In situ studies on dynamic properties of carbon nanotubes with metal clusters

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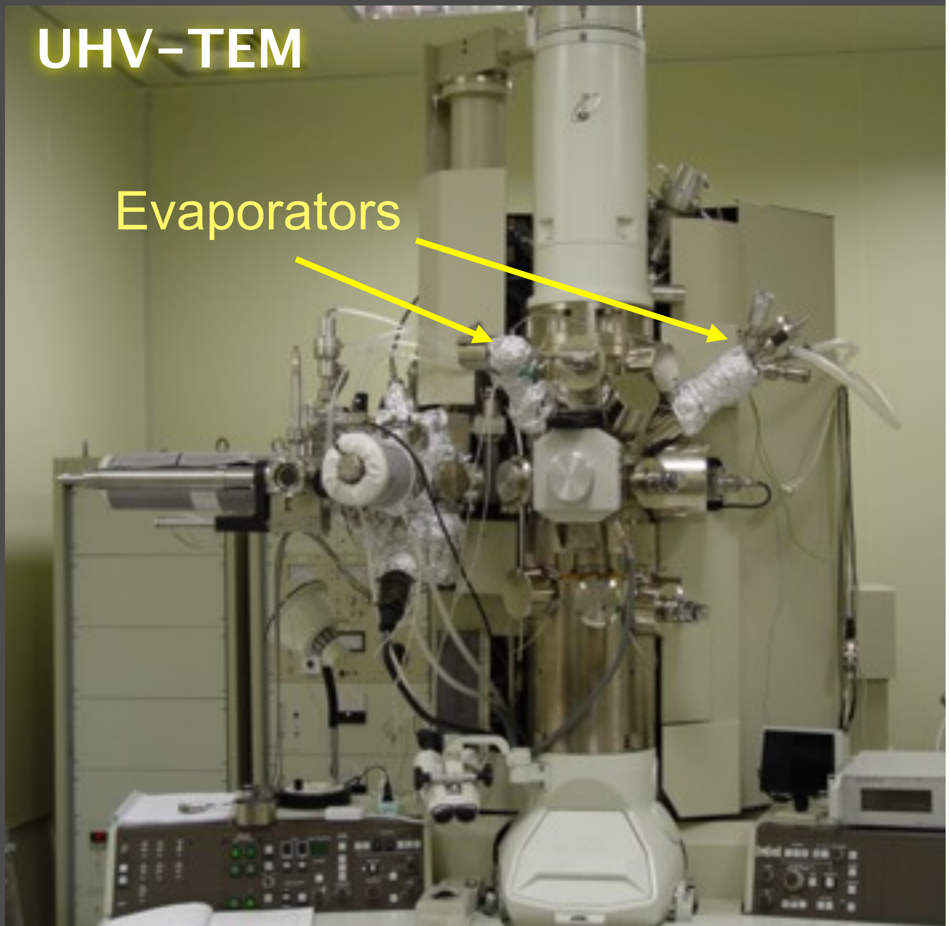
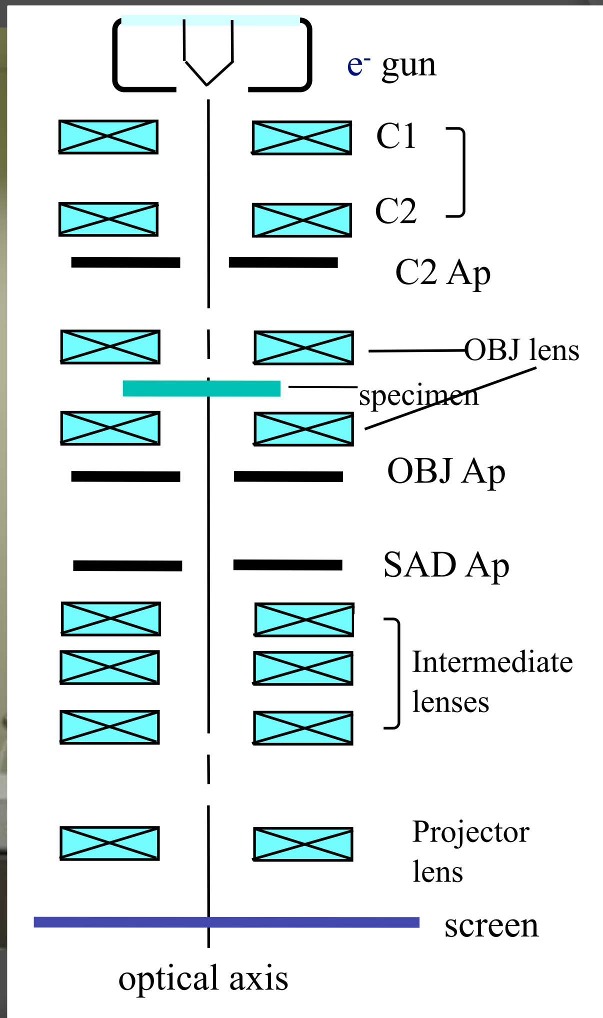
Outline

- Growth of Ag clusters on carbon nanotubes
- Mass detection using CNT as a resonator
- Capillarity of molten silver droplets

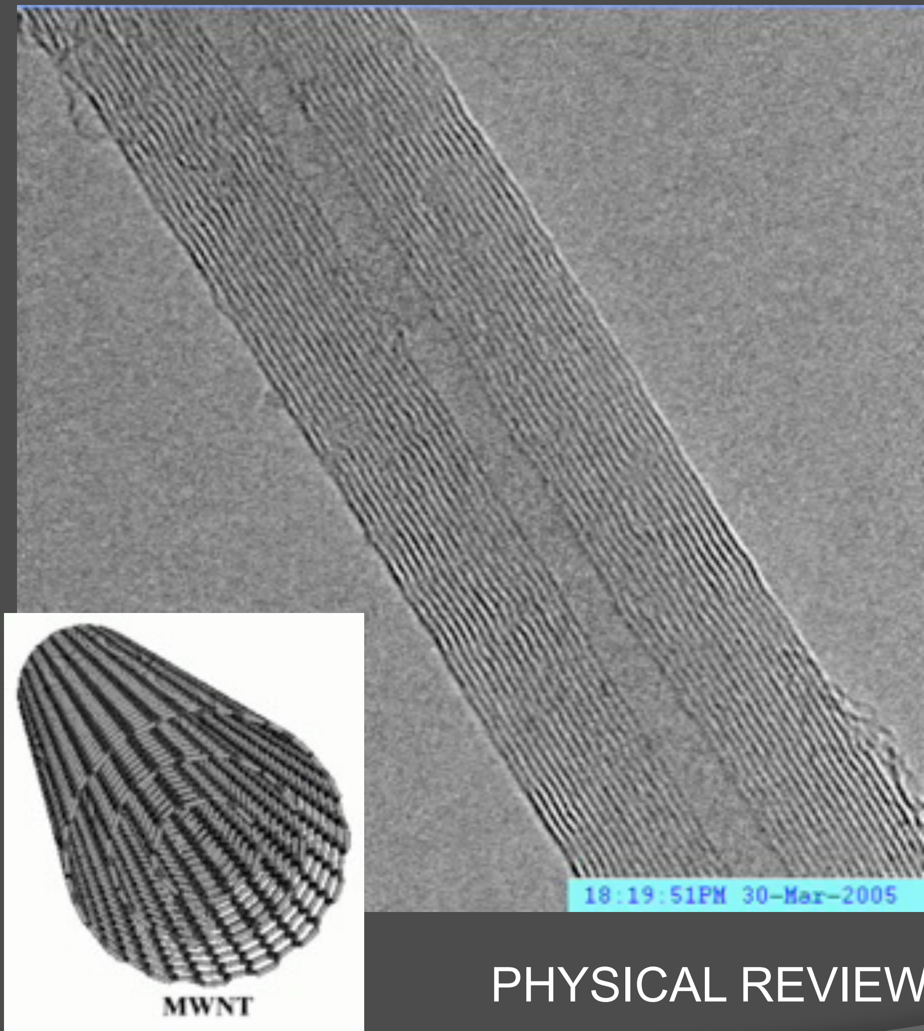
Ultrahigh vacuum HR-TEM

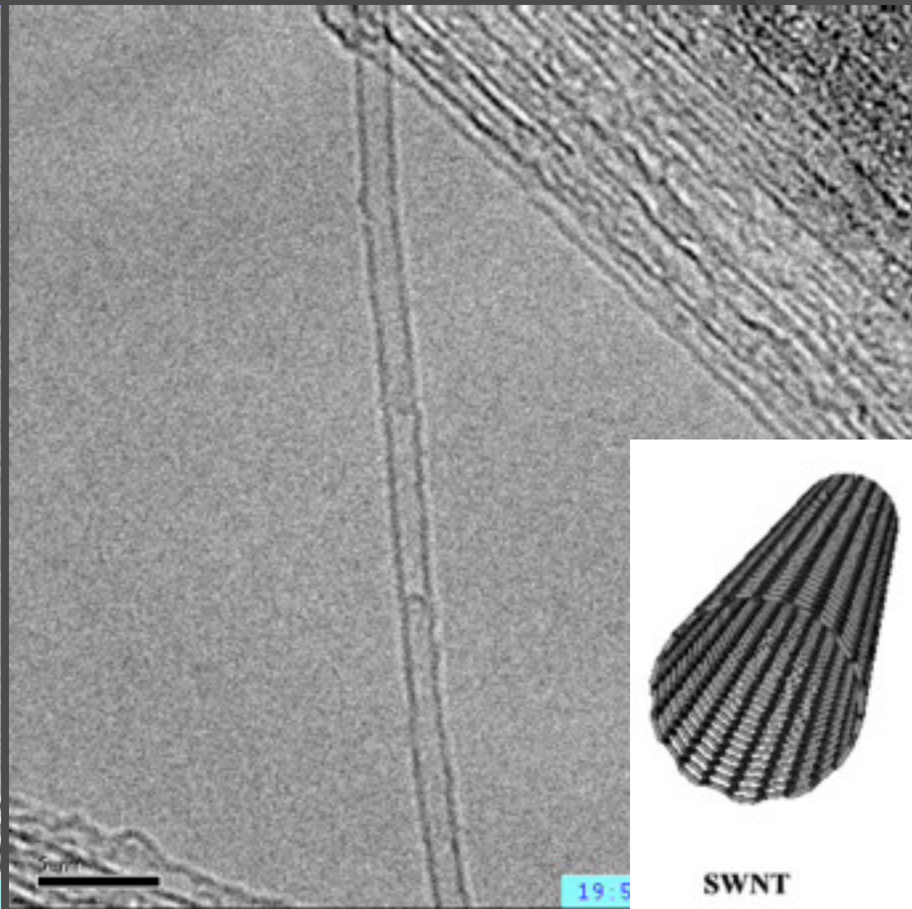




Base pressure 2 x 10^{-10} torr

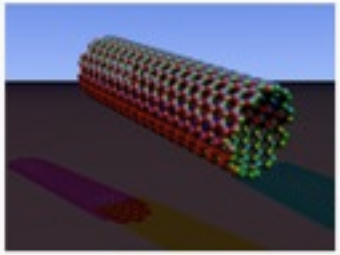
In situ deposition



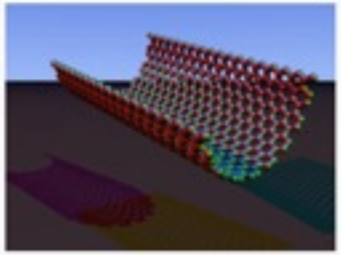


PHYSICAL REVIEW B **74**, 125424 (2006)

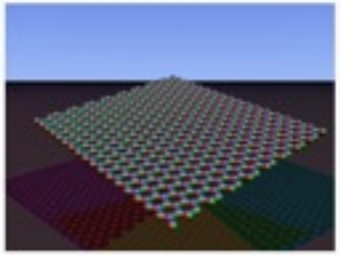
Structure of carbon nanotube



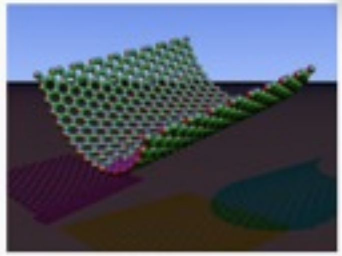
Armchair (*n*,*n*)



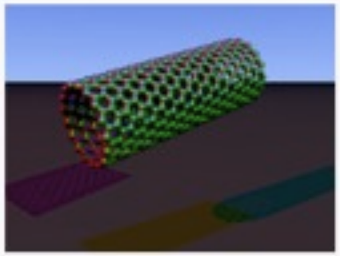
The chiral vector is bent, while the translation vector stays straight



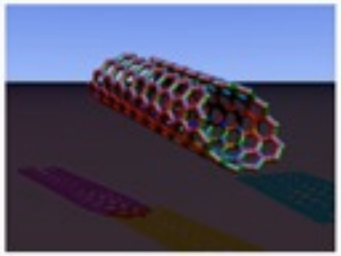
Graphene nanoribbon



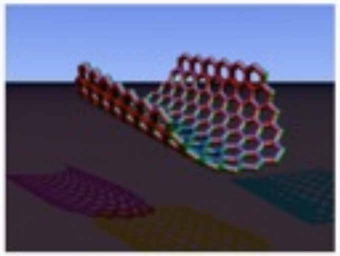
The chiral vector is bent, while the translation vector stays straight



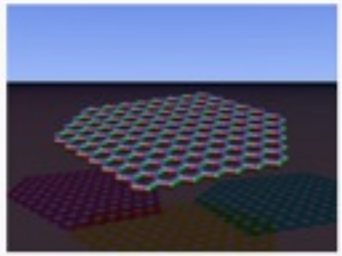
Zigzag (*n*,0)



Chiral (*n*,*m*)

