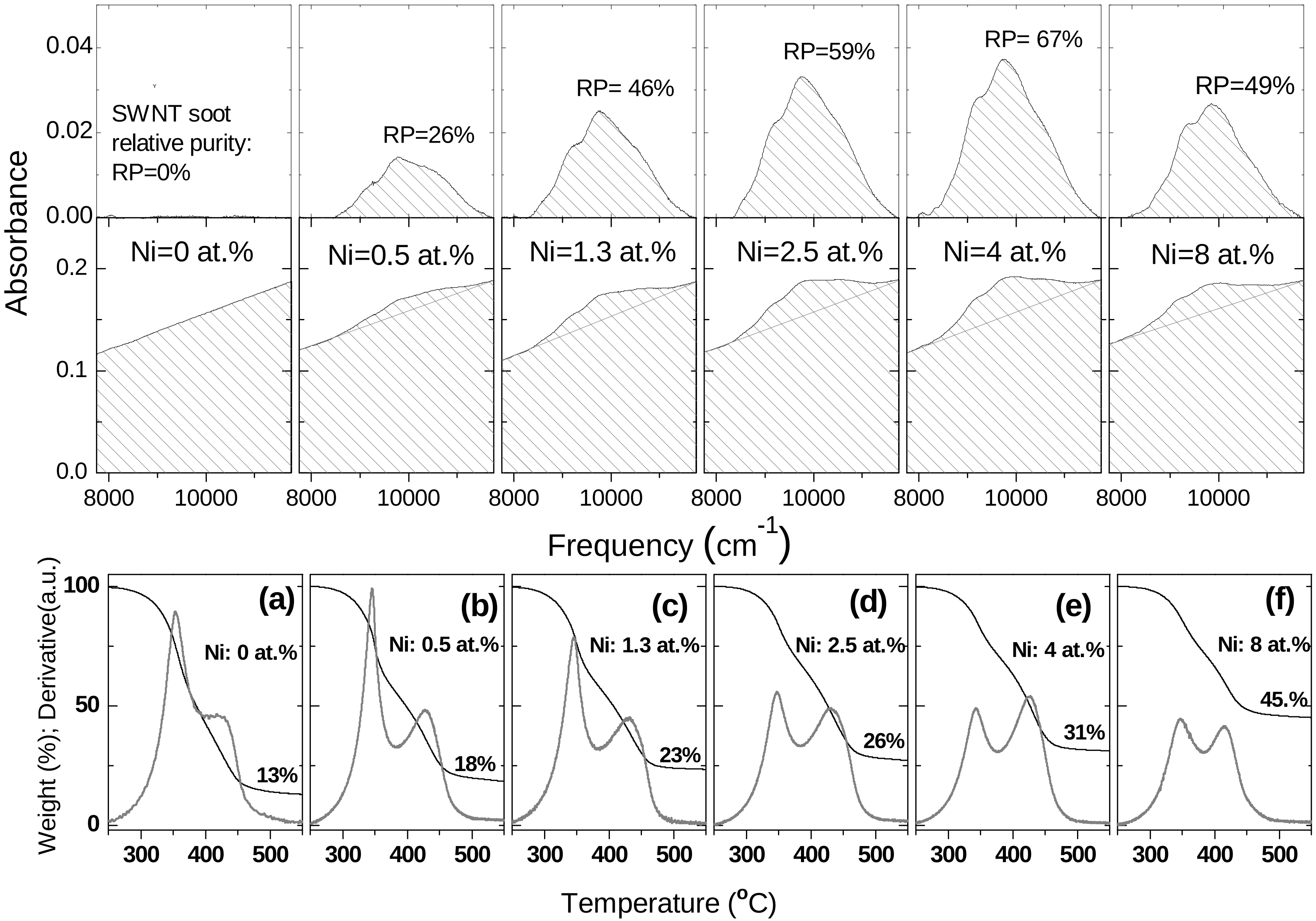
Co, Co/Ni, Co/Y, Co/Fe, Co/Pt, Co/Cu, Ni/Fe, Fe, Rh/Pt

Ni:Y 4:1 at.%, C=95 at.% , ***Journet et al Nature 1997, 388, 756-758.***

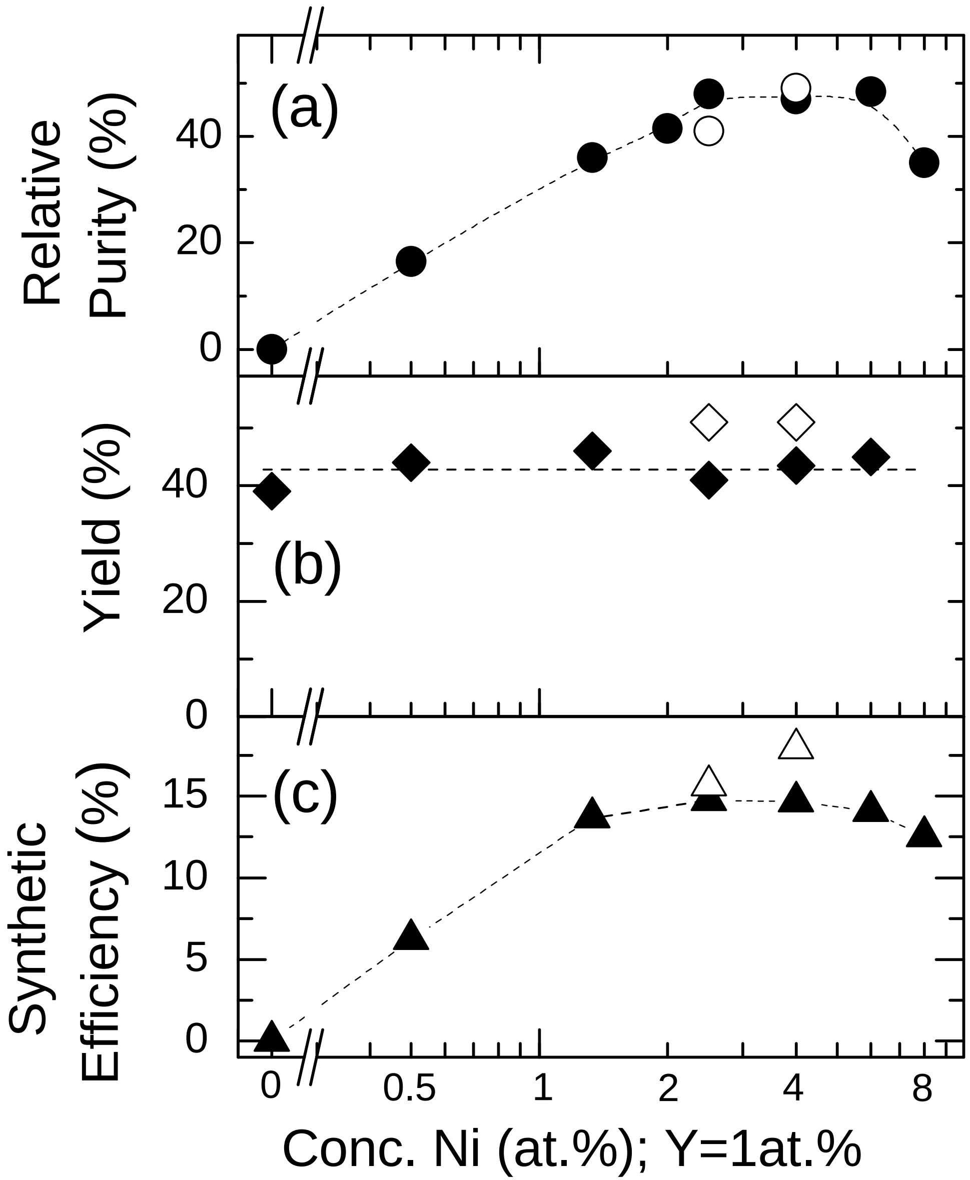
Ni:Y (0.6-0.4):0.1 at.% , ***Takizawa et al Chem. Phys. Lett. 2000, 326, 351-357.***

Analysis: SEM, TGA, Raman
(milligram scale)

