Freie Universität Berlin

Synthesis of Carbon Nanotubes

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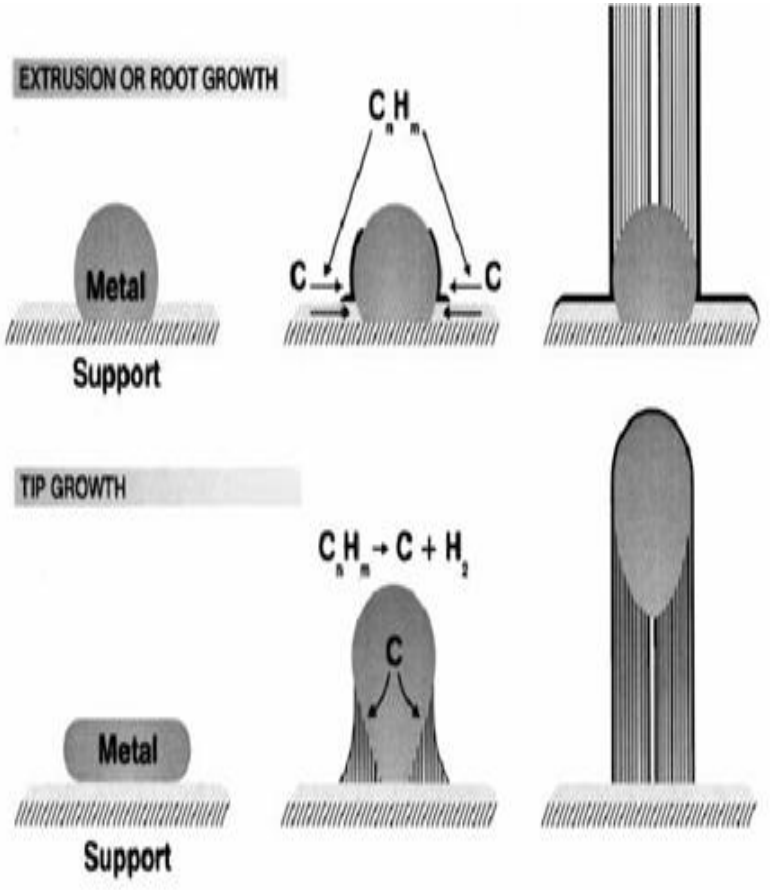
Synthesis of CNT's

- Arc Discharge (1991)
- Laser Ablation (1995)
- Chemical Vapour Deposition (CVD) (1959/ 1993)
- High Pressure Carbon Monoxide (HiPco) (1999)
- CoMoCat (2000)
- New Ideas...

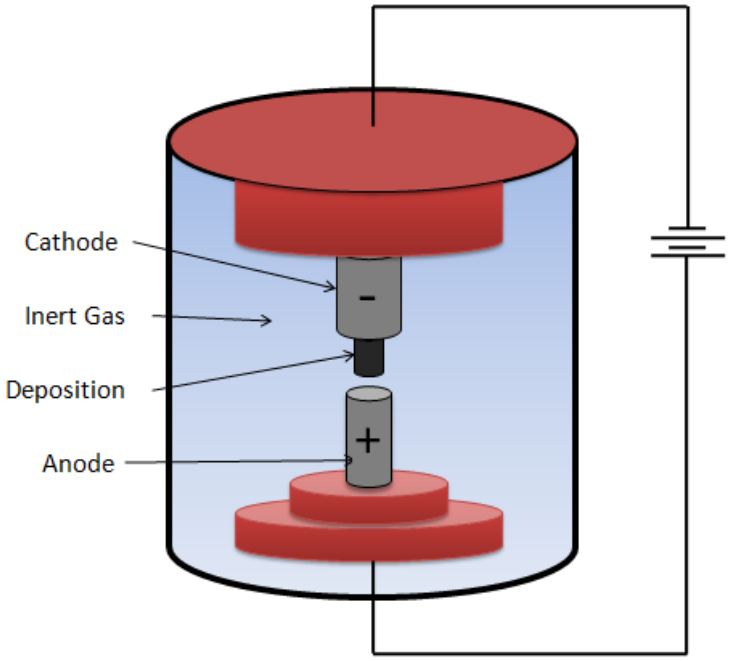
Growth Mechanism



- metal catalyst particles
- deposition on one half
- extrusion (base-growth)
- tip-growth