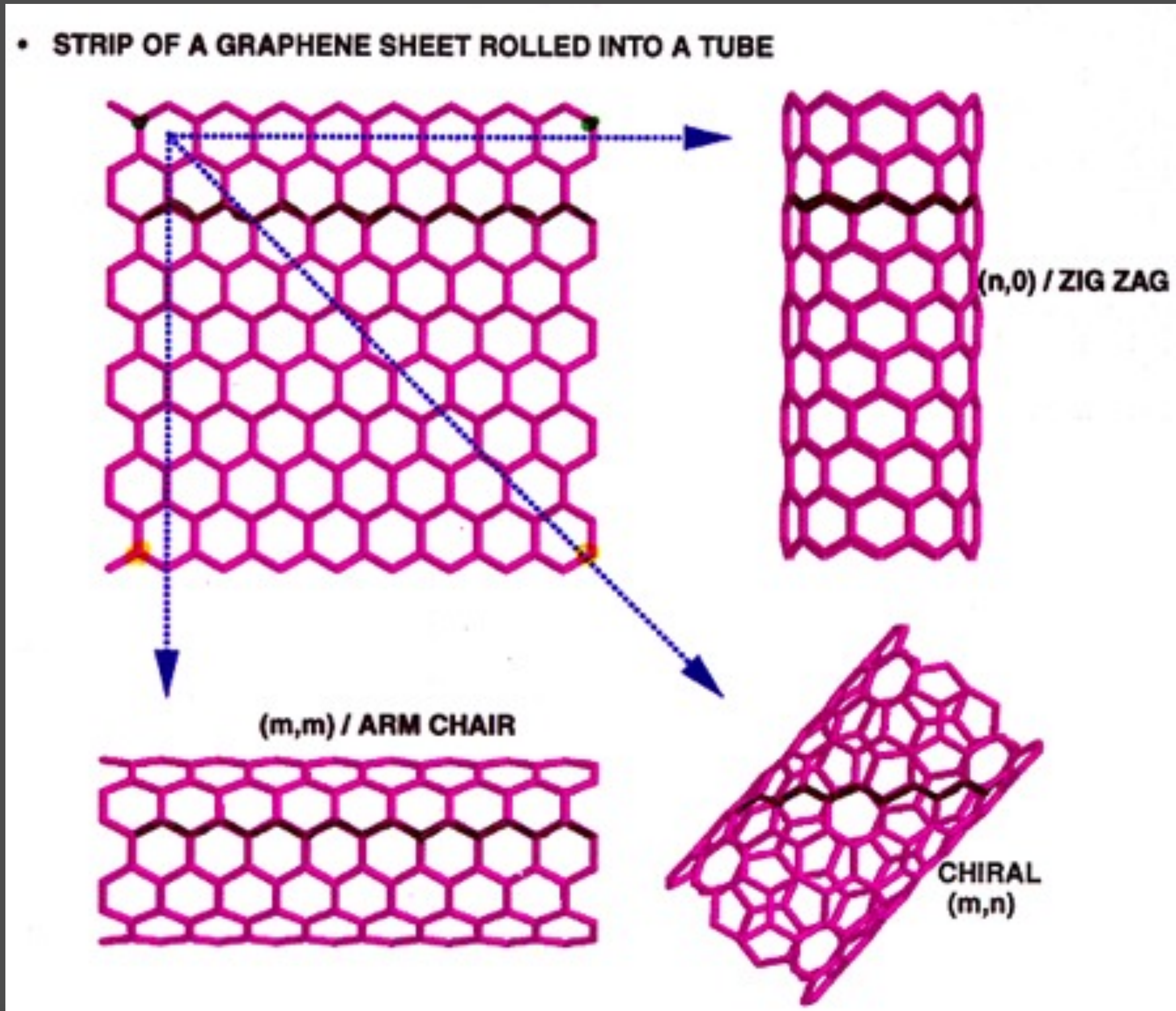


n and *m* can be counted at the end of the tube



Graphene nanoribbon

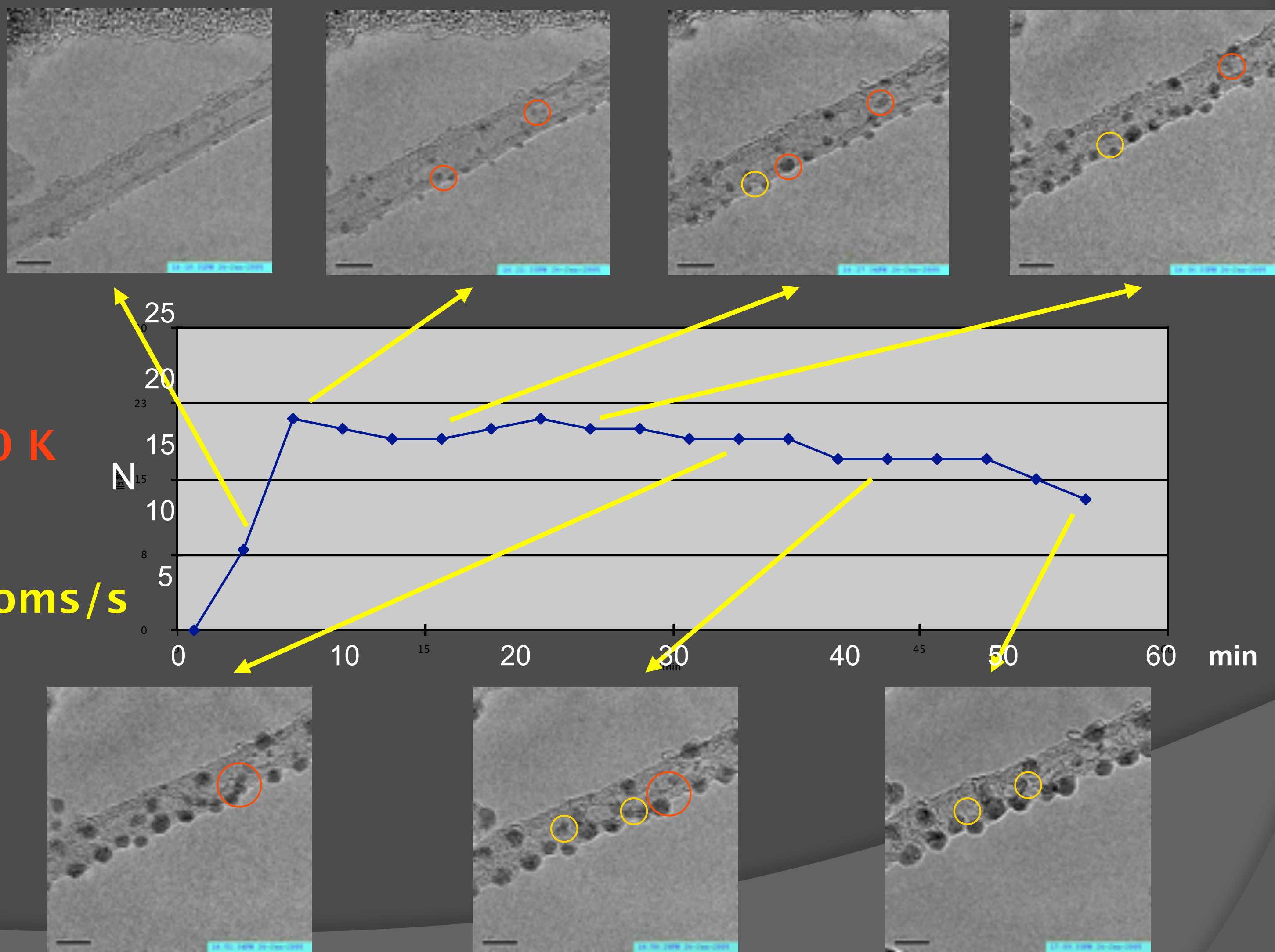
Structure of carbon nanotube



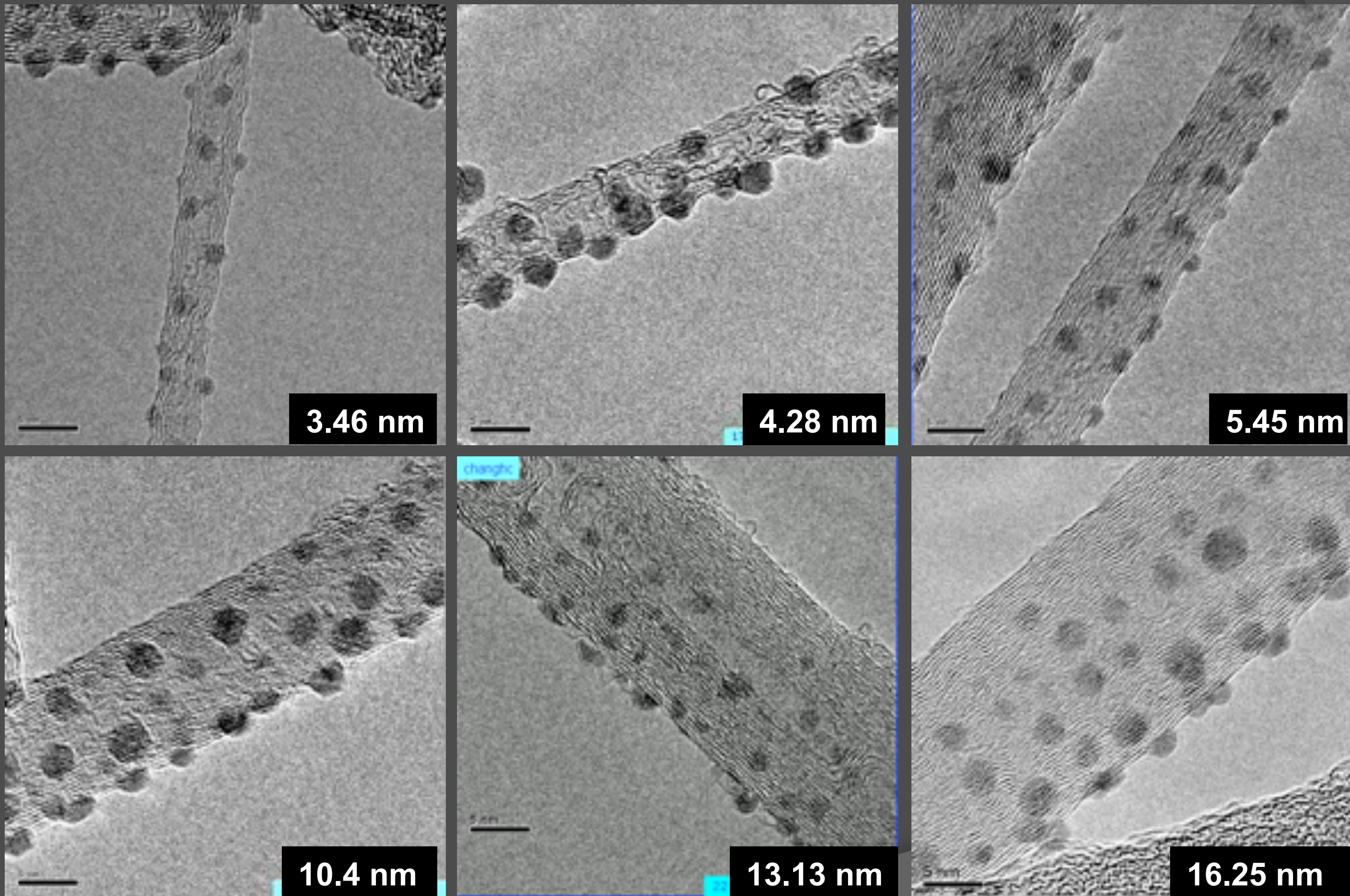
From nucleation to coalescence

T ~ 300 K

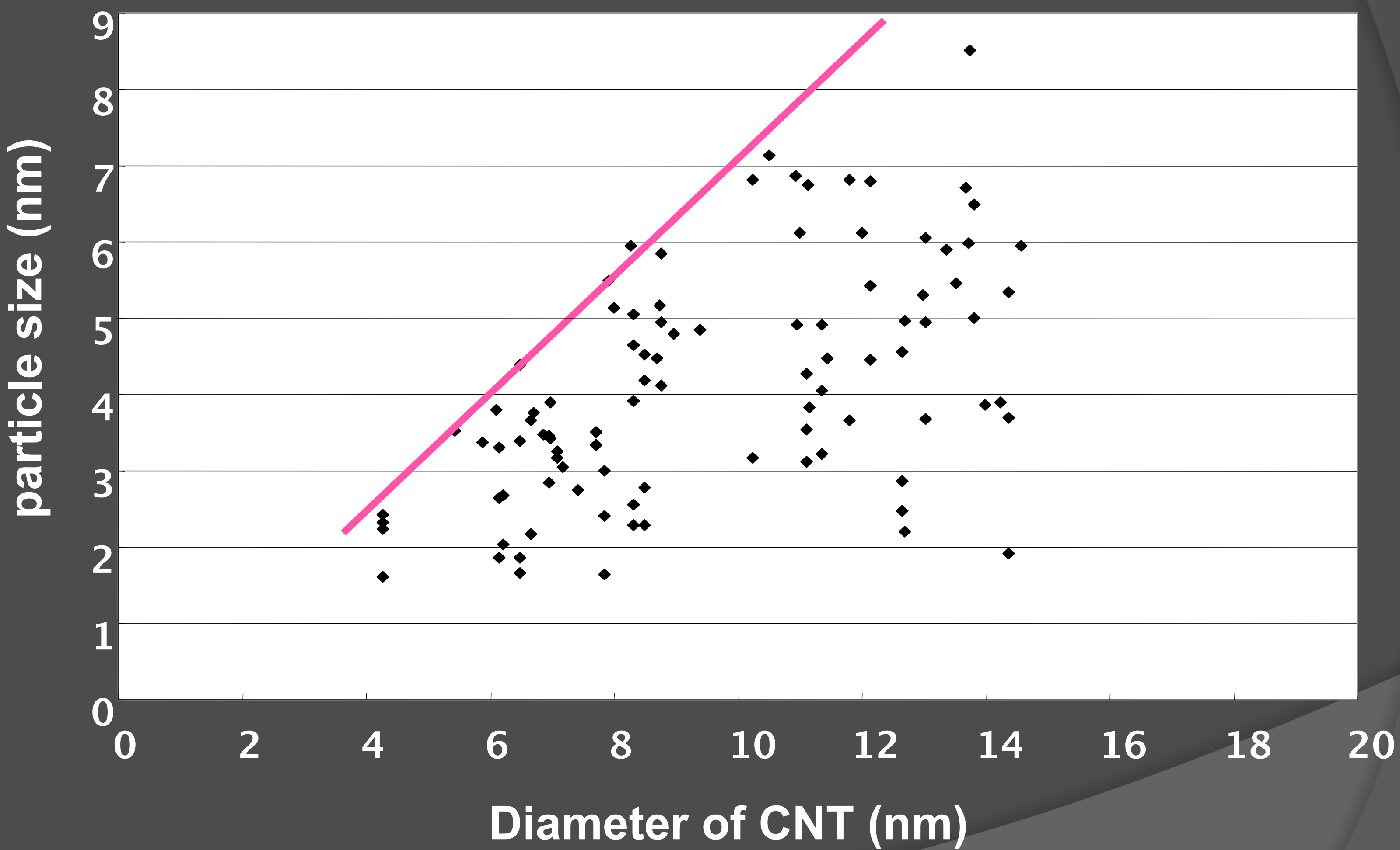
Flux
~ 125 atoms/s



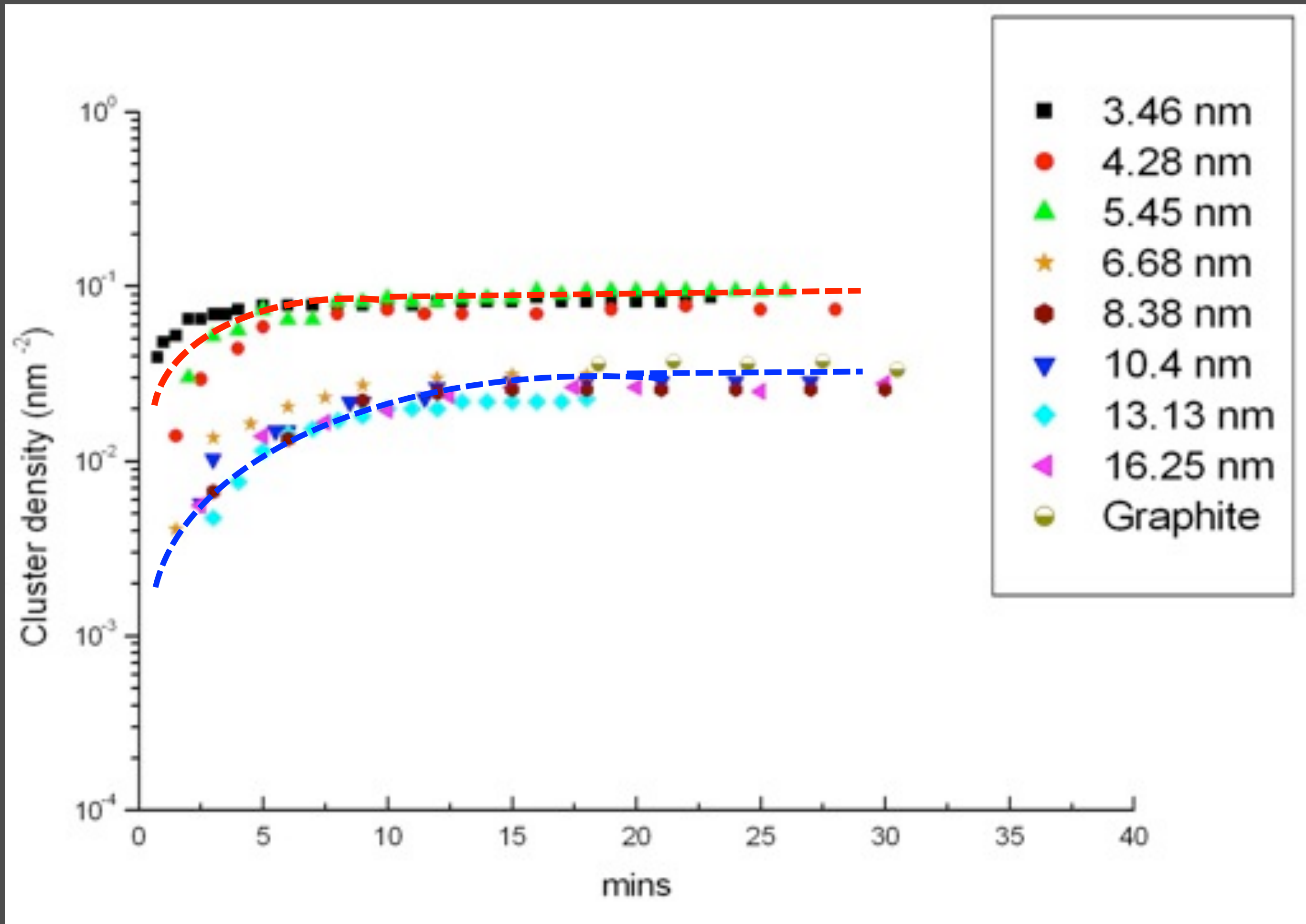
Growth of Ag clusters on CNTs



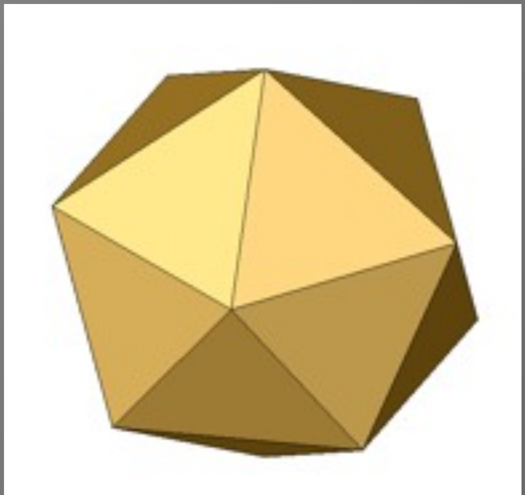
Boundary effect



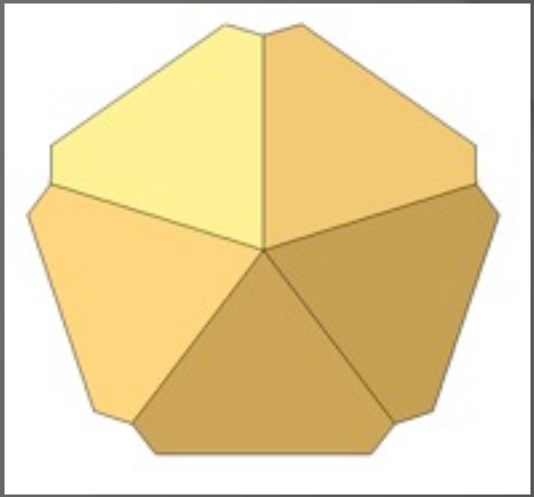
Cluster density vs deposition time



Multi-twinned phases in clusters



Icosahedra



Marks' decahedra

Size-dependent structures calculated for Ni clusters:

Icosahedra for 142 – 2300 atoms;

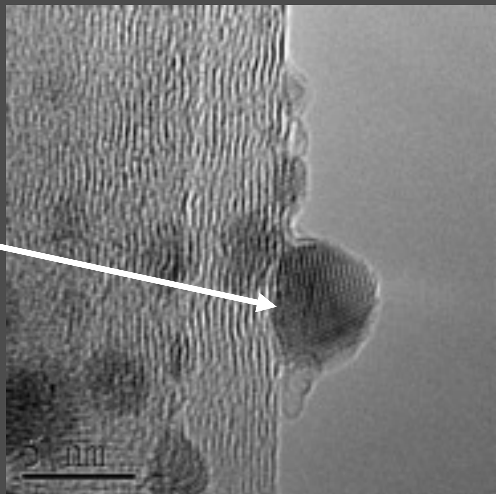
Marks' decahedra for 2300 – 17000 atoms;

Single crystal for > 17000 atoms.

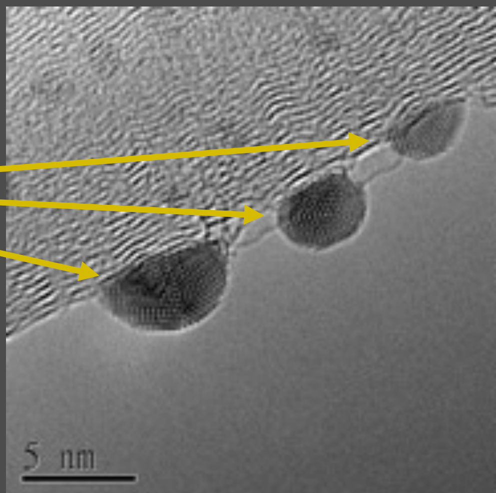
C.L. Cleveland and Uzi Landman, J. Chem. Phys. 94, 7376 (1991).