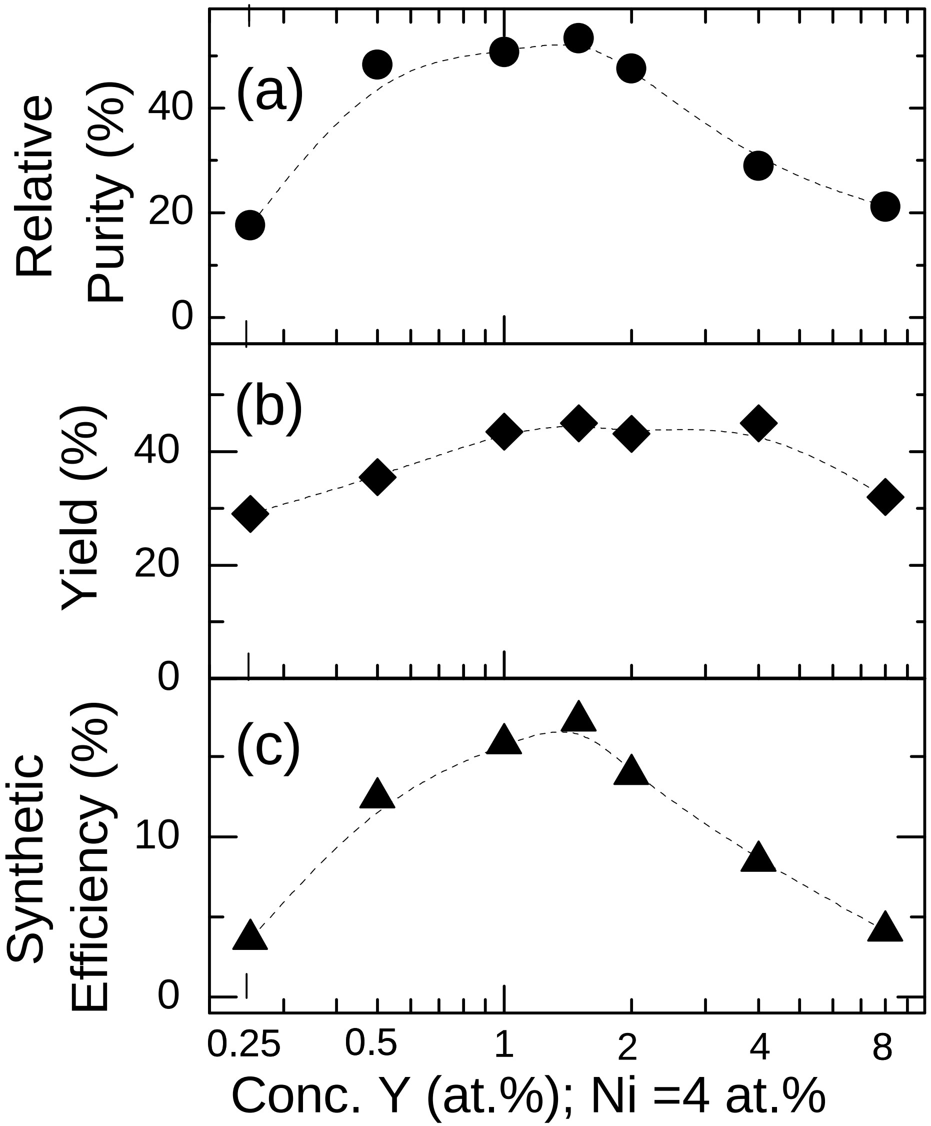
Variation of Ni with Y held constant at 1 at%