http://students.chem.tue.nl/ifp03/synthesis.html

Arc Discharge

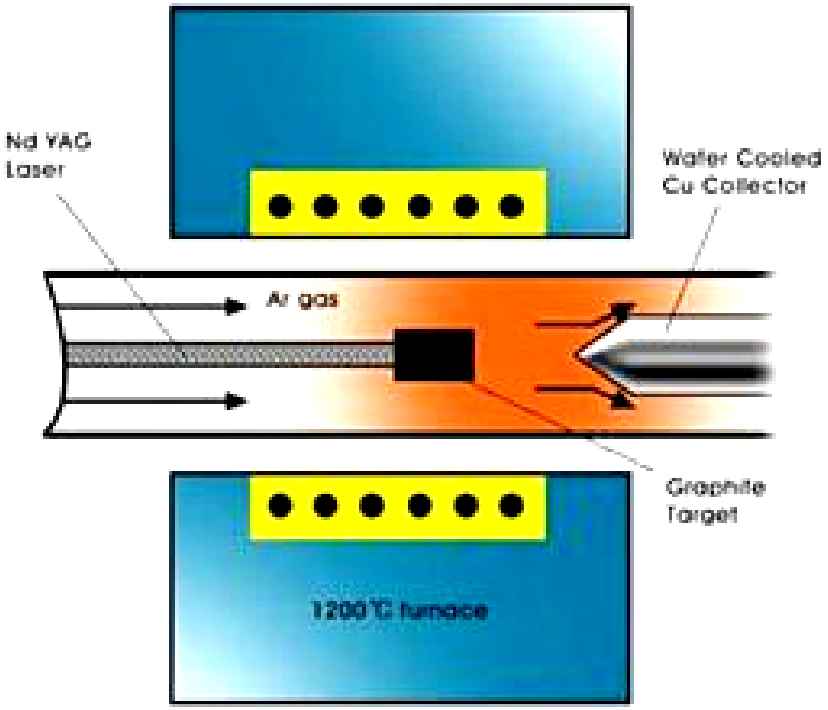


- 1991: **Iijima** [1]
- two carbon rods as electrodes
- NTs on the cathode & on walls
- high temperatures, ~3000°C [2]
- ~30% of Carbon evaporates [3]
- catalysts: Fe, Y, Ni, Co, Mo...
- Synthesis Product Yield: 60%[3]
- Purification Yield: 70% [3]

[1] Iijima,S, Nature 354,56-58 (1991)
[2]http://students.chem.tue.nl/ifp03/synthesis.html
[3] J.A.Isaacs, A.Tanwani, M.L.Healy, L.J.Dahlben. J Nanopart Res. 2010, 12:551-562