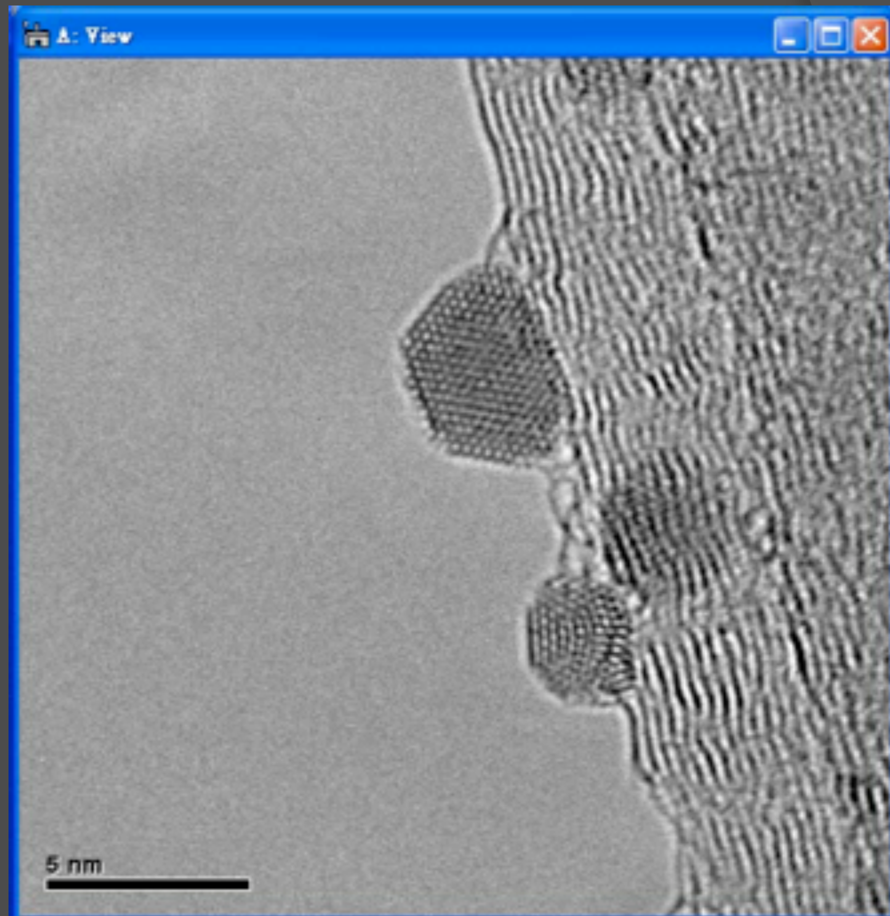
Varying structures of Ag clusters

stable

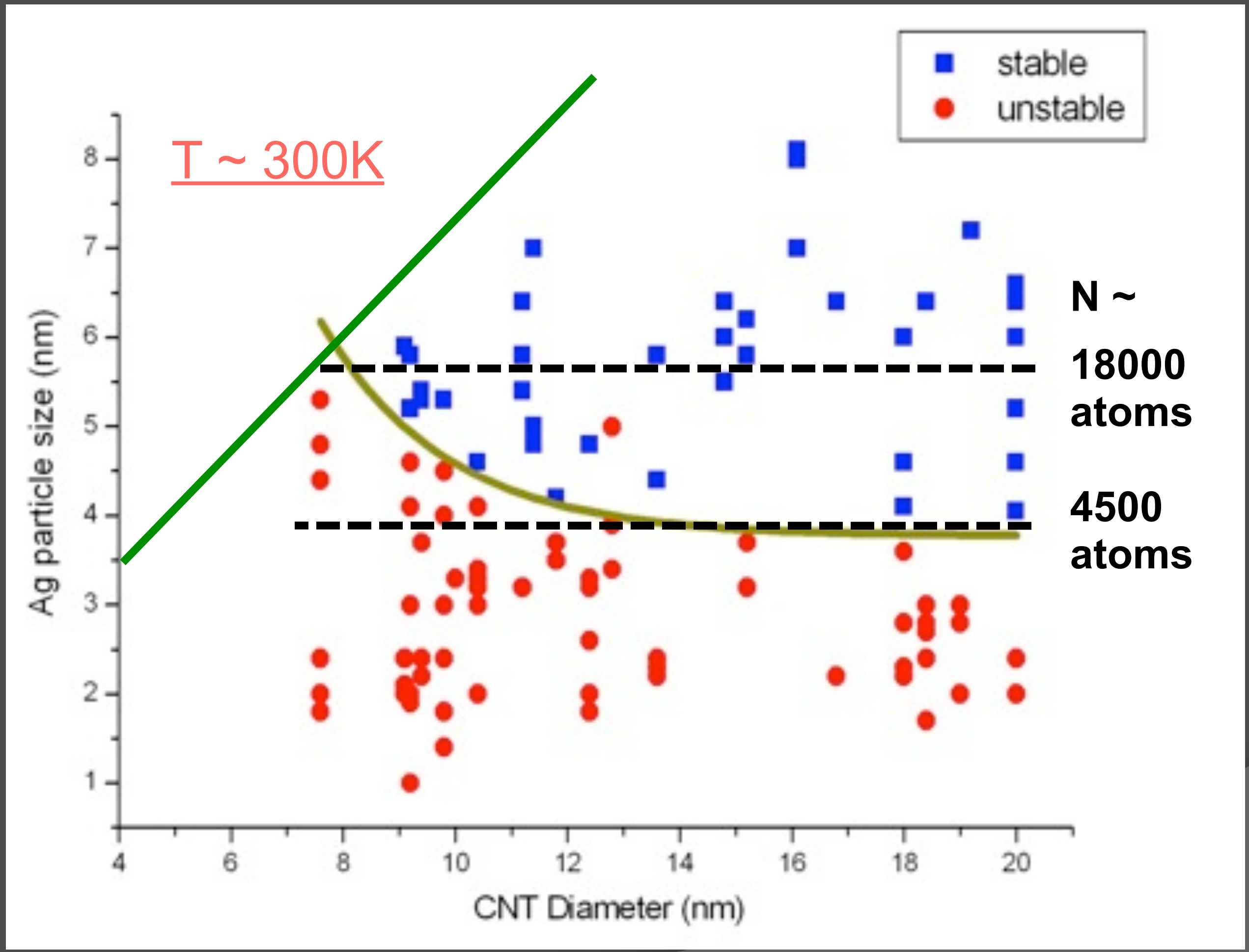


Unstable





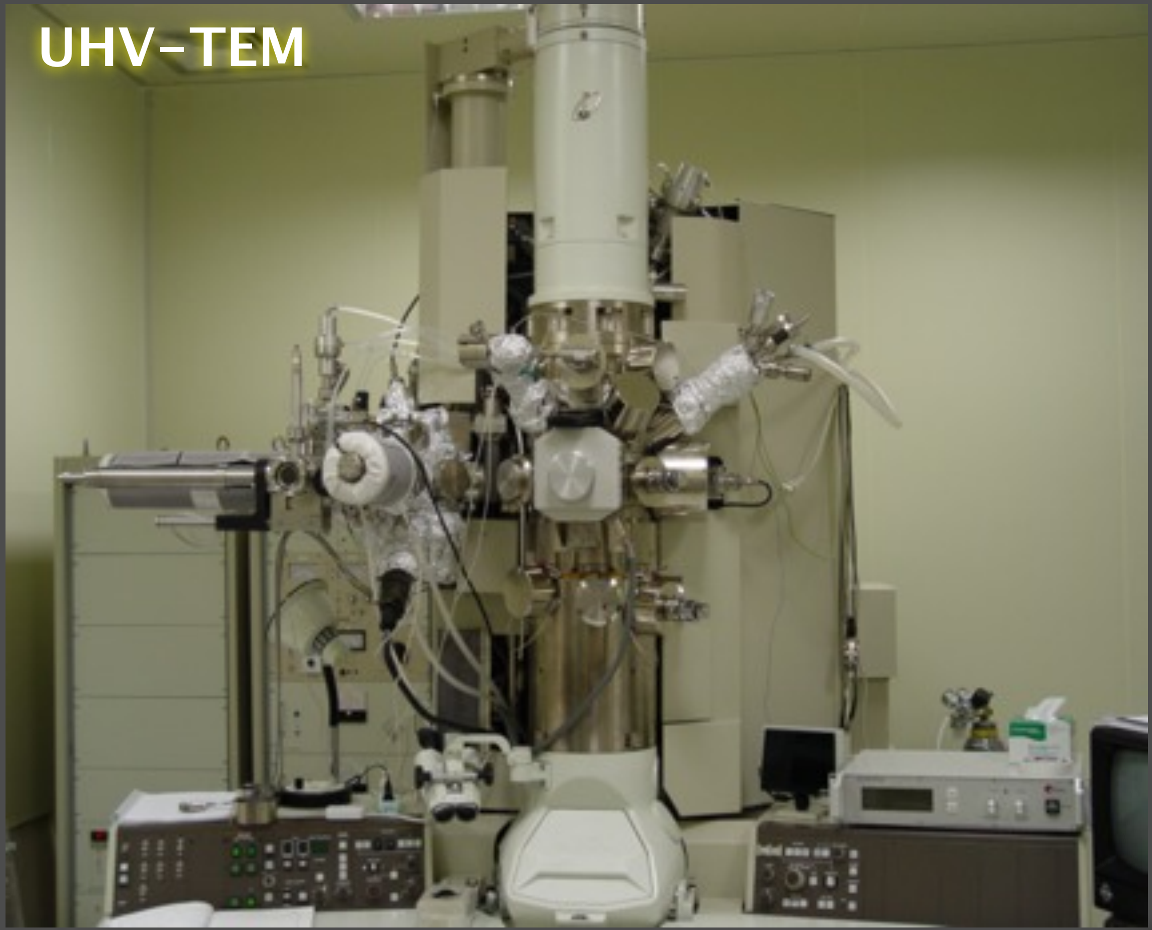
Stability of crystalline phases



Summary

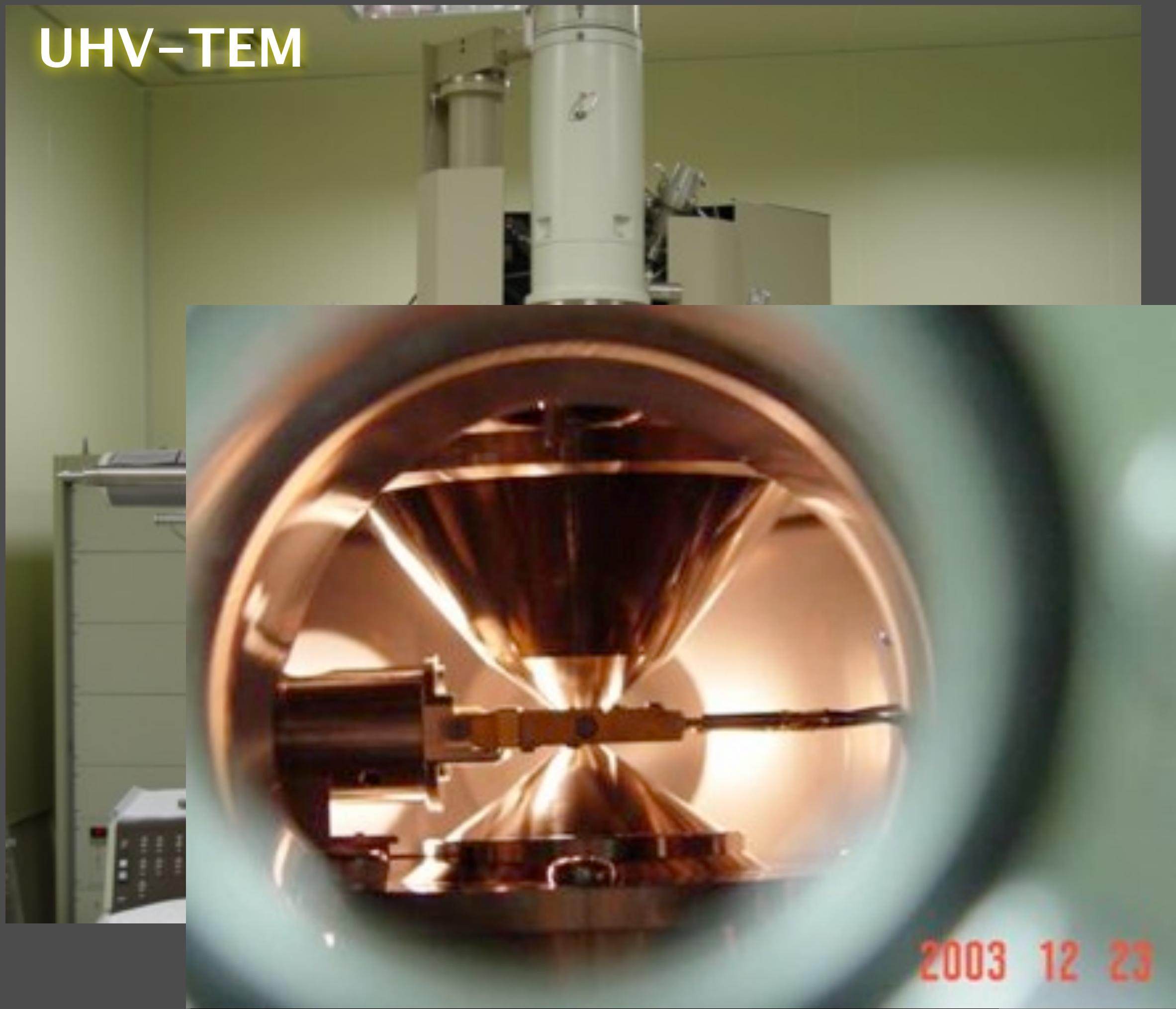
- *The growth of Ag clusters on carbon nanotubes has revealed that the ultimate size, the nucleation density, and the stable crystalline structure of a grown cluster are closely related to the size of the tube.*
- *The effect can be attributed to the curvature change of the tube surface that is determined by its size and chirality.*