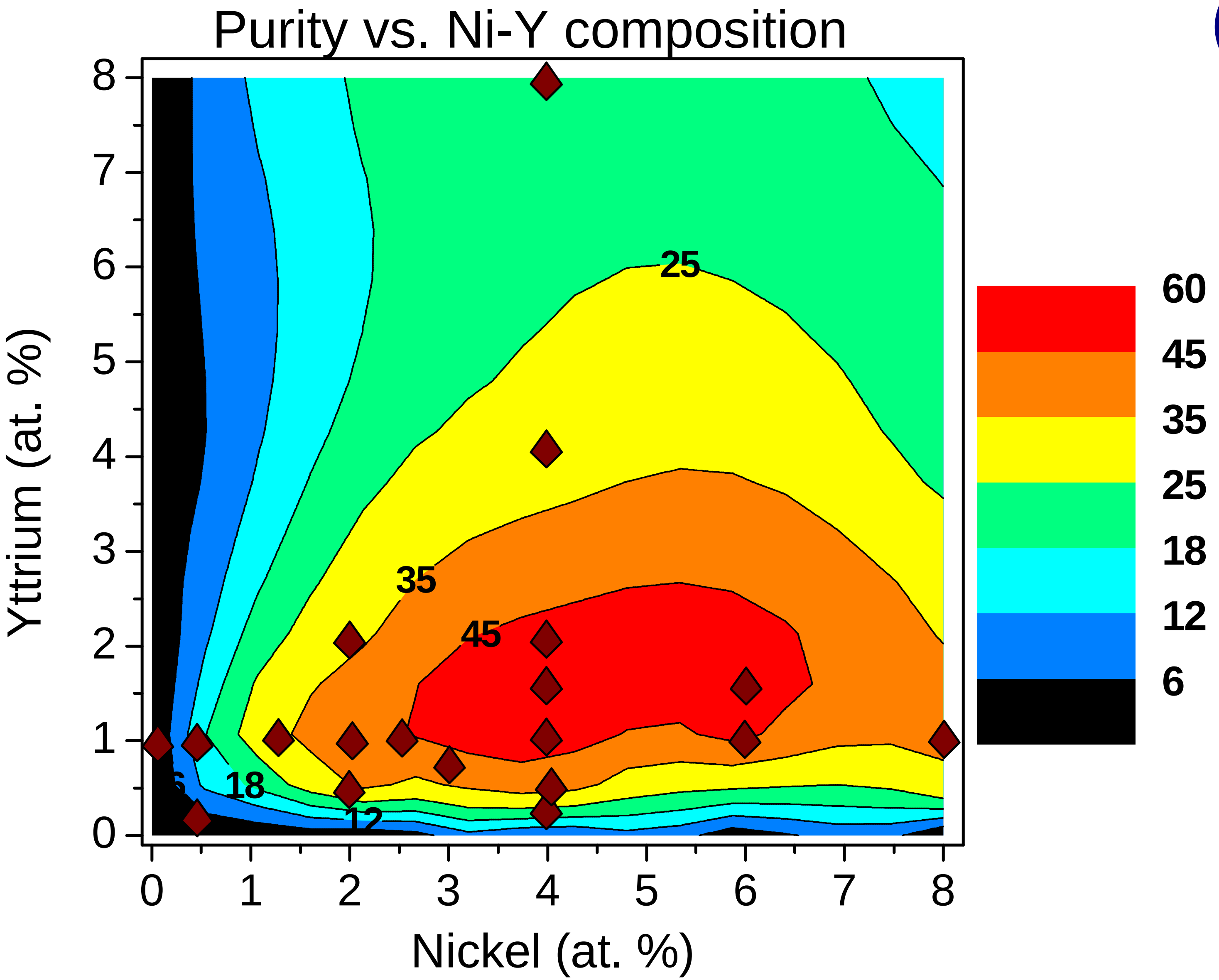


Variation of Ni with Y held constant at 1 at%



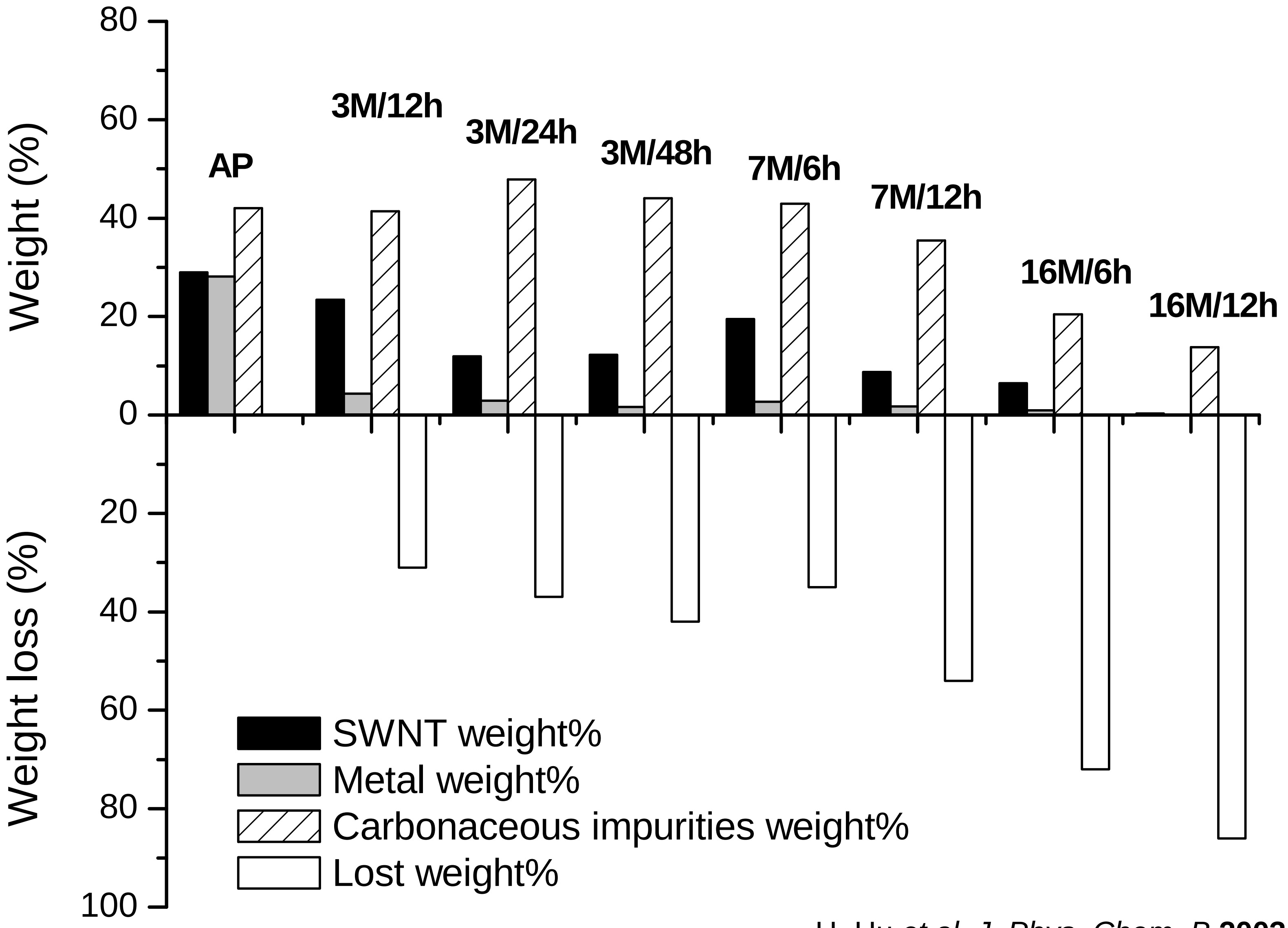
Variation of Y, with Ni held constant at 4 at%





Itkis, M. E.; Perea, D.; Niyogi, S.; Love, J.; Tang, J.; Yu, A.; Kang, C.; Jung, R.; Haddon, R. C., Optimization of the Ni-Y Composition in Bulk Electric Arc Synthesis of Single-Walled Carbon Nanotubes by Using Near-Infrared Spectroscopy. *J. Phys. Chem. B* **2004,** 108, 12770-12775.

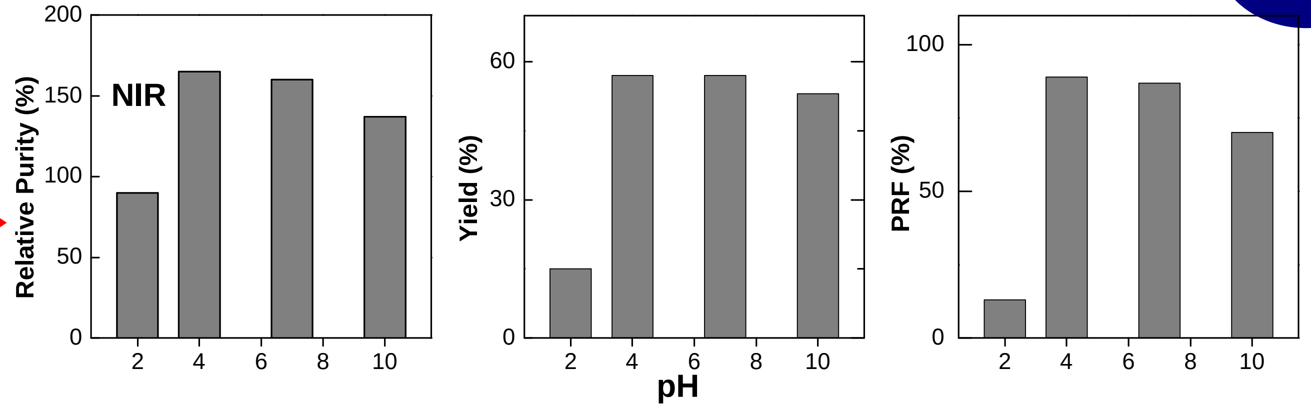
Nitric Acid Purification of Single-Walled Carbon Nanotubes



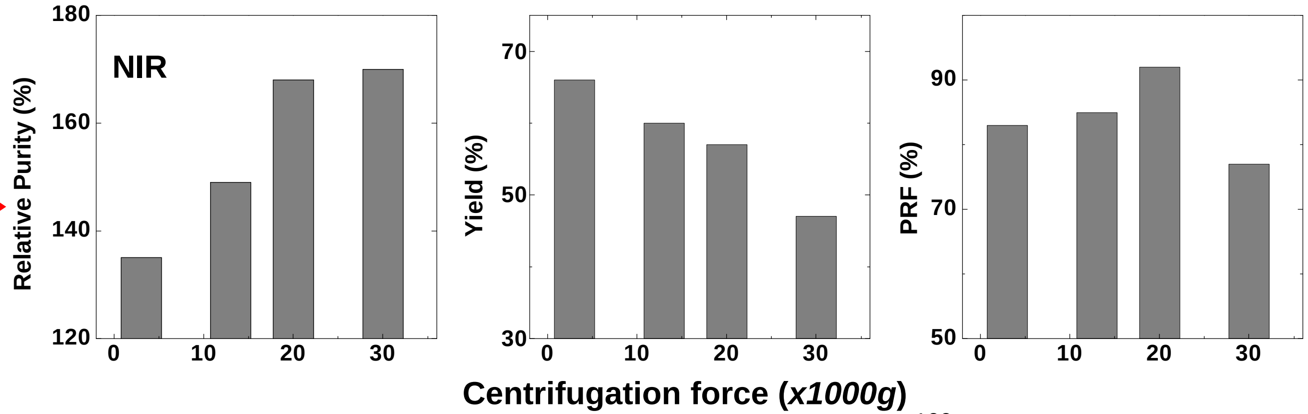
H. Hu *et al*. *J. Phys. Chem. B* **2003**, 107, 13838.