http://www.celnav.de/hv/hv4.htm

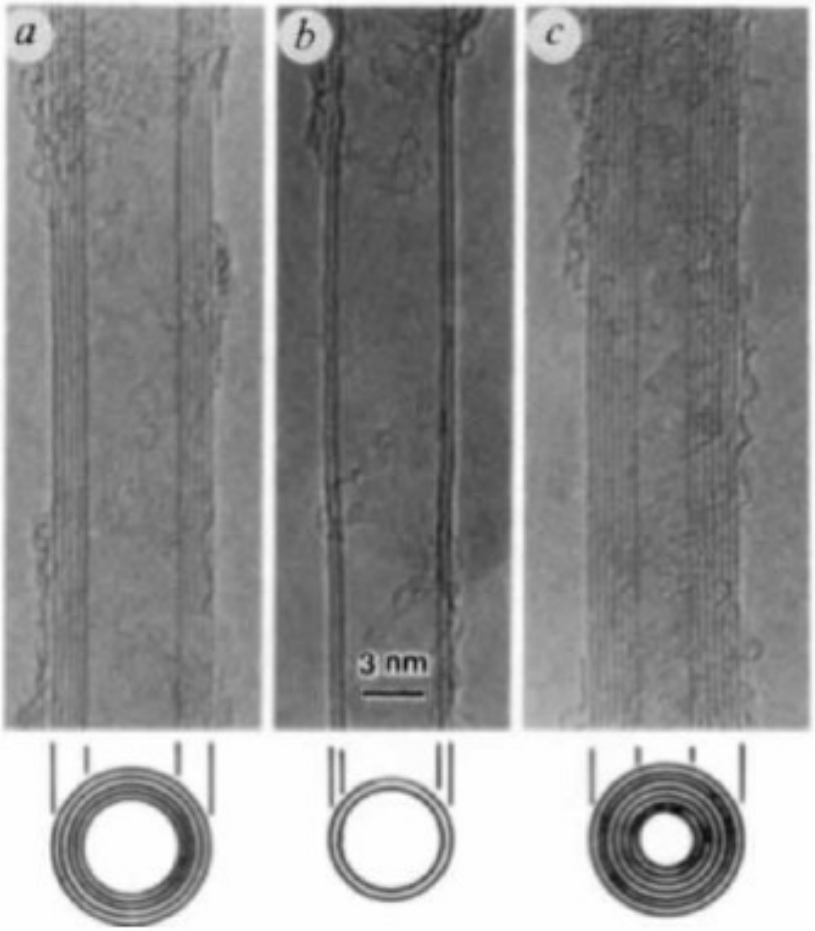
Laser Ablation



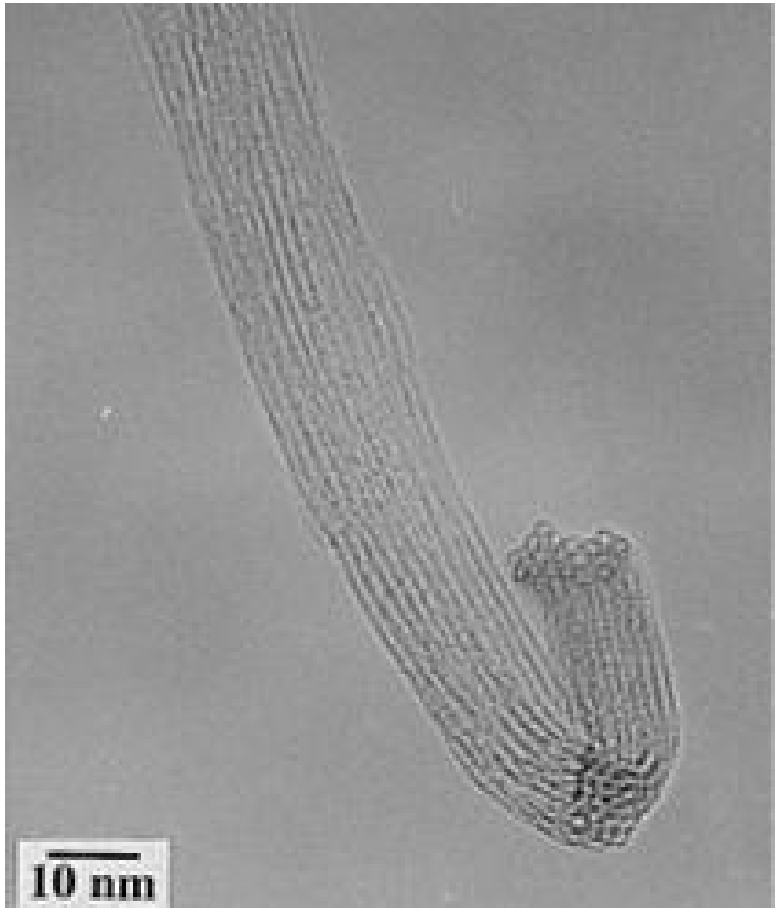
- 1995: **Smalley**, USA [1]
- const pressure due to He or Ar
- 1100-1500 °C
- vaporisation of graphite target
- catalysts: Co, Fe, Ni, Y...
- best yield: Ni/Y-mixture[3]

[1]Guo, T., Nikolaev, P., Thess, A., Colbert, D. T., Smalley, R. E.Chem.Phys.Let. 243(1,2), 49-54.1995.
[2]http://students.chem.tue.nl/ifp03/synthesis.html
[3]Journet,C;Maser,W.K;Bernier,P;Loiseau,A;et al, Nature 388, 756-758 (1997)

Arc Discharge - Laser Ablation



Iijima,S, Nature 354,56-58 (1991)



Maser, W. K., Munoz, E., Benito, A. M., Martinez, M. T., de la Fuente, G. F., Maniette, Y., Anglaret, E., and Sauvajol, J. L. Chem.Phys.Let. 292(4,5,6), 587-593. 1998.

Problems...

☹ evaporation of the carbon source

☹ very high temperatu C

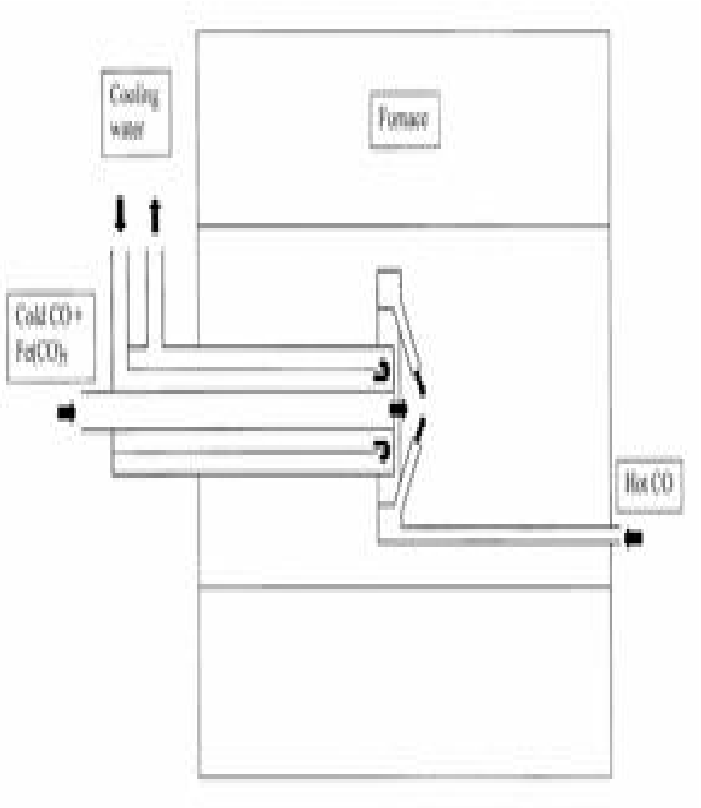
☹ N

ture possible

☹ lots of purification needed

We need something else!