STM@UHV-TEM



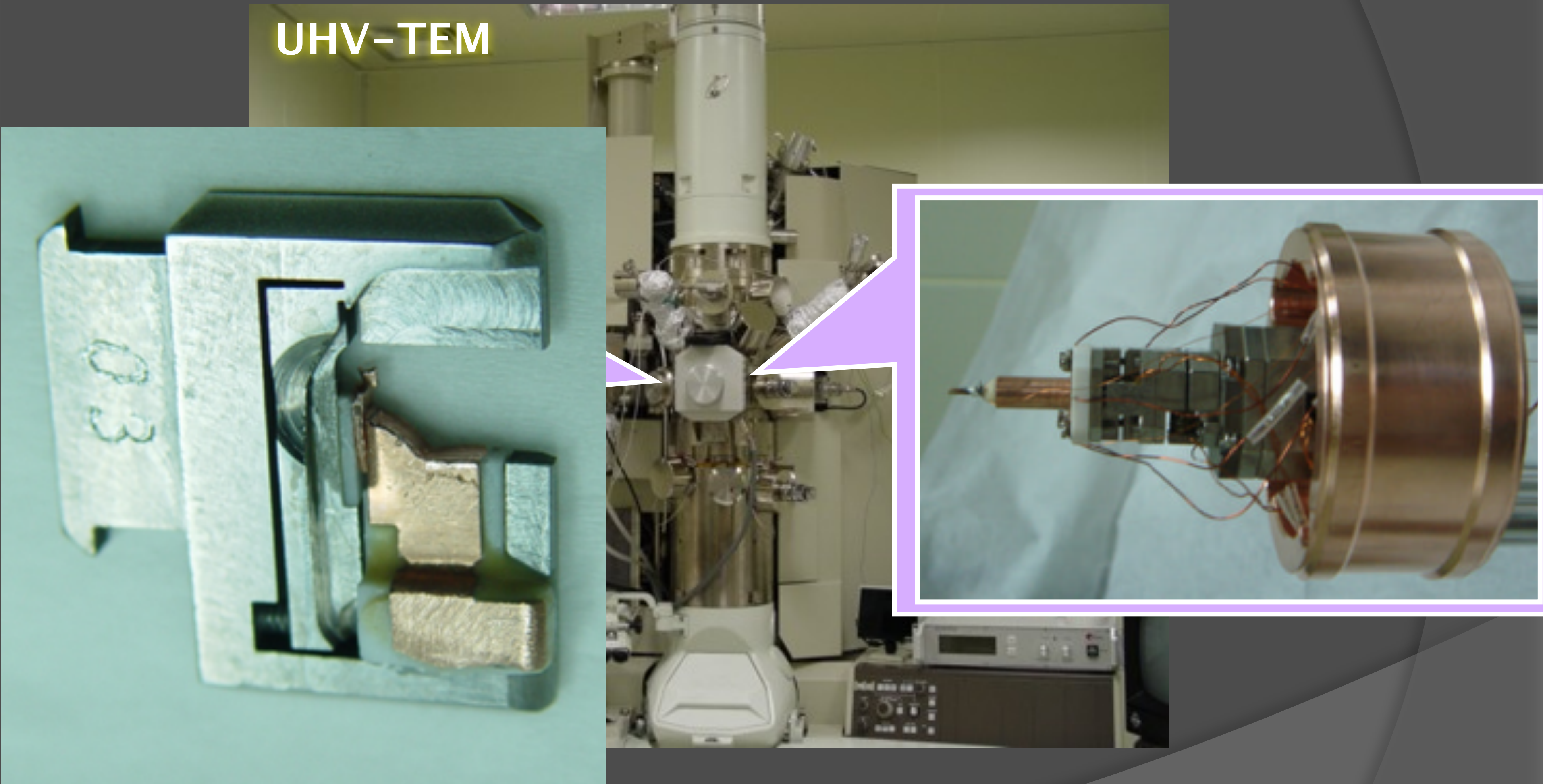
Base pressure 2 x 10^{-10} torr

STM@UHV-TEM



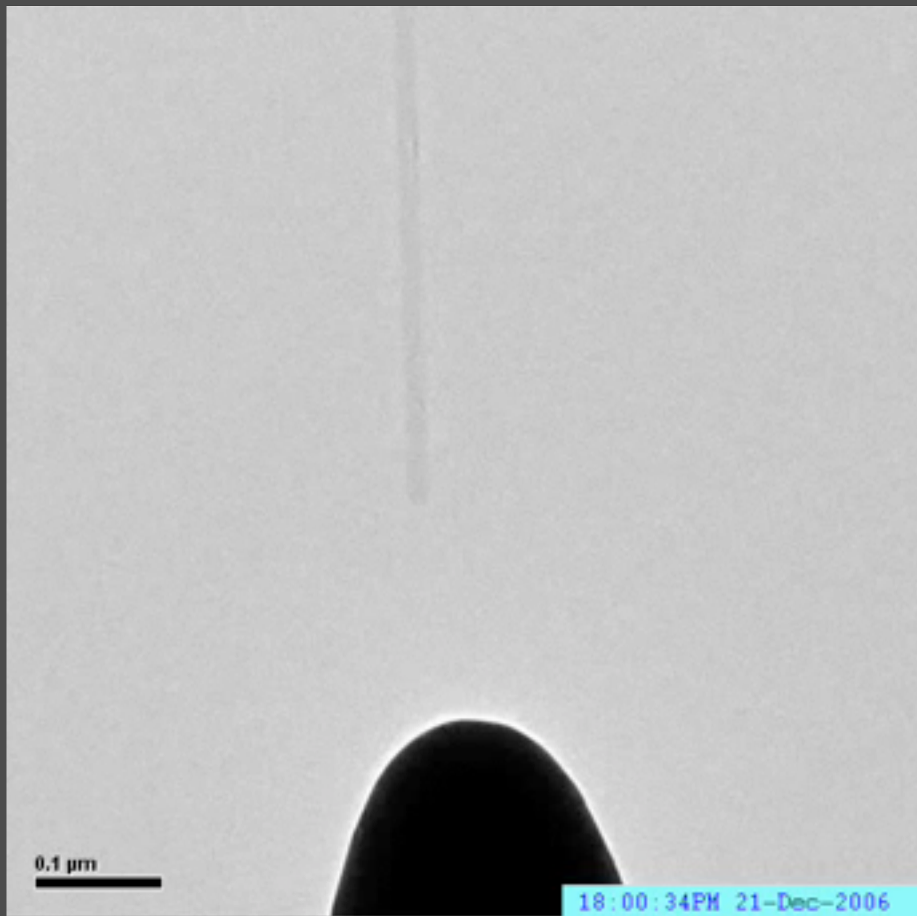
Base pressure 2 x 10^{-10} torr

STM@UHV-TEM

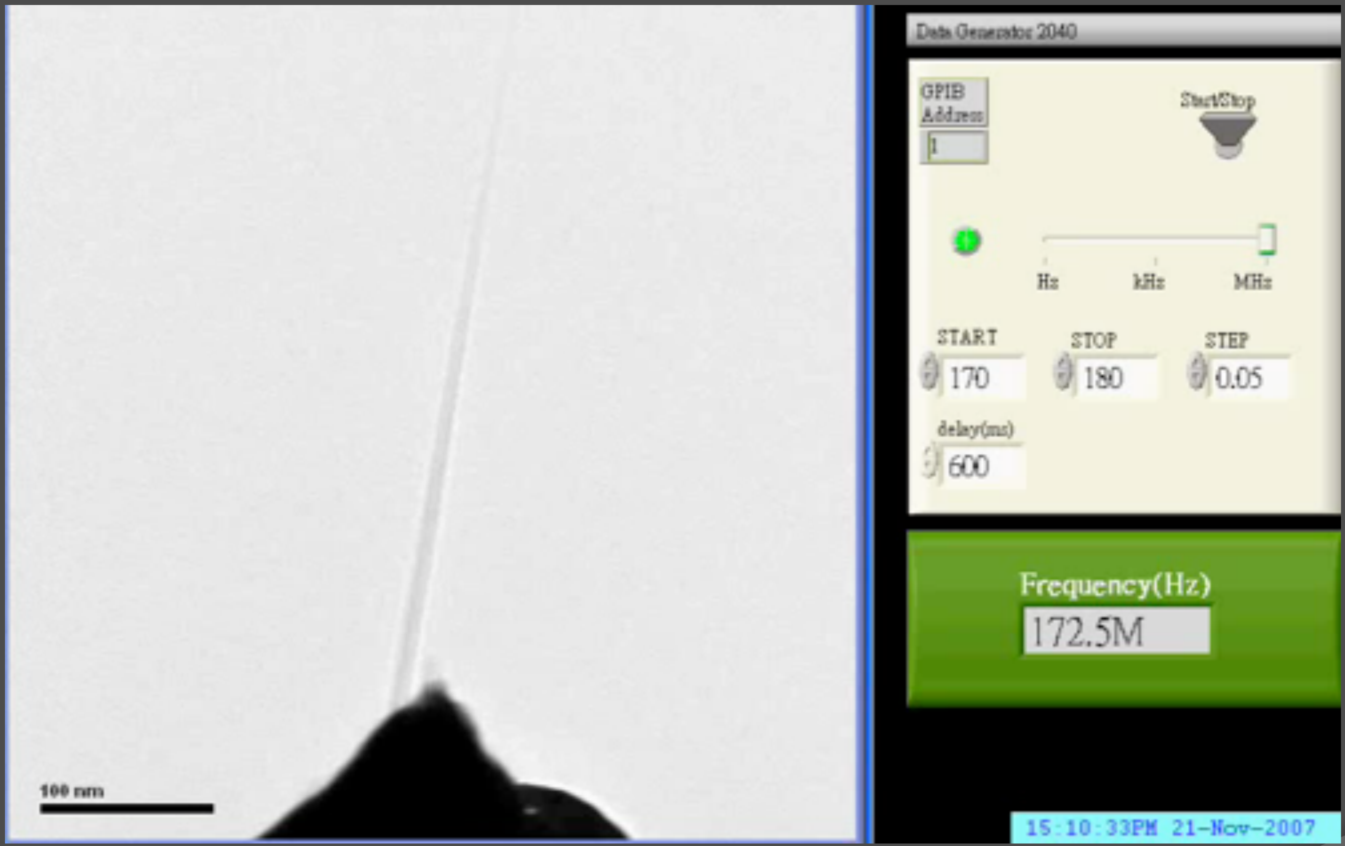


Base pressure 2 x 10^{-10} torr

Making CNT tips by STM@TEM

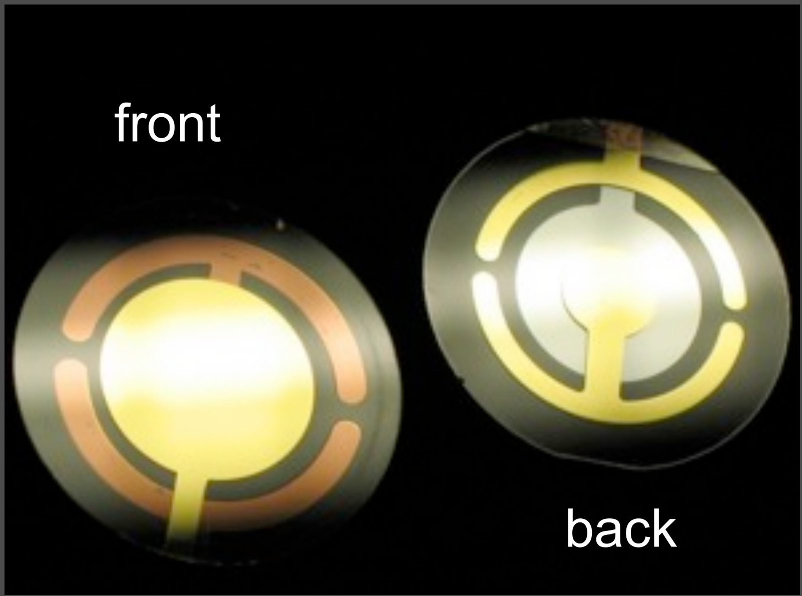


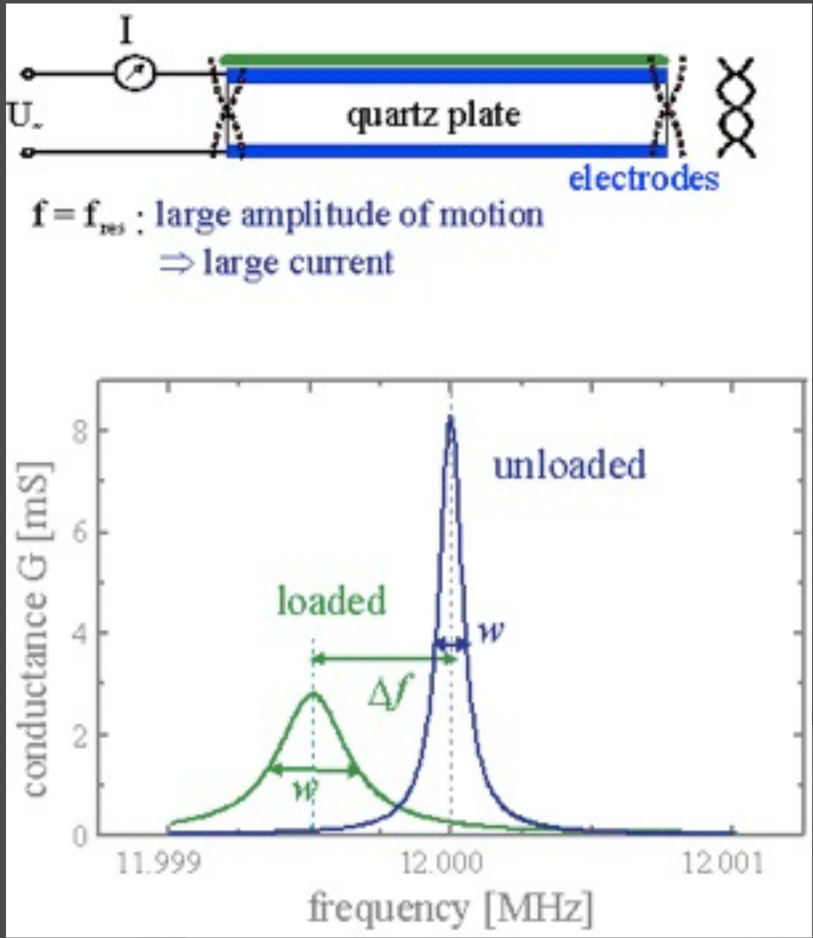
Nano electromechanical oscillator



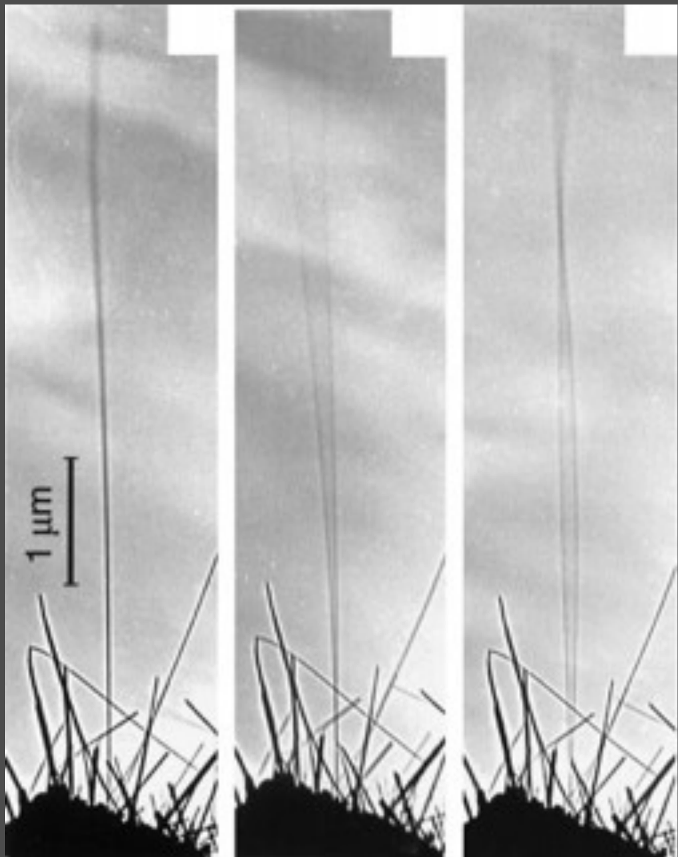
$$\nu_i = \frac{\beta_i^2}{8\pi}\frac{1}{L^2}\sqrt{\frac{(D^2+D_i^2)E_\beta}{\rho}}$$

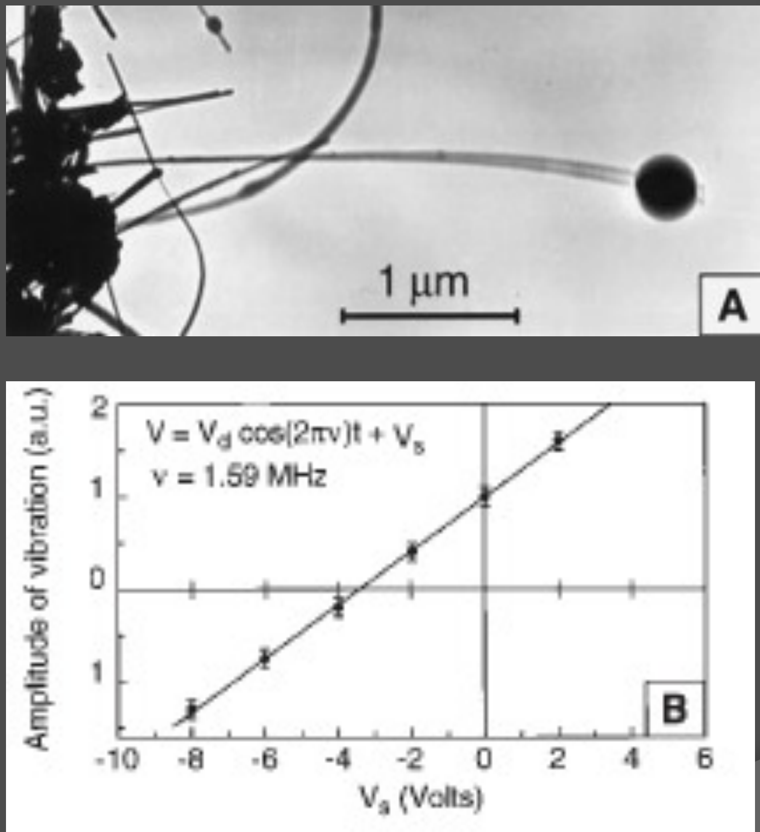