Process Optimization using NIR Spectroscopy

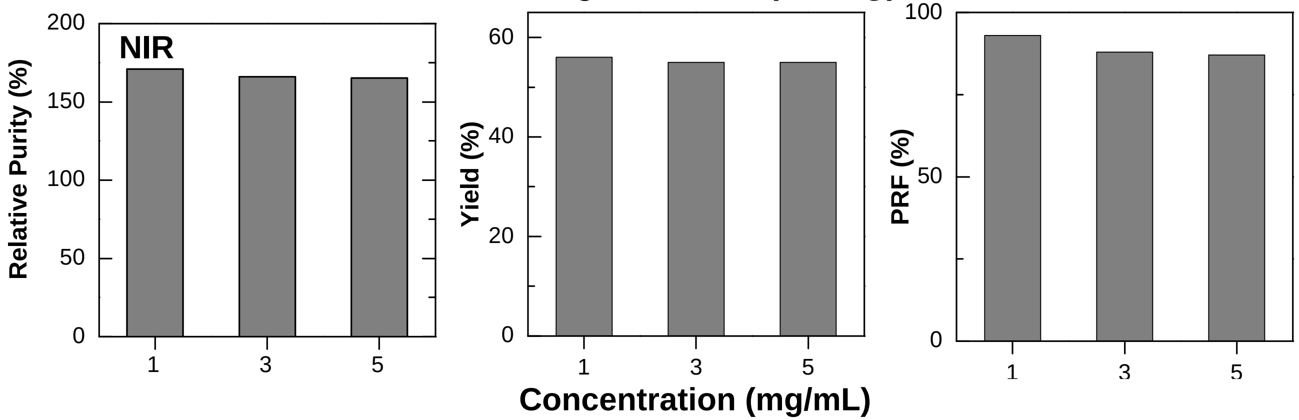
pH



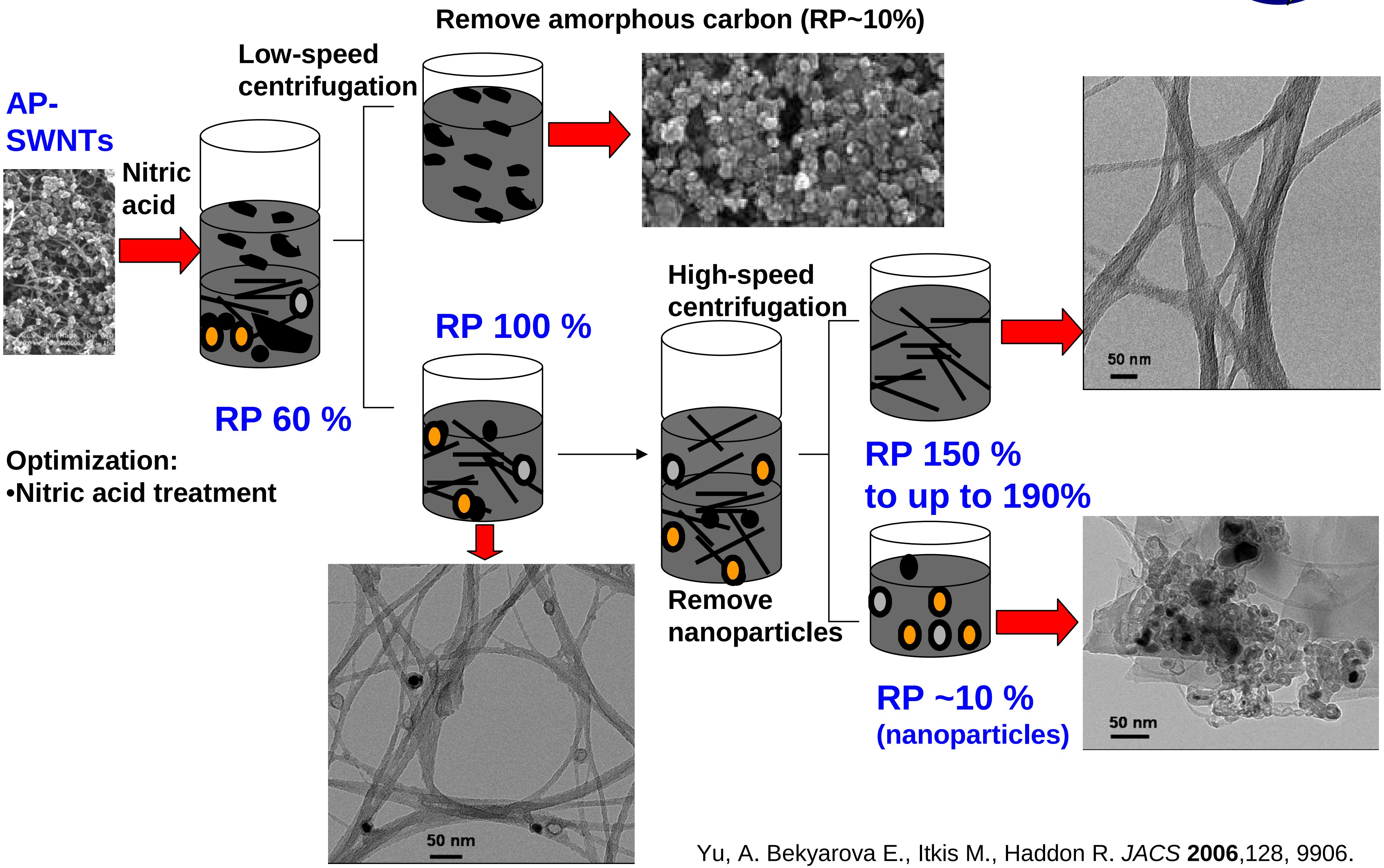
Centrifugation force



Starting concentration

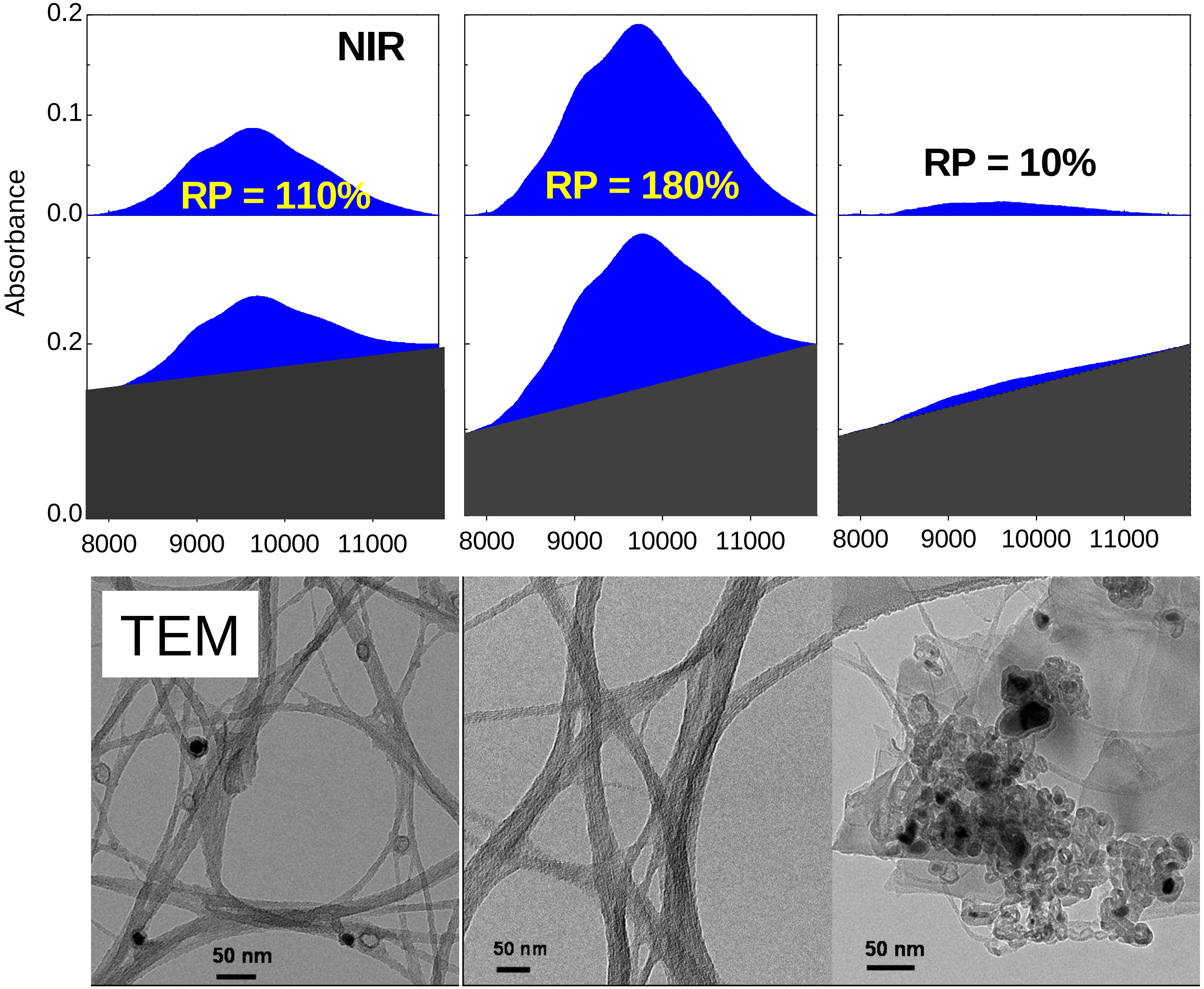


Large scale purification procedure



Yu, A. Bekyarova E., Itkis M., Haddon R. *JACS* **2006**,128, 9906.