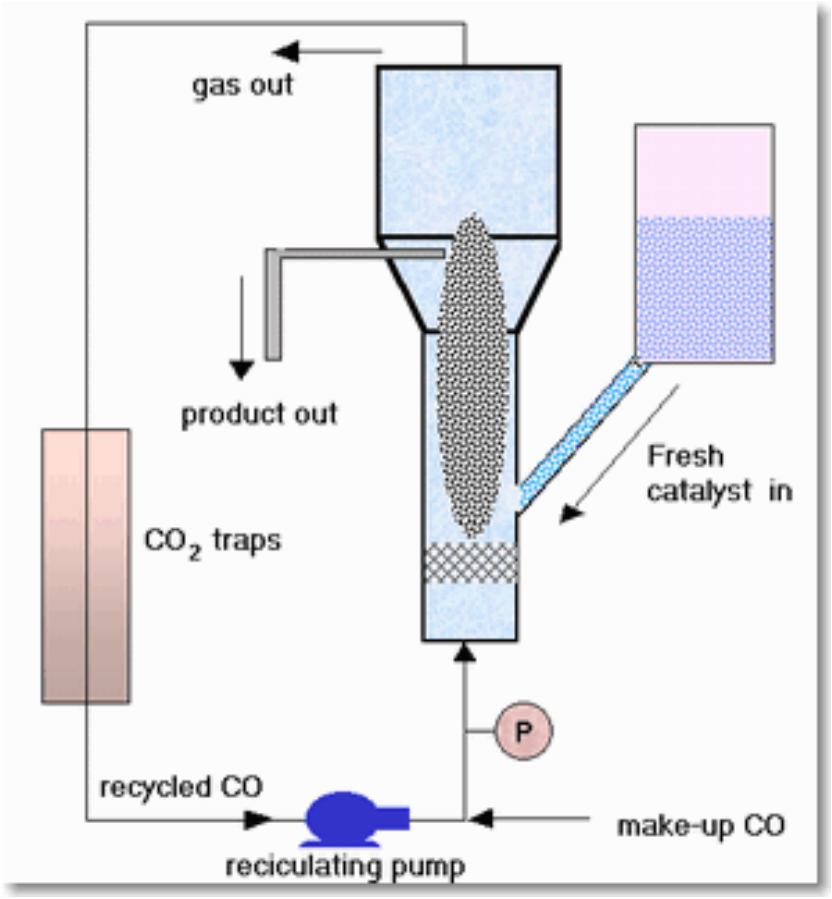
High Pressure CO (HiPco)



- **Smalley**'s Group, USA (1999) [1]
- continuous-flow gas phase
- CO: carbon feedstock
- Fe(CO)5: catalyst
- the smallest stable SWNTs [2]
- Synthesis Product YIeld: 97%
- Purification YIeld: 90% [3]

http://students.chem.tue.nl/ifp03/synthesis.html;
[1]Nikolaev, Pavel, Bronikowski, Michael J., Bradley, R. Kelley, Rohmund, Frank, Colbert, Daniel T., Smith, K. A., and Smalley, Richard E. Chemical Physics Letters 313(1,2), 91-97. 1999.
[2]Smalley, Richard E. and Yakobson, Boris I. Solid State Com 107(11), 597-606. 1998.
[3]J.A.Isaacs, A.Tanwani, M.L.Healy, L.J.Dahlben. J Nanopart Res. **2010**, 12:551-562