Quartz crystal microbalance





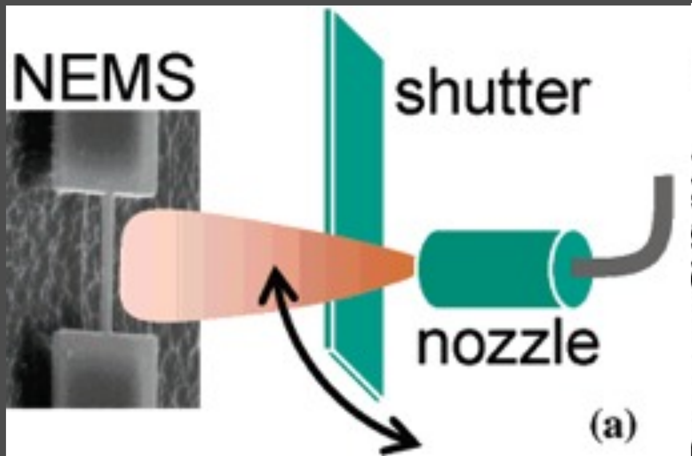
Electromechanical Resonances of Carbon Nanotubes

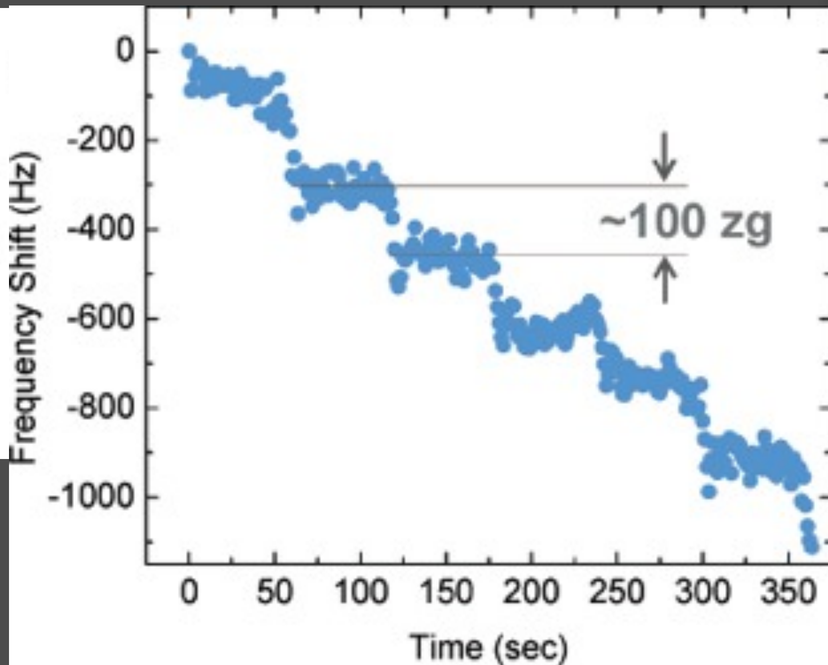




Philippe Poncharal, Z. L. Wang, Daniel Ugarte, and Walt A. de Heer, *Science* **283**, 1513 (1999).

Zeptogram Nanomechanical Sensing





$$\partial M_D/\partial t = mA_D(\partial N_C/\partial t)/\pi L^2$$

$$\delta M \sim (M_{eff}/Q)10^{-DR/20}$$

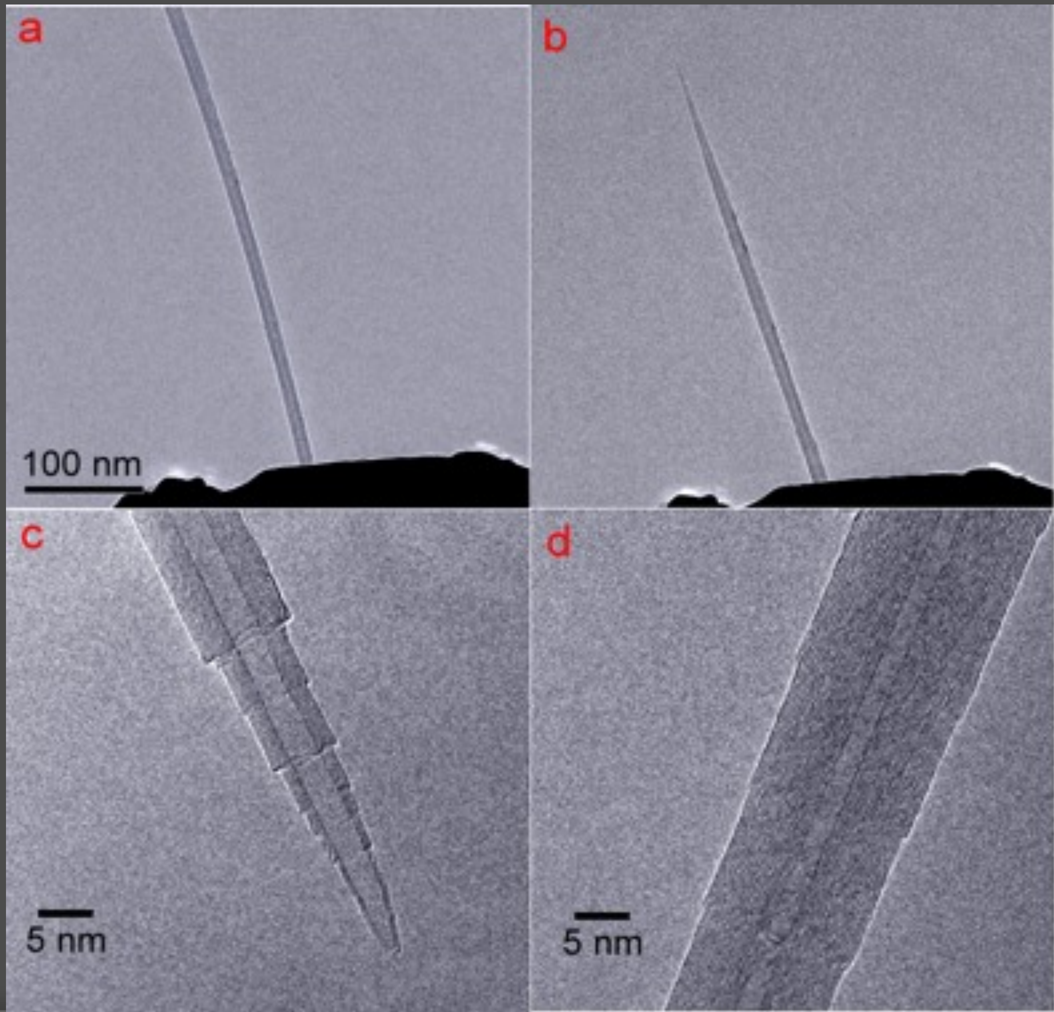
Y. T. Yang, C. Callegari, X. L. Feng, K. L. Ekinci, and M. L. Roukes, *Nano Lett.* **6**, 583 (2006).