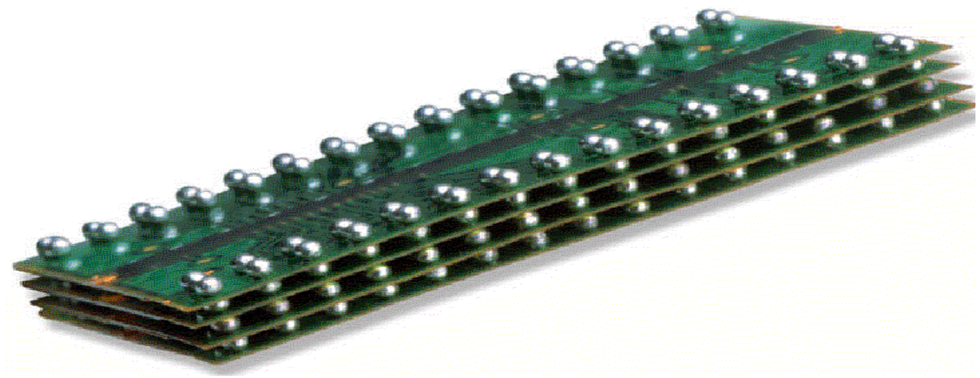
Results of Purification: Removing of Nanoparticles



Yu, A. Bekyarova E., Itkis M., Haddon R., *J. Am. Chem. Soc.* **2006,** 128, 9902-9908.

Effect of Carbon Nanotube Purity on Physical Properties

Thermal management in high density modules: bonding, thermal interfaces



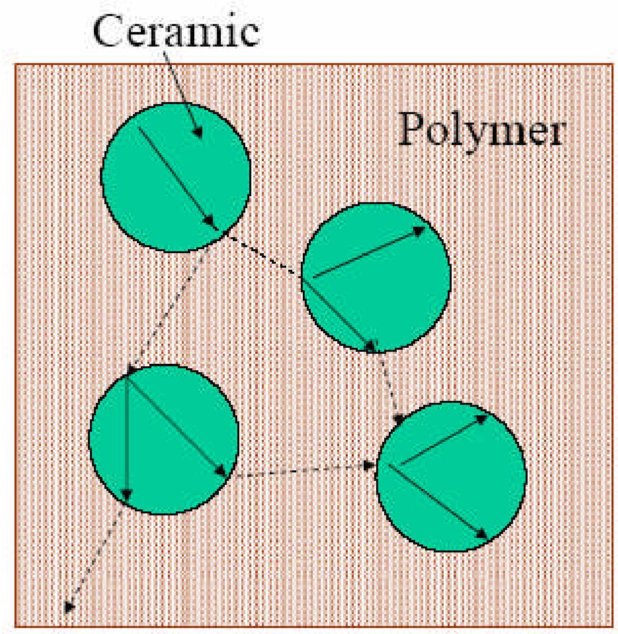
Component	Material	k (W/m.K)
Die	**Silicon**	**f(T)**
Tape	**Polyimide**	**0.2**
Elastomer	**Silicone**	**0.2**
Solder ball	**Eutectic**	**50.1**
Board dielectric	**FR4**	**0.3**
Traces	**copper**	**390**

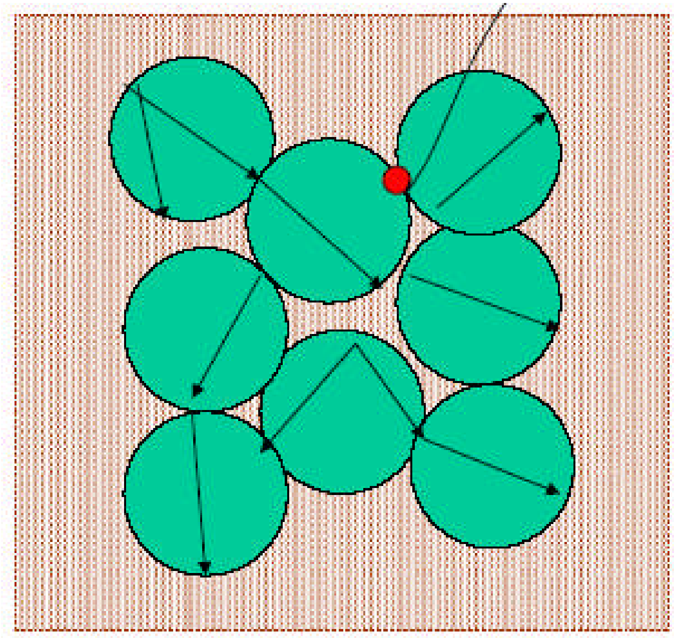
Thermal interface materials need improvement

Source: Tessera

Current approaches in thermal management

Addition of Ag, Al_2O_3 or SiC particles to polymer





$k_{polymer} \sim O\,(0.1)$ W/m-K

$k_{filler} \sim O\,(1\text{-}1000)$ W/m-K

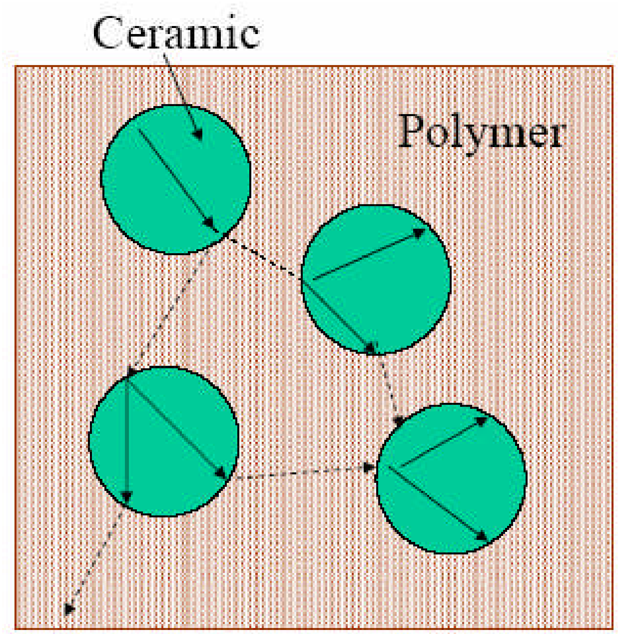
$k_{TIM} \sim O\,(1)$ W/m-K

Drawbacks:
Poor particle-particle contact is a severe problem

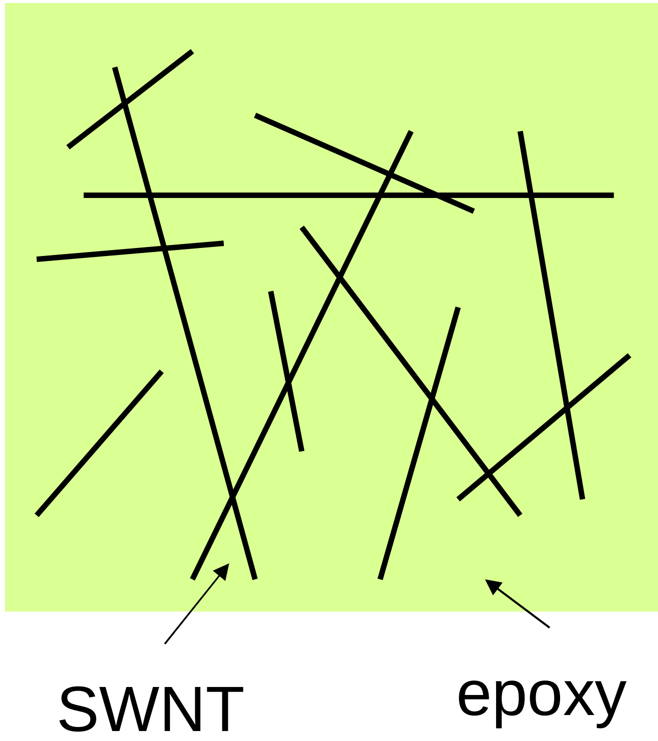
Problem: Very high filler loading required (60-80wt%) – viscosity increases faster than thermal conductivity