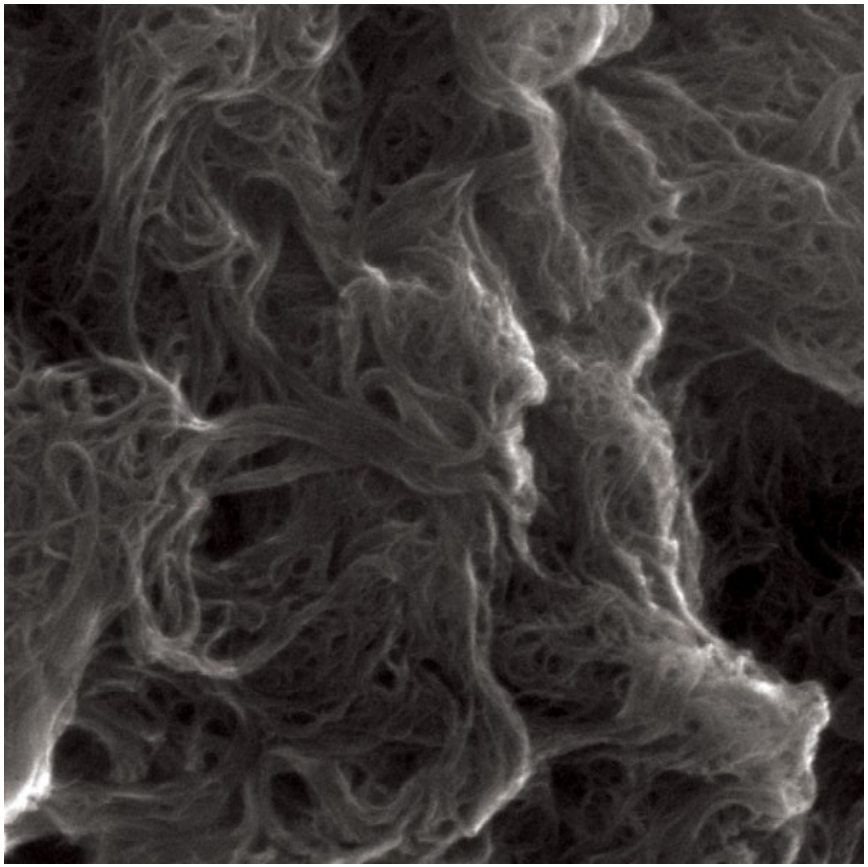
CoMoCat

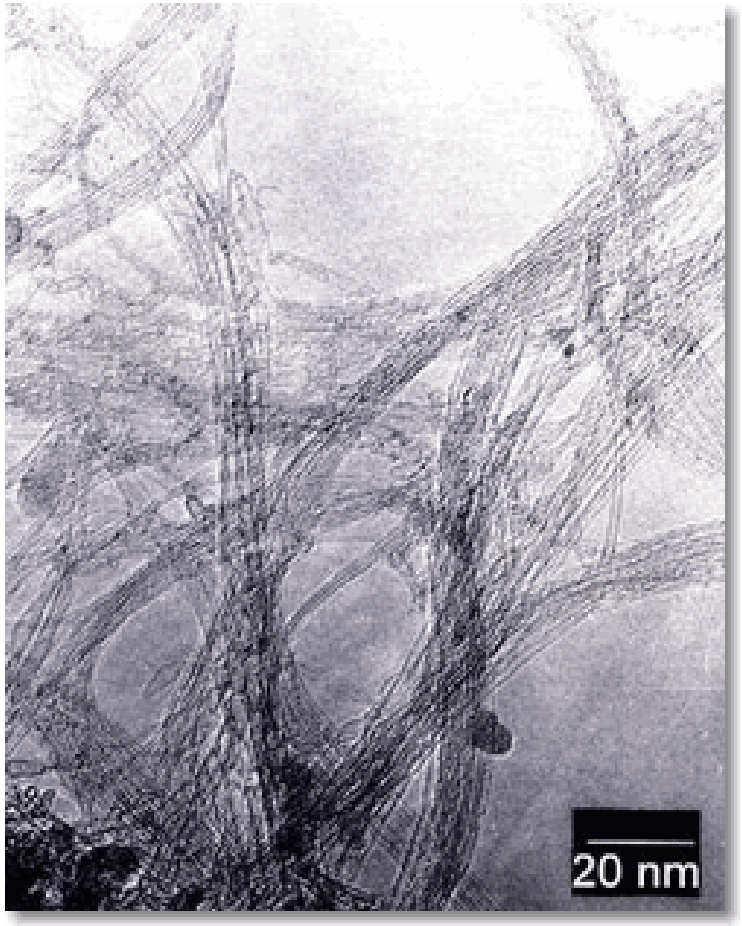


- 2000: Kitiyanan, USA (2000)
- CO decomposititon into C and carbon dioxide
- 700 - 950°C
- unique Co-Mo catalyst
- inhibits the formation of the by-products

[1]B. Kitiyanan, W.E. Alvarez, J.H. Harwell, D.E. Resasco. Chem.Phys.Let. 317 2000 497-503
[2]http://www.ou.edu/engineering/nanotube/comocat.htm