Criteria for an atom balance

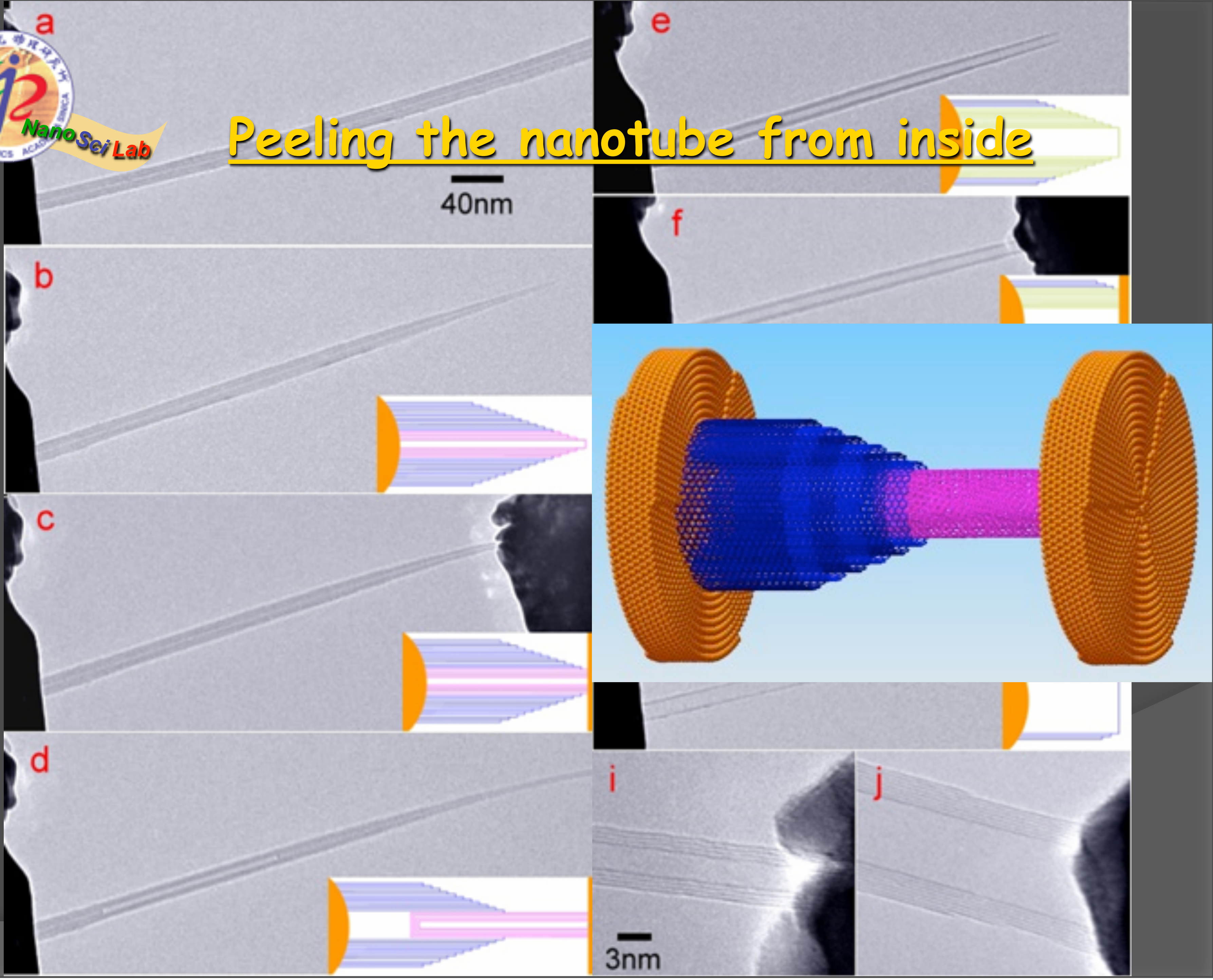
$$\delta m \sim 2m_0(kT/E_c)^{1/2}(\delta f/Qf_0)^{1/2}$$

- Small balance mass
- Sensitive detection mechanism
- Minimal thermal effects
- Well-controlled environment

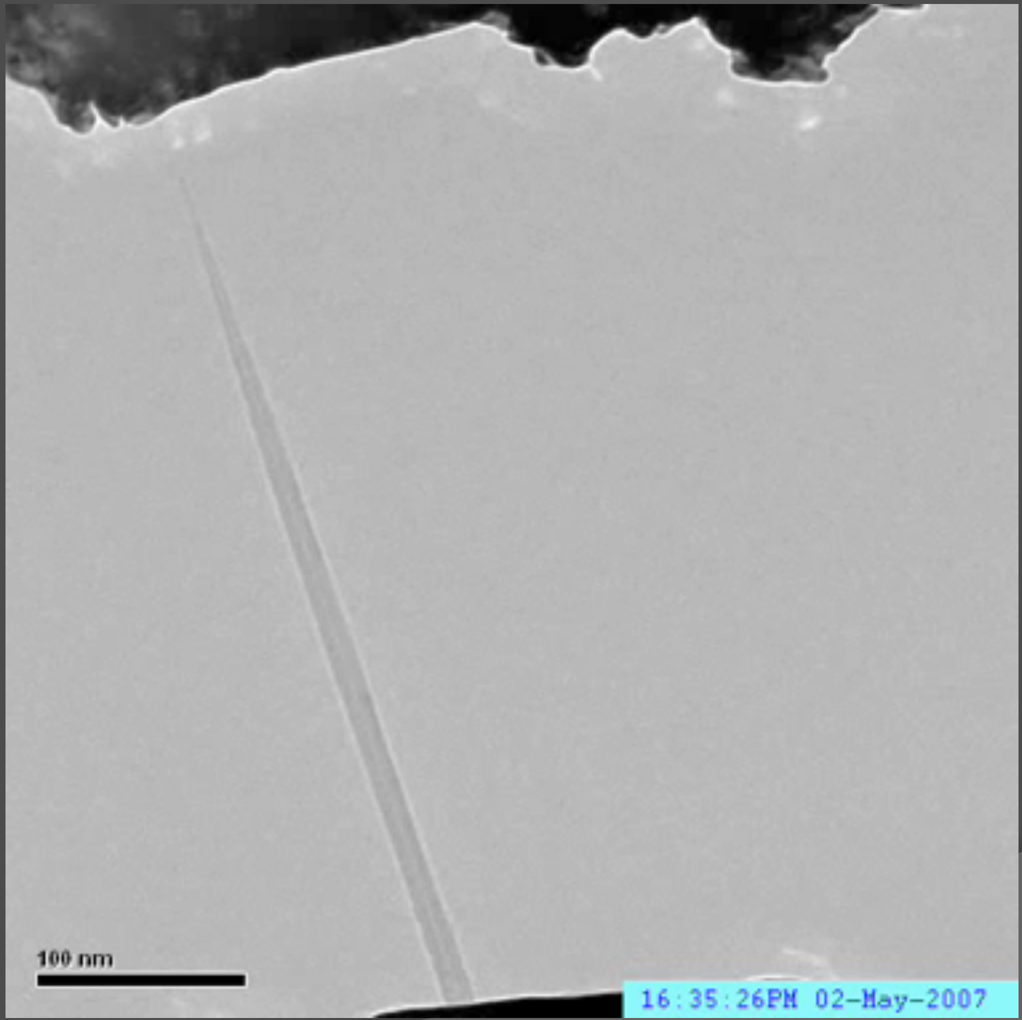
Shaping a nanotube into telescope



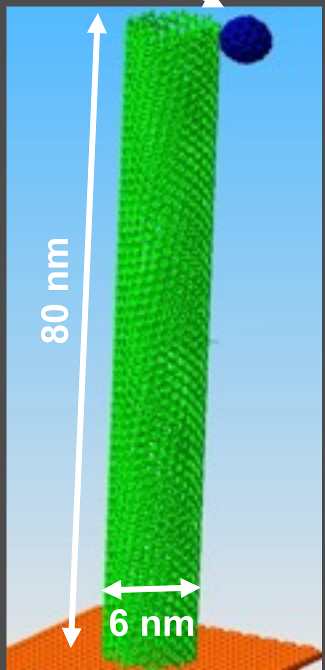
Peeling the nanotube from inside

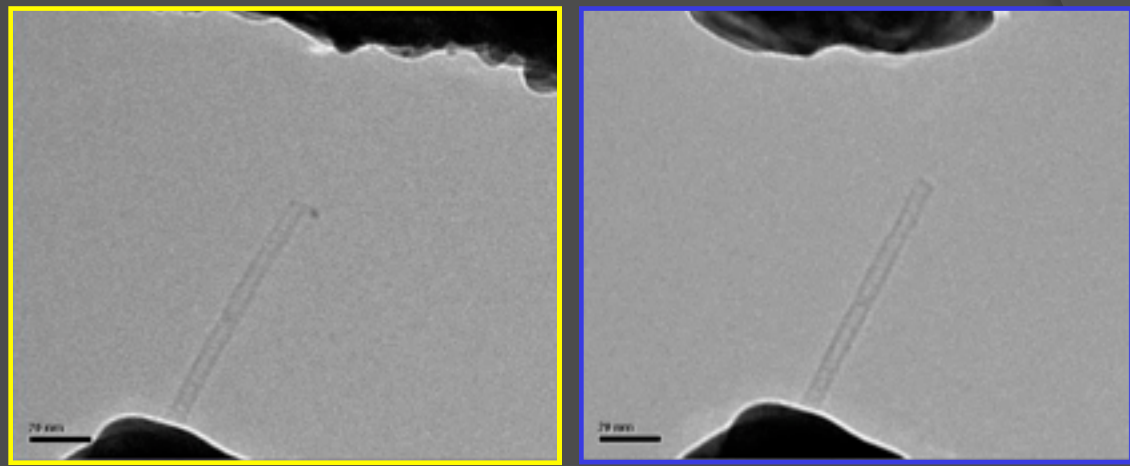


Peeling the nanotube from inside

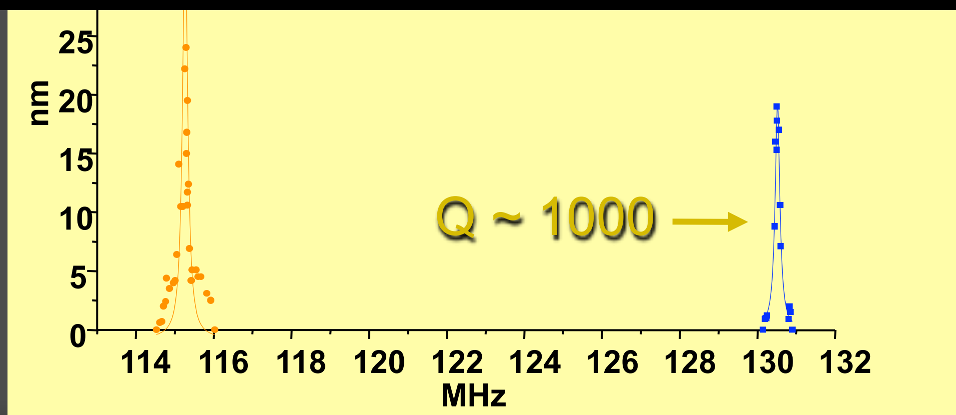


"Atom" balance





$m \sim -m_0(\Delta f/2f_0) \sim 1.8\times10^{-19}$ g (mass of 1000 Ag atoms)



Y.C. Chang *et al.*, *Small* **4**, 2195 (2008).

Mass resolution

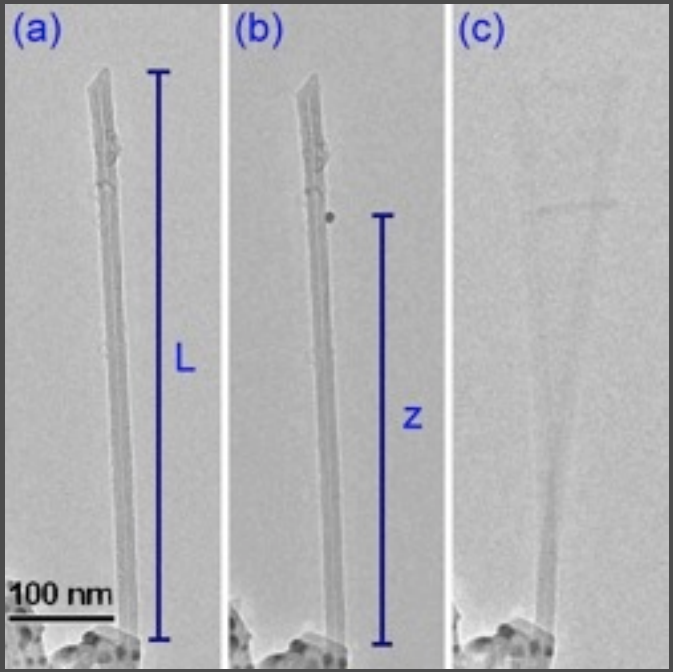
$$\delta m \sim 2m_0(kT/E_c)^{1/2}(\delta f/Qf_0)^{1/2}$$

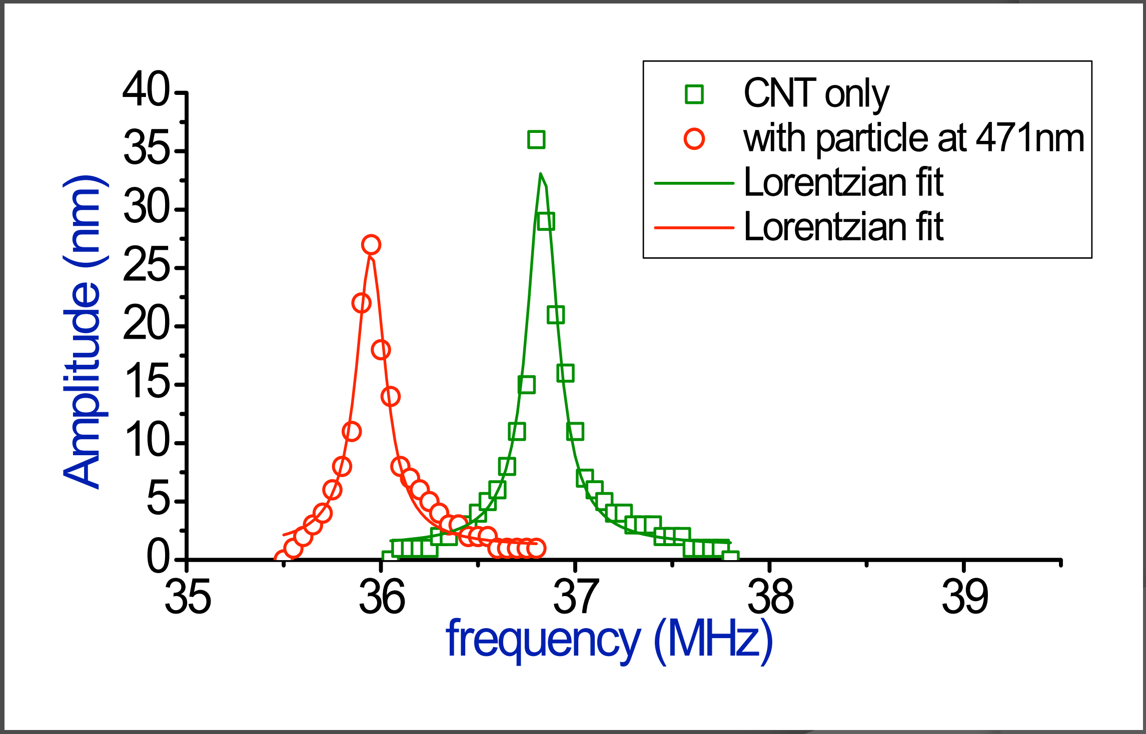
Parameters of the tailored CNT resonator:

Mass of balance : m_0 = 3.1 ag
Thermal energy: kT = 26 meV
Drive energy: $E_c \sim$ 200 meV
Measurement bandwidth: $\delta f \sim$ 100Hz
Quality factor: $Q \sim$1000
Resonance freq: f_0 ~130 MHz

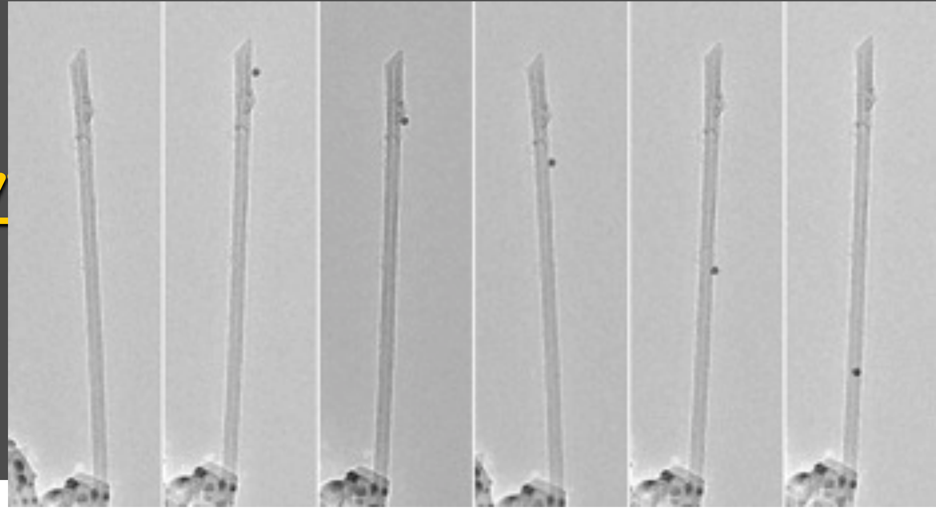
$\delta m \sim$ 0.1 zg < 0.18 zg (mass of Ag atom)

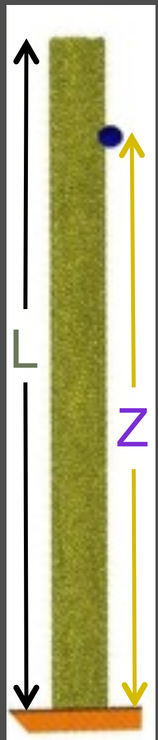
Shift of resonance frequency

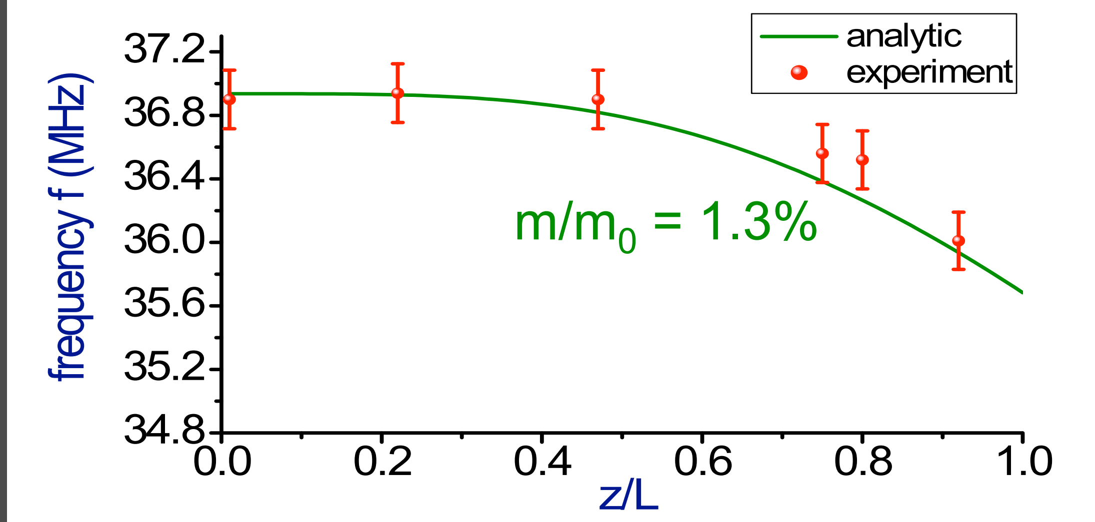




Analy ... sults



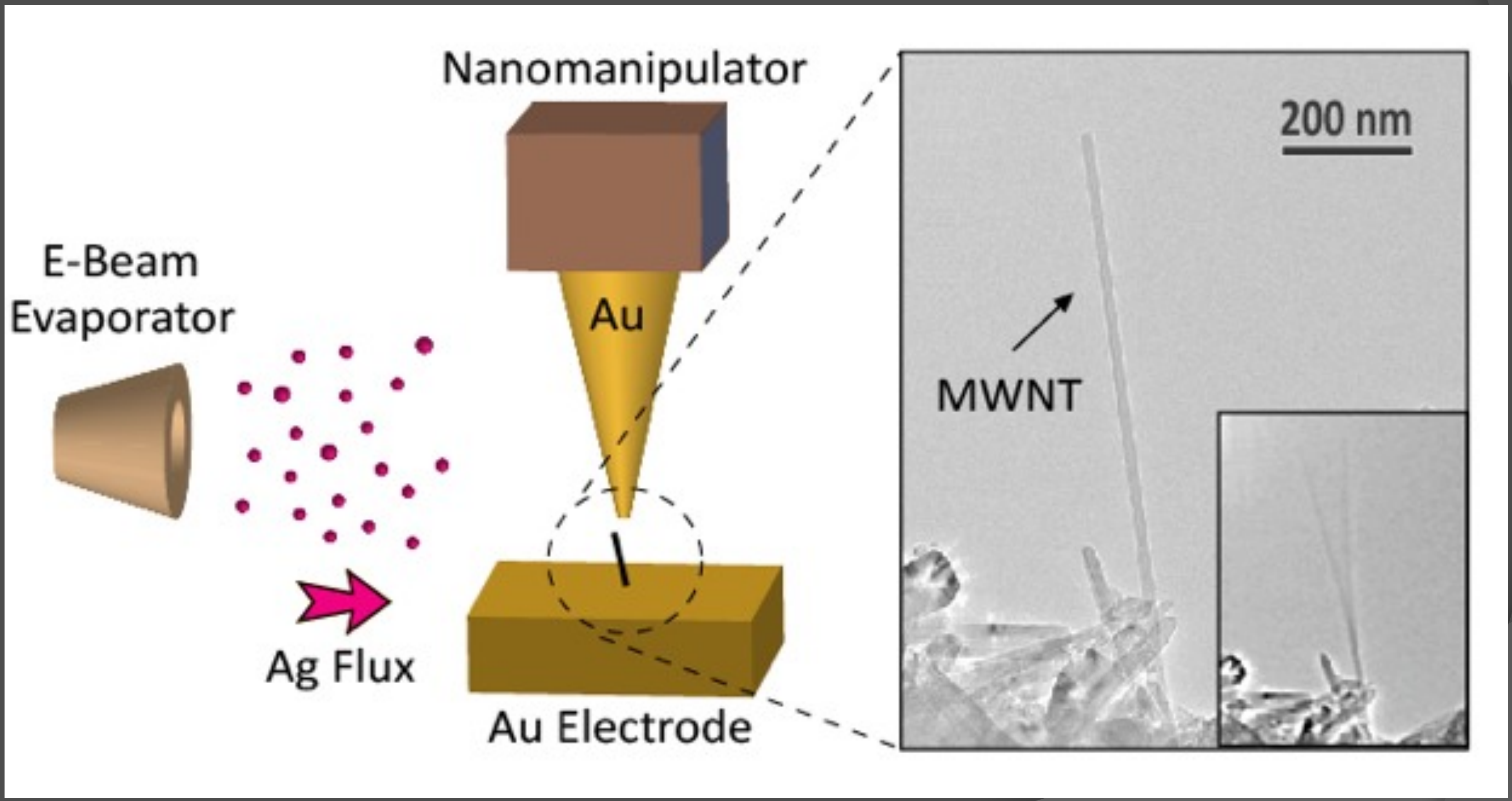




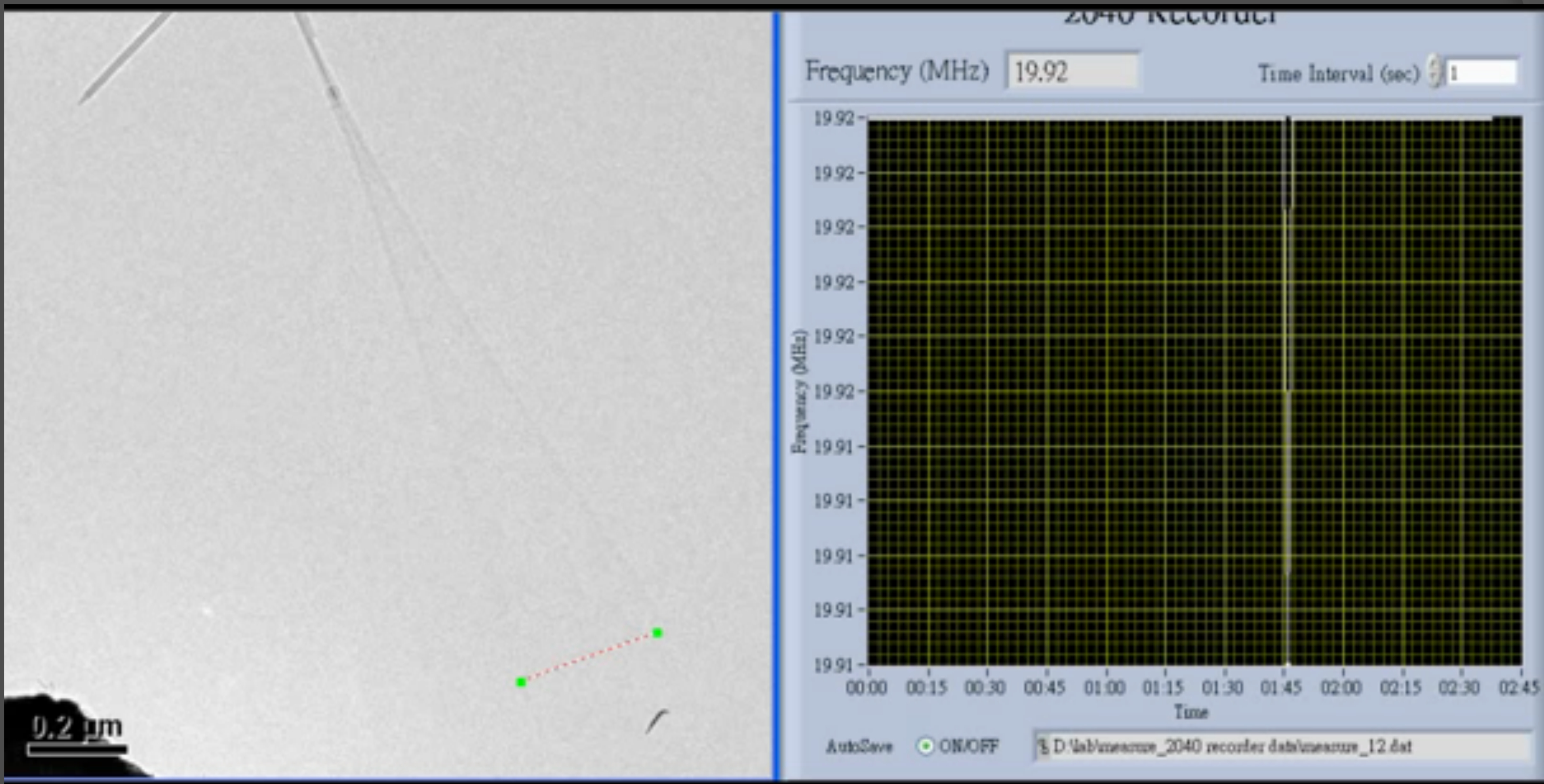
$$f^2 = f_0^{\,2}\left(1 + \frac{m}{m_0}U^2(z)\right)^{-1} \qquad f_0 = \frac{3.516}{8\pi L^2}\sqrt{(D^2 + D_i^{\,2})\frac{E_b}{\rho}}$$

$$U = -1.0002\left[\cos\left(1.875\frac{Z}{L}\right) - \cosh\left(1.875\frac{Z}{L}\right)\right] + 0.7344\left[\sin\left(1.875\frac{Z}{L}\right) - \sinh\left(1.875\frac{Z}{L}\right)\right]$$