Source: IBM

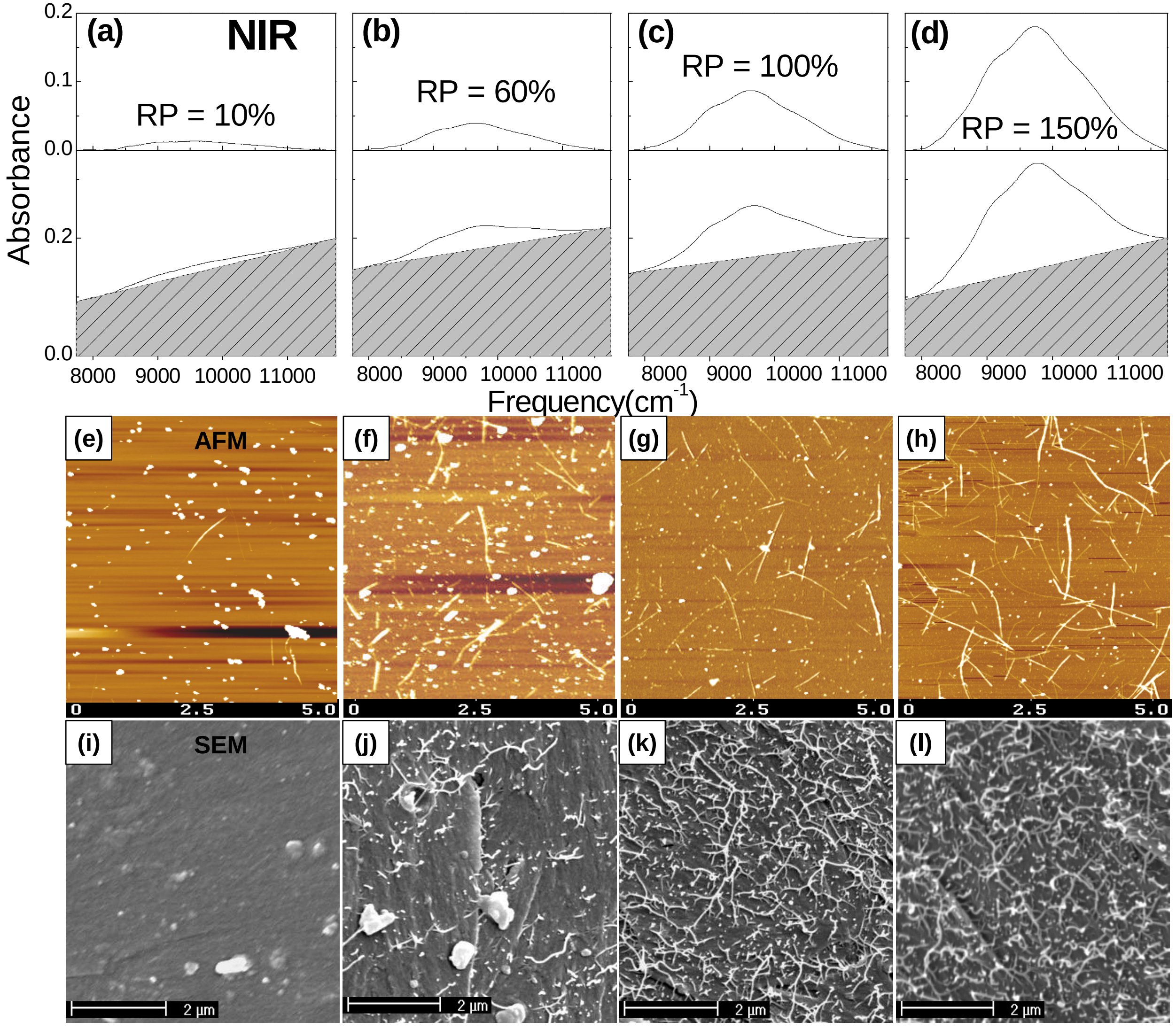
Utilization of carbon nanotubes



Source: IBM



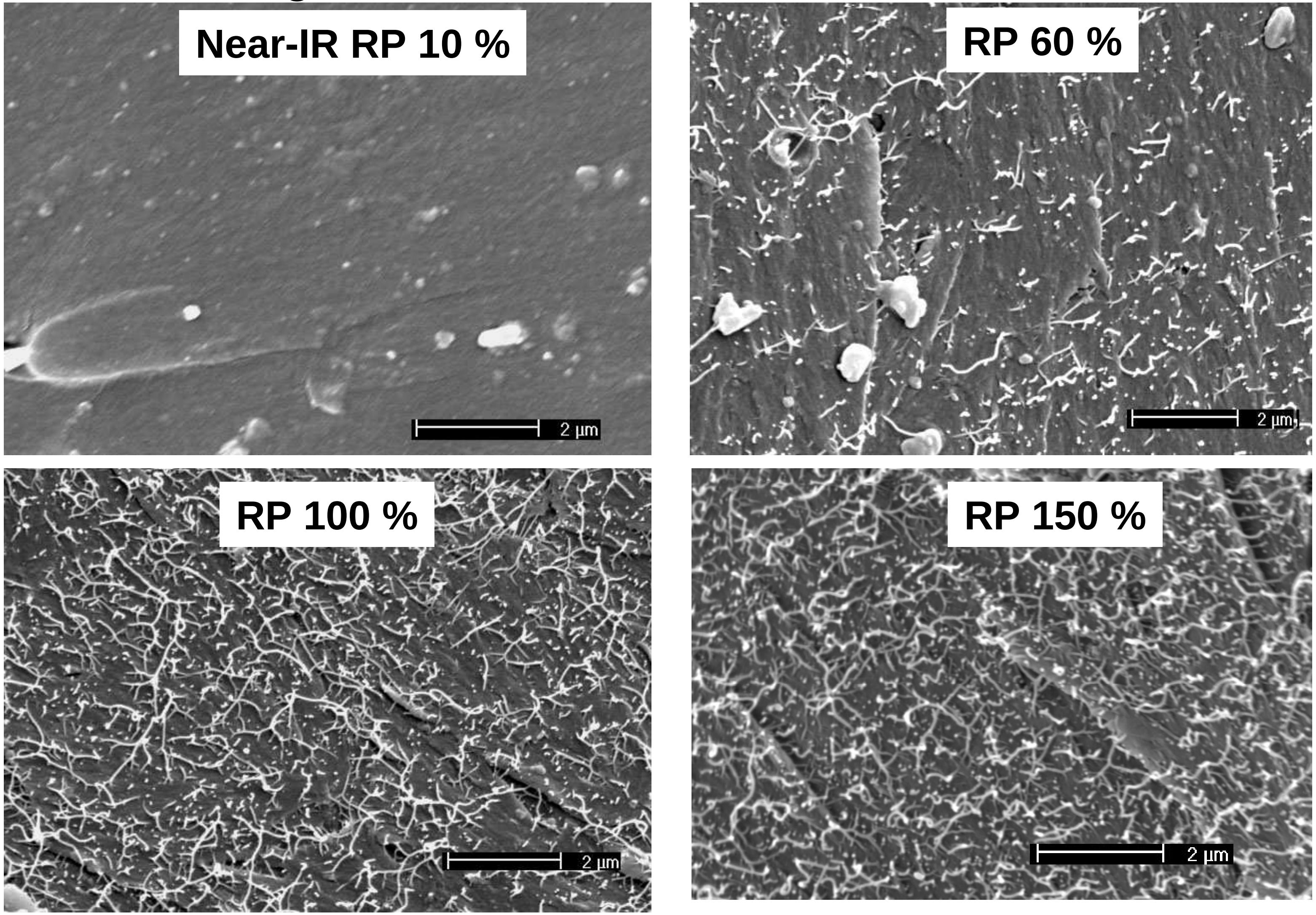
Single-walled carbon nanotube (SWNT) epoxy composite thin films as a function of SWNT purity



Yu, A.; Bekyarova, E.; Itkis, M. E.; Fakhrutdinov, D.; Webster, R.; Haddon, R. C., Application of Centrifugation to the Large-Scale Purification of Electric Arc Produced Single-Walled Carbon Nanotubes. *J. Am. Chem. Soc.* **2006,** 128, (30), 9902-9908.