HiPco - CoMoCat

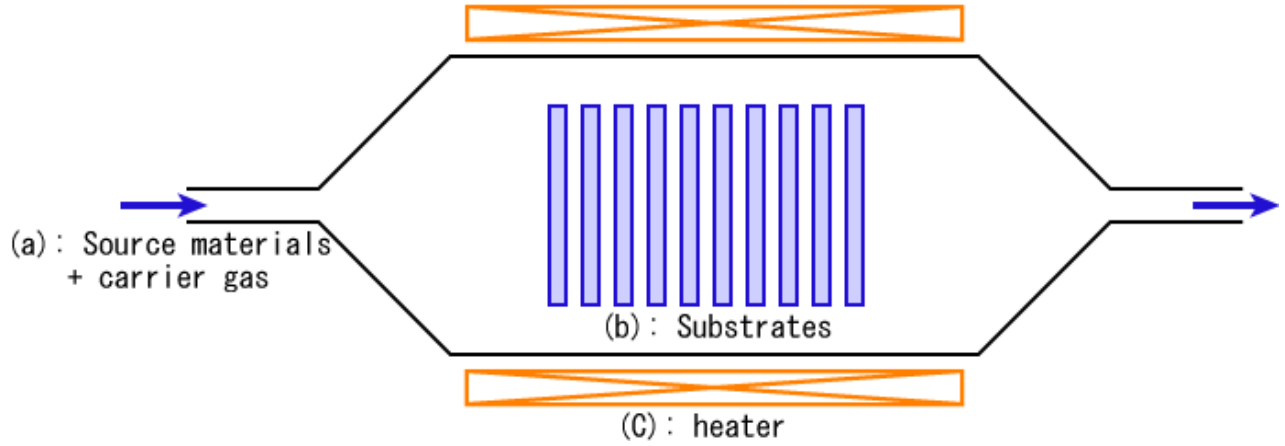




http://www.nanointegris.com/en/hipco

http://www.ou.edu/engineering/nanotube/comocat.htm

Chemical Vapour Deposition



- hydrocarbon gases: acetylene (C2H2), methane (CH4)...
- process gas: nitrogen, hydrogen, argon
- catalysts: Ni, Co, Fe...
- substrate heating ~700°C
- Synthesis Product Yield: 90% [3]
- Purification Yield: 90% [3]

[1]http://en.wikipedia.org/wiki/Chemical_vapor_deposition
[2]José-Yacamán, M.; Miki-Yoshida, M.; Rendón, L.; Santiesteban, J. G.Appl. Phys. Lett. 62 (6): 657 1993
[3]J.A.Isaacs, A.Tanwani, M.L.Healy, L.J.Dahlben. J Nanopart Res. **2010**, 12:551-562

New directions in CVD

- **Selective growth** (1999) [1]
Surface pretreatments provide selective deposition of catalysts - photolitography

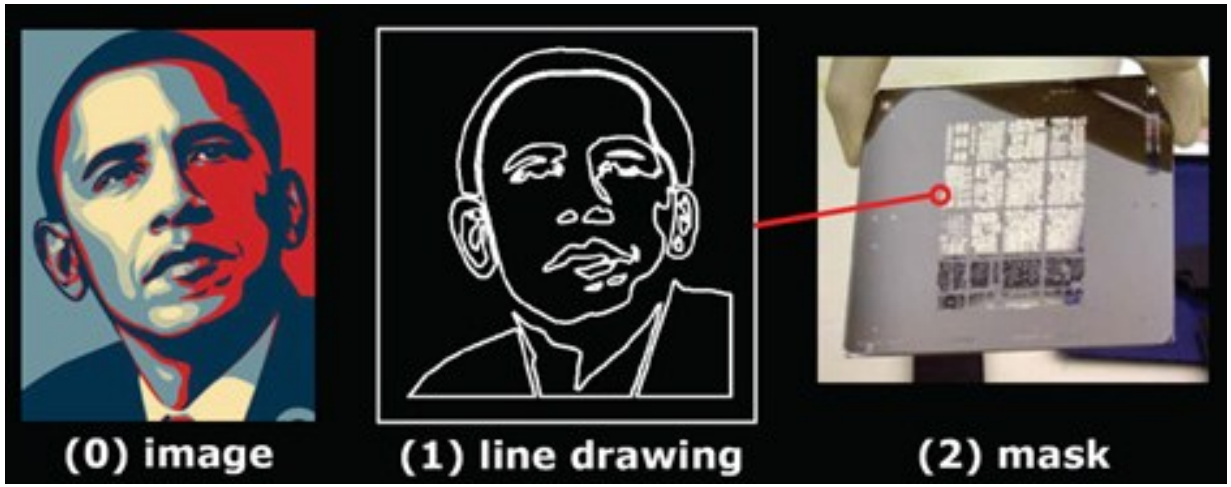
- **Super-growth CVD** (2004)
Water.assisted CVD - well-aligned „forests“ [2]