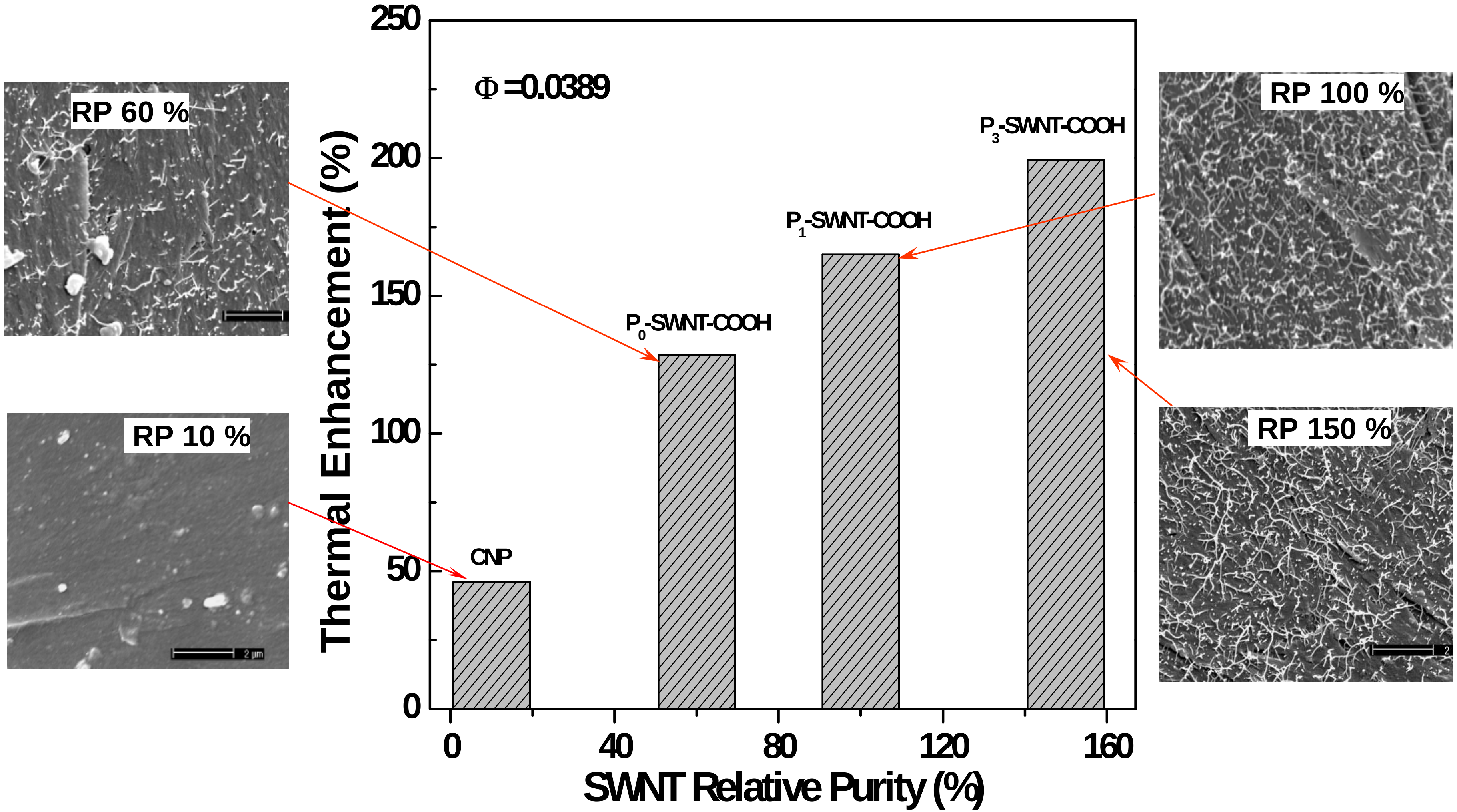
SEM of composites from different purity SWNT

5 wt% loading



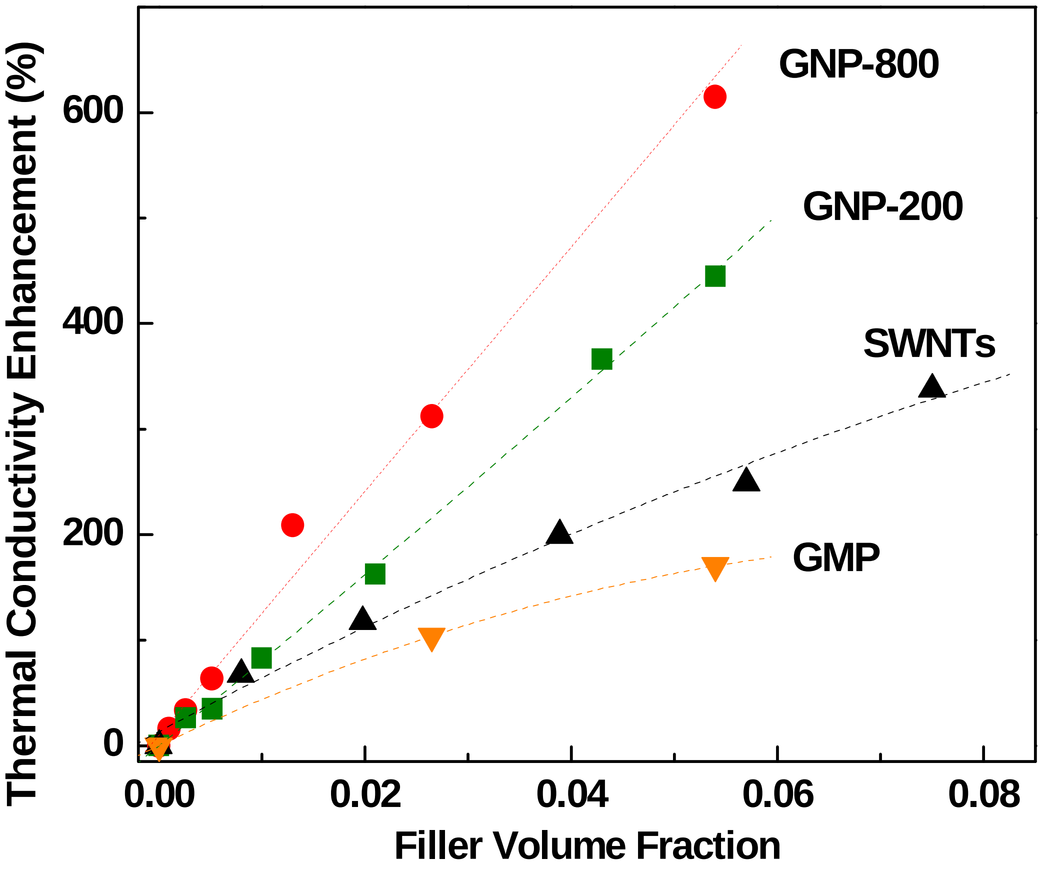
aspect ratio & thermal conductivity

SWNT purity effect on thermal conductivity of composites



Yu, A.; Itkis, M. E.; Bekyarova, E.; Haddon, R. C., Effect of Single-Walled Carbon Nanotube Purity on the Thermal Conductivity of Carbon Nanotube-Based Composites. *Appl. Phys. Lett.* **2006,** 89, (13), 133102.