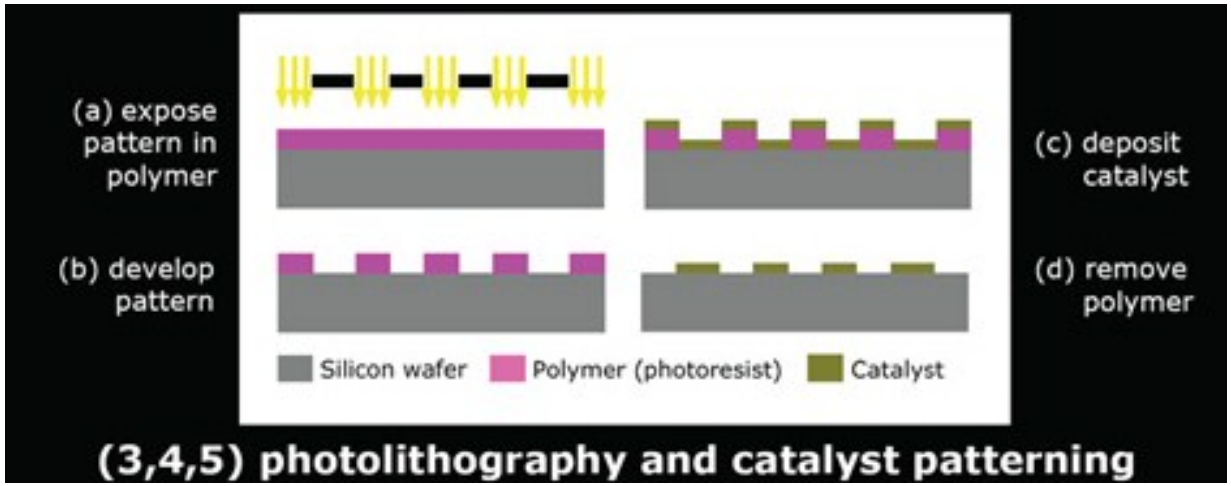
- **Low temperature** (2006) [3]
W filament increases the decomposition of precursor gases

- **High-efficiency CVD** (2007)
Hydrocarbon gas: Camphor (C10H16O) [4]

[1]Li,J;Papadopoulos,C;Xu,J.M. Appl.Phys.Lett.75-3-19Juli1999
[2] http://en.wikipedia.org/wiki/Carbon_nanotube
[3] Cantoro; Hoffman;, Pisana; Robertson. NanoLetters,Vol6,No6,1107-1112,2006
[4]Kumar,M; Ando,J. Journal of Physics: Conference Series 61: 643. 2007

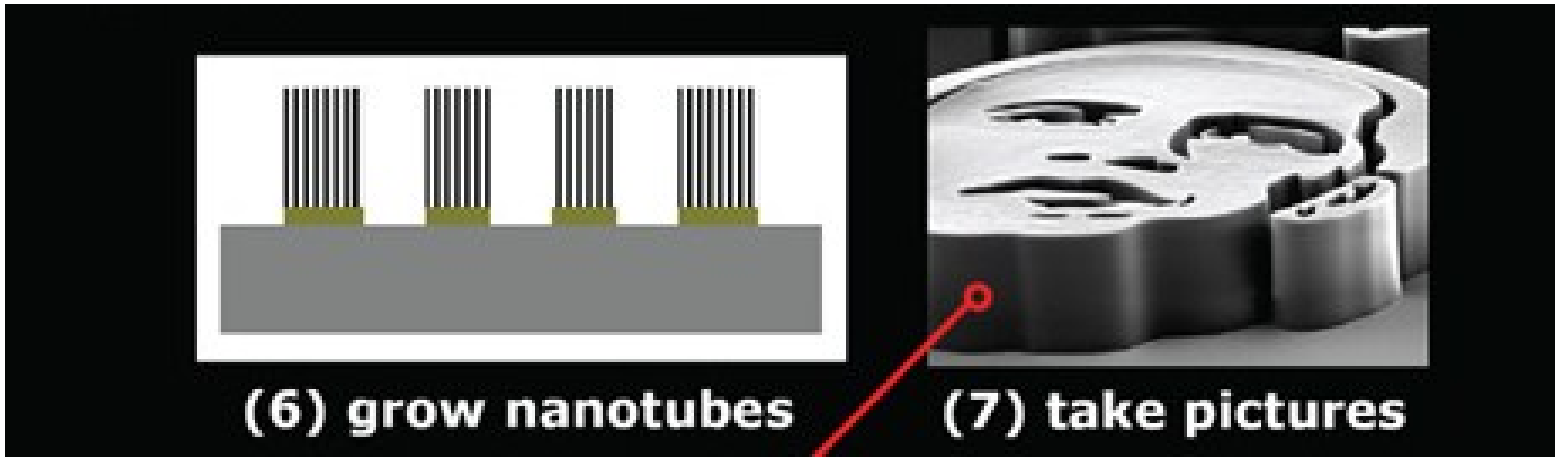
Structures!

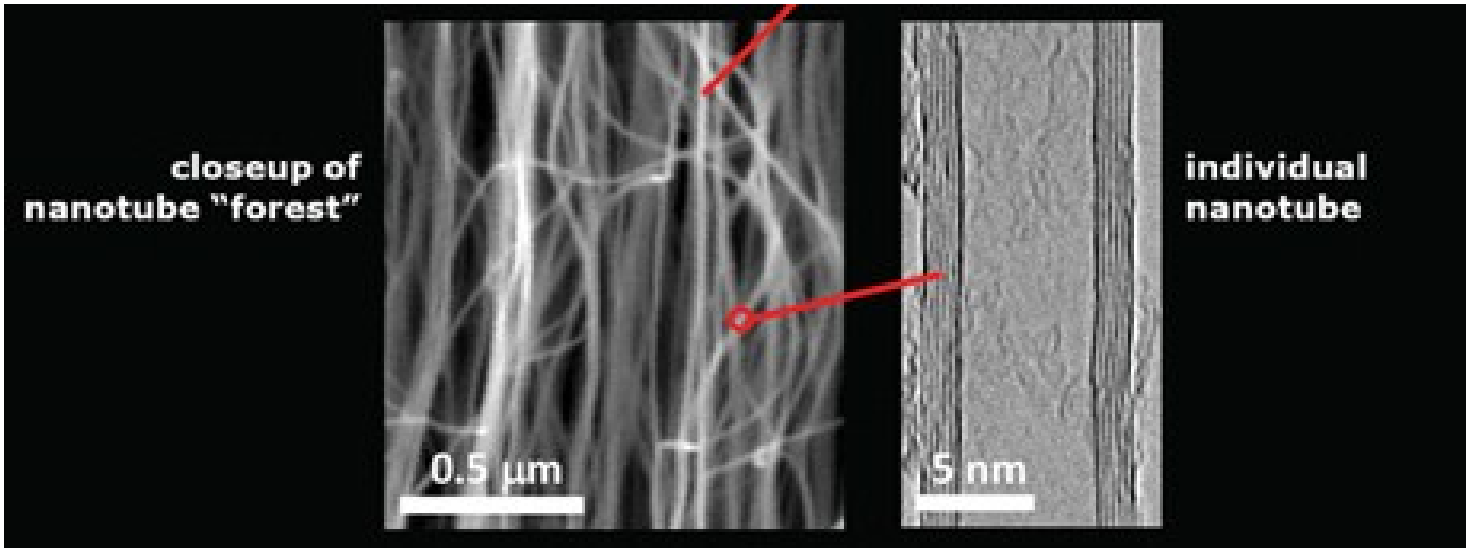




http://www.nanobama.com/how/how.htm

Structures!





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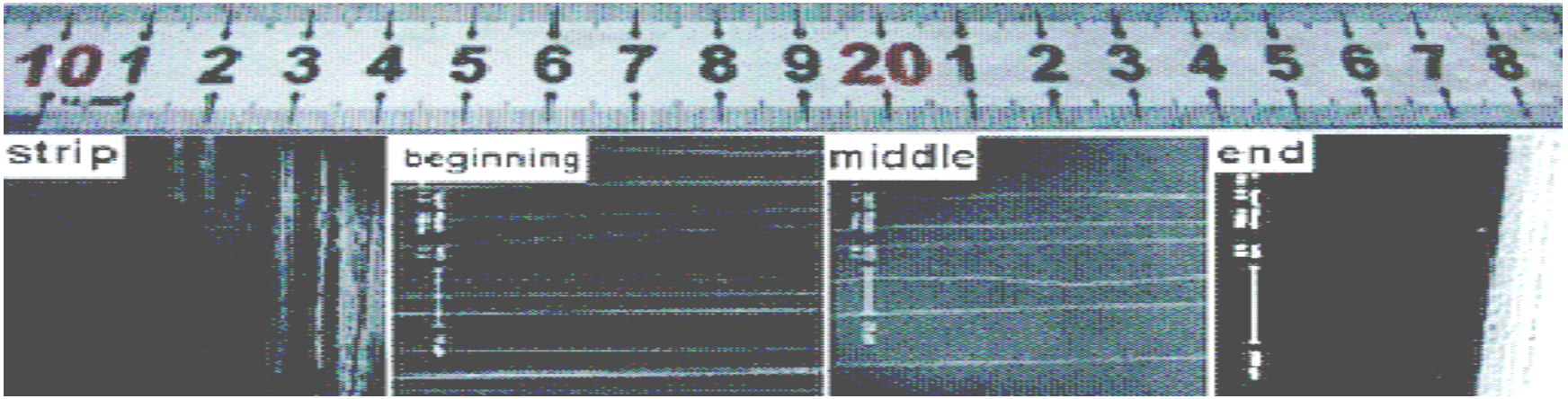
Ultralong Nanotubes - CVD



Wang, X.; Li, Q.; Xie, J.; Jin, Z.; Wang, J.; Li, Y.; Jiang, K.; Fan, S.: Nano Letters (2009)

- CNTs over 18.5 cm long
- Fe−Mo on Si substrates
- length/ diameter ratio ~ 10^8:1
- 1/50,000th of the width of a human hair

Nanotubes in the macroworld

- 3,4 cm wide, 1 m long sheet of drawn NTs
- catalytic super-growth CVD
- thickness of the sheet - 50 nm
- diaphanous
- good conductivity

http://nanotechweb.org/cws/article/tech/22915
M.Zhang, S.Fang, R-H.Baughman et al, University of Texas at Dallas, USA; Science 19.08.05: Vol. 309 no. 5738 pp. 1215-1219
DOI: 10.1126/science.1115311