Graphene Nanoplatelets

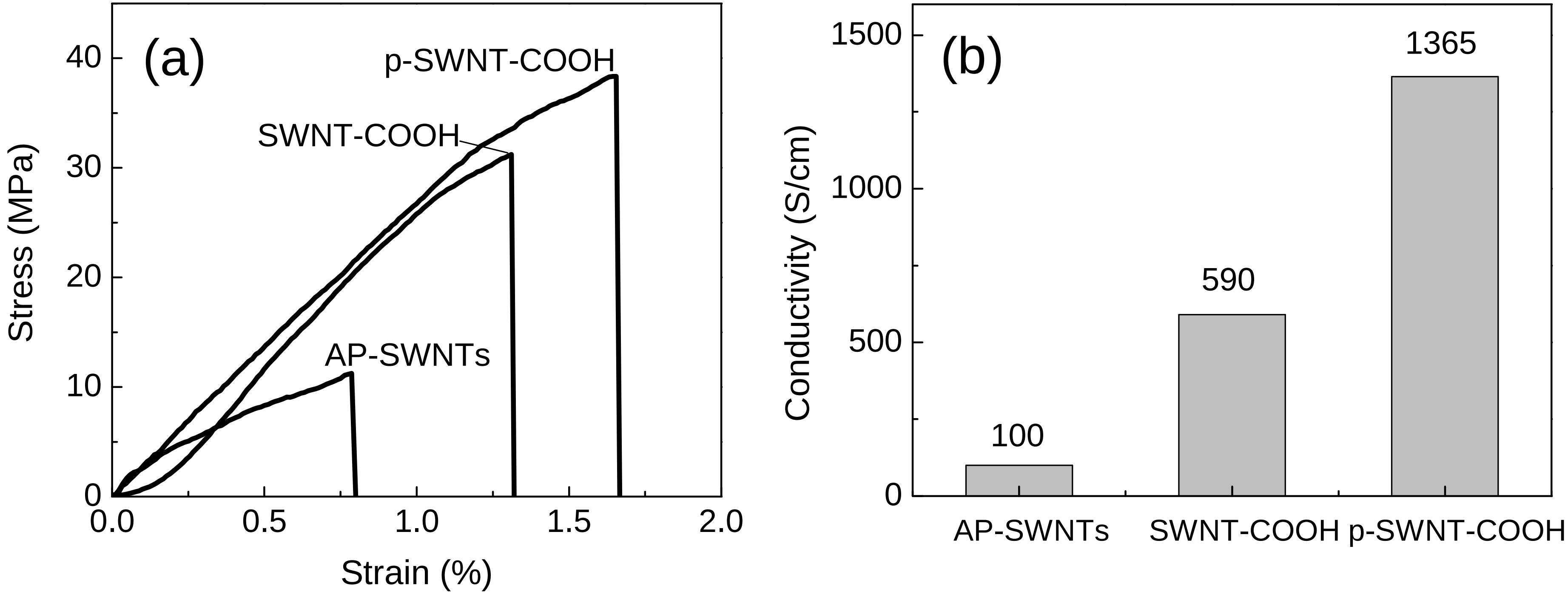


Yu, A.; Ramesh, P.; Itkis, M. E.; Bekyarova, E.; Haddon, R. C., Graphite Nanoplatelet-Epoxy Composite Thermal Interface Materials. *J. Phys. Chem. C* **2007,** 111, 7565-7569.

Properties of SWNT thin films as a function of purity

Free-standing films of thickness 40-70 μm prepared by vacuum filtration for three samples at various stages of purification:

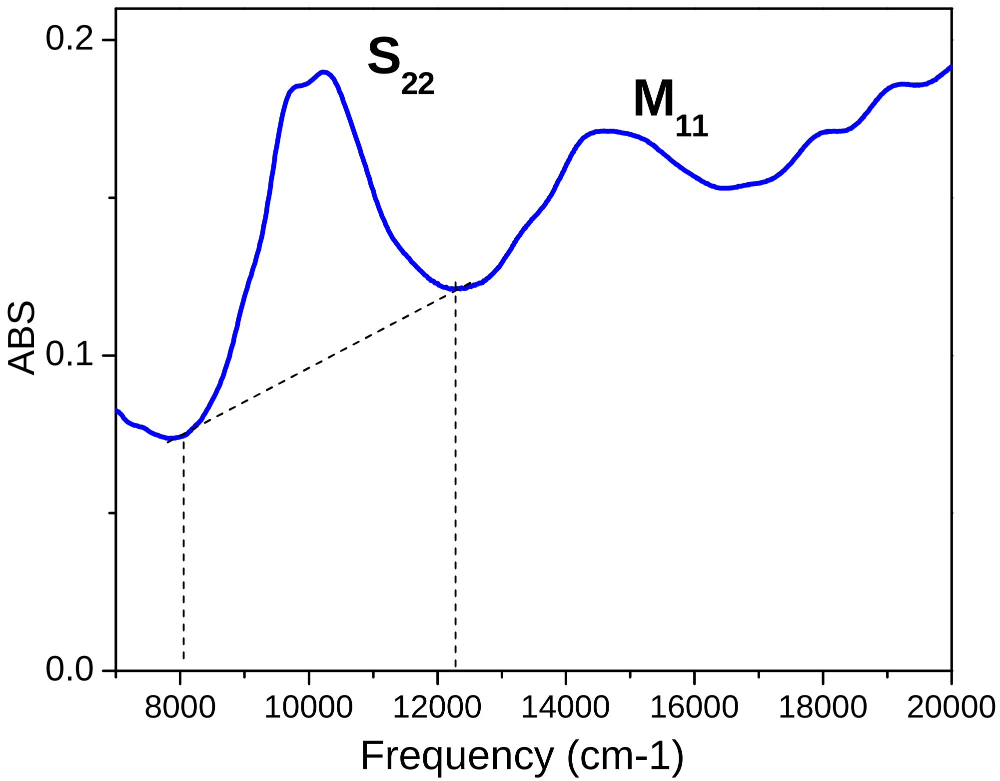
•As-prepared (**AP-SWNTs,** relative purity RP=60%)
•Nitric acid purified AP-SWNTs after removal of amorphous carbon (**SWNT-COOH**, RP=110%)
•SWNT-COOH after removal of carbon nanoparticles (**p-SWNT-COOH**, RP=170%)

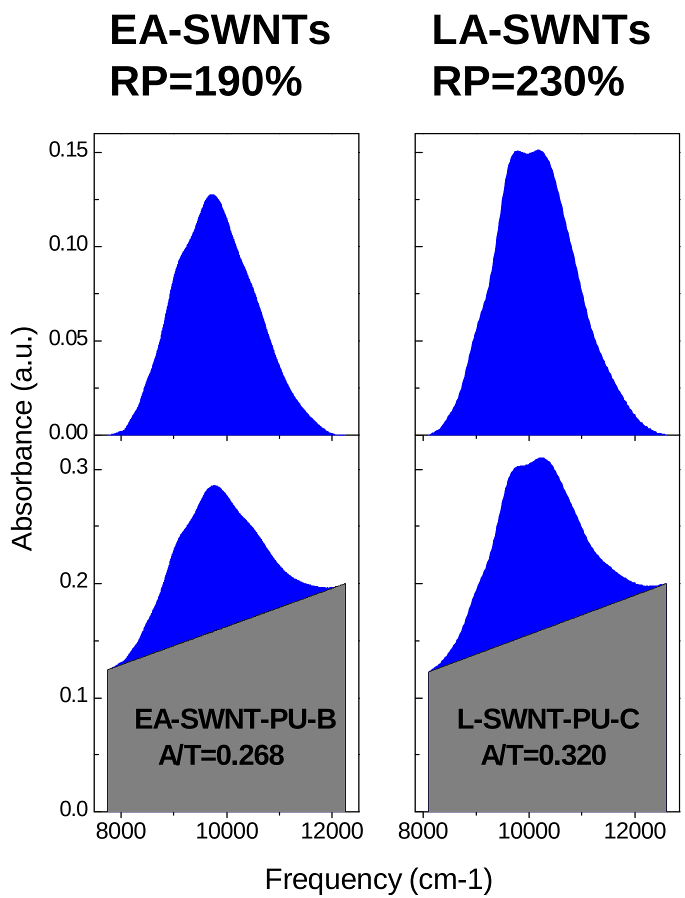


Yu, A.; Bekyarova, E.; Itkis, M. E.; Fakhrutdinov, D.; Webster, R.; Haddon, R. C., Application of Centrifugation to the Large-Scale Purification of Electric Arc Produced Single-Walled Carbon Nanotubes. *J. Am. Chem. Soc.* **2006,** 128, (30), 9902-9908.

Application to laser ablation SWNTs

from A.C. Dillon (NREL)





Quest for an absolute purity standard

Conclusions

• Solution phase NIR spectroscopy provides a simple metric for the relative carbonaceous purity of SWNTs

• Sensitive to nanostructure and SWNT chemistry

• Efficient tool for optimizing SWNT synthesis, purification and processing

• Well suited for providing quality control and quality assurance specifications for SWNT applications

•Absolute purity standards are within reach

• Wide distribution of SWNT diameters in HiPco and CVD makes the application of the NIR technique more difficult; not applicable to MWNTs

• Individual and separated SWNTs remain to be addressed

• Simplest approach - linear baseline subtraction

• Extinction coefficients of all carbon atoms are assumed to be equal