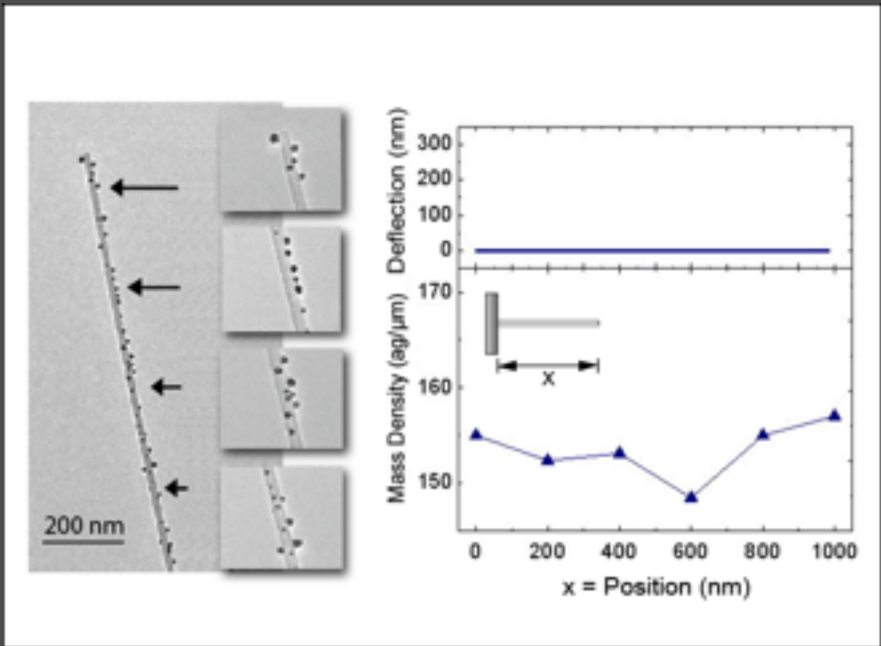
Nanotube resonator as mass sensor

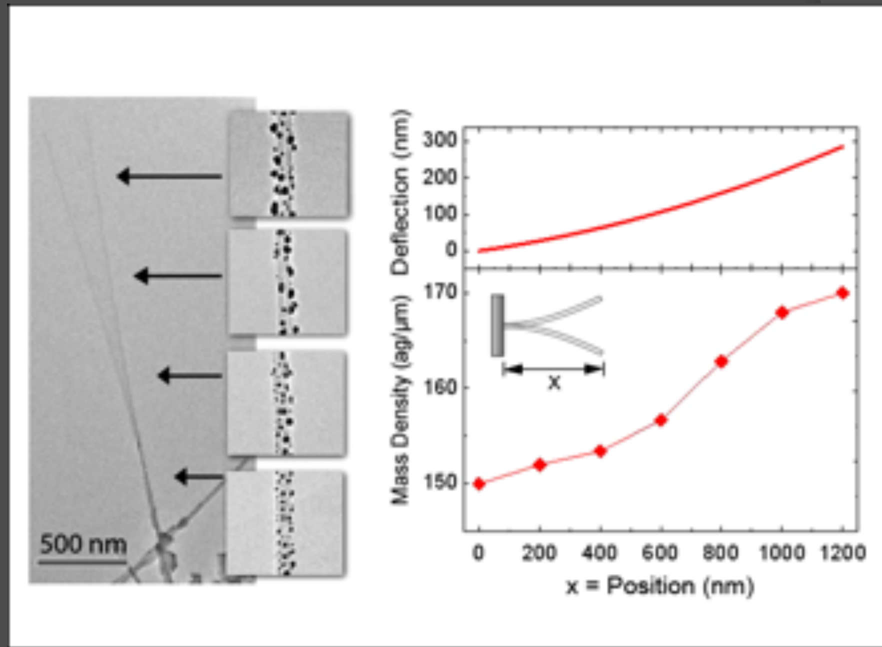


In situ measurement of freq. shift

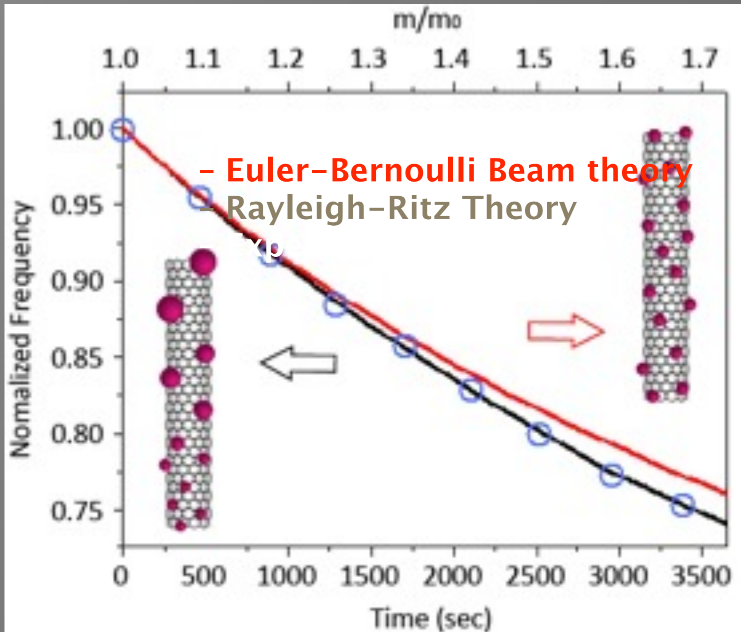


Gradient Coating Effect of Vibrating CNTs





Self-weighting ability

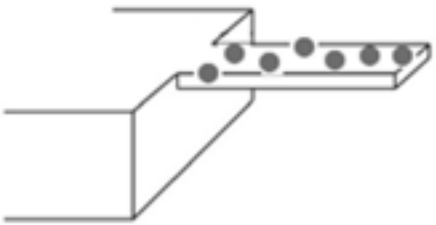


Euler-Bernoulli Beam theory

$$f = \frac{1}{2\pi}\sqrt{\frac{k}{m_0 + \Delta m}}$$

(Δm must be uniformly distributed on the cantilever)

Rayleigh-Ritz Theory



$$E_{strain} = E_{kin} + E_{kin,\Delta m1} + E_{kin,\Delta m2} + E_{kin,\Delta m3} \cdots$$

$$\omega = \omega_0 \left\{1 + \frac{1}{m_0}\int_0^L U^2(z)\,\lambda(z)\,dz\right\}^{-2}$$

$$U(z) = A_n(\cos k_n z - \cosh k_n z) + B_n(\sin k_n z - \sinh k_n z)$$

$$\lambda(z) = a_0 z + a_1$$ (Linear mass density)

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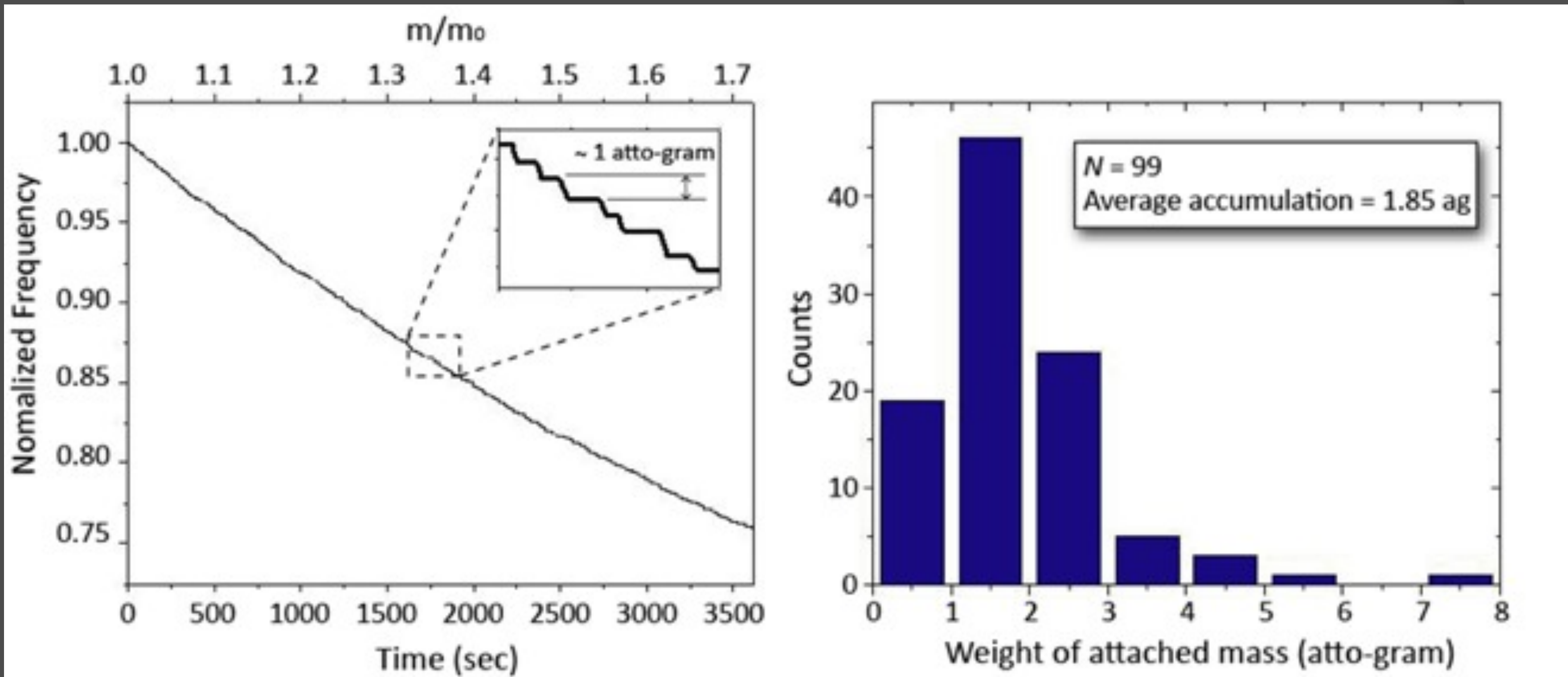
Weighting resolution



Flux (E-Beam Evaporator): 10 nA ~ 250 atoms/s

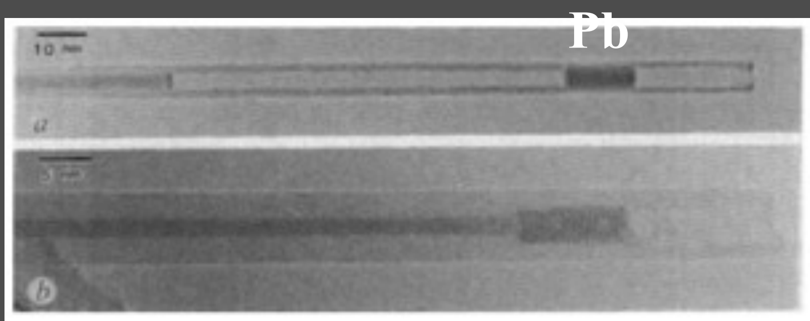
Summary

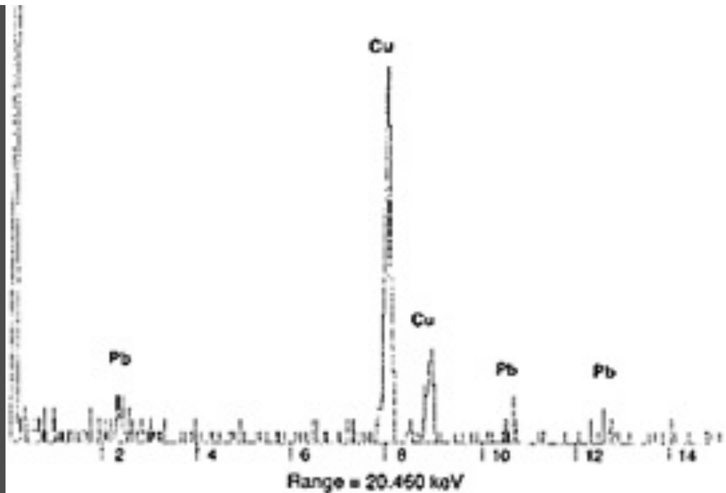
- Several in situ techniques under the UHV environment have been developed in the STM-TEM system to design a suitable CNT resonator for measuring neutral atoms/ molecules.
- A mass resolution of a single Ag atom has been indirectly demonstrated with the tailored CNT resonator.
- The shift of resonance frequency subject to the cluster's position on the CNT has been measured and analyzed with the classical analytical formula.
- In real time detection, the distribution of adsorbed mass on the vibrating CNT cannot be assumed uniform but close to linear.

Capillarity-induced filling of carbon nanotubes

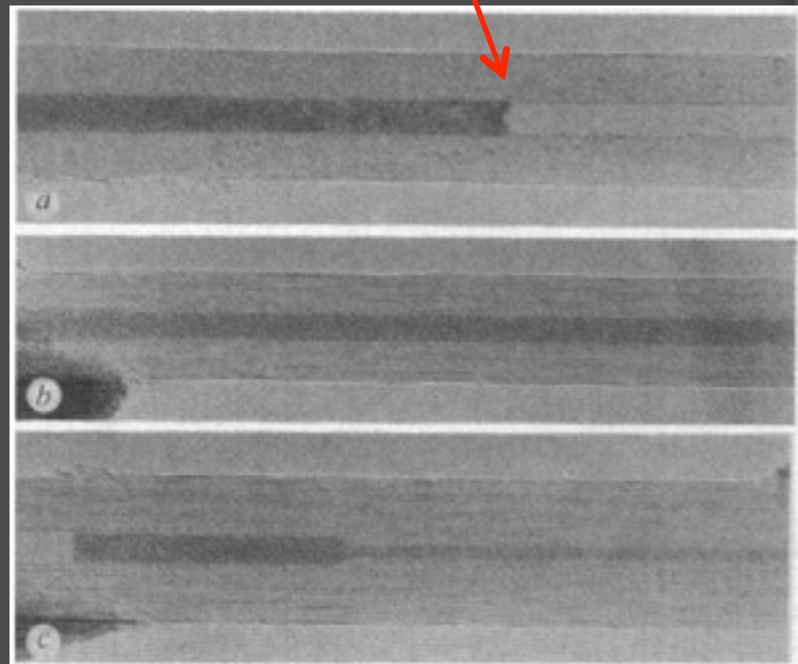
P. M. Ajayan & Sumio Iijima

Paper : Nature Vol. 361, 333-334, 1993



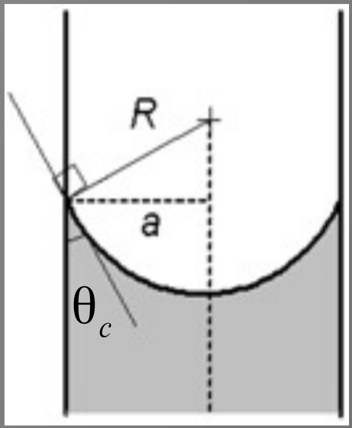


Pb seems to wet CNT



Macroscopic capillarity

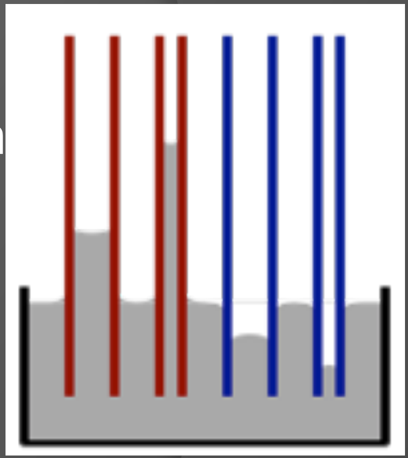
Sign and magnitude of the pressure ΔP across the liquid meniscus depend on contact angle θ_c



$$\Delta P = 2\gamma \cos\theta_c / a$$

$\theta_c < 90°$ → resulting in spontaneous absorption of the liquid into the capillary tube

$\theta_c > 90°$ → not be drawn inside the hollow unless external forces are applied



With this model, Dujardin *et al.* (*Science* **265** (1994) 1850) predicted the capillary action can happen only for the materials with surface tension γ < 200 mN/m.

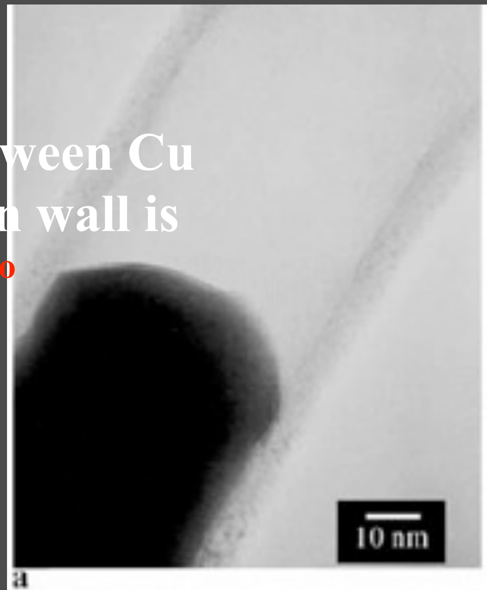
Surface tension (γ) for Ag ~ 900 mN/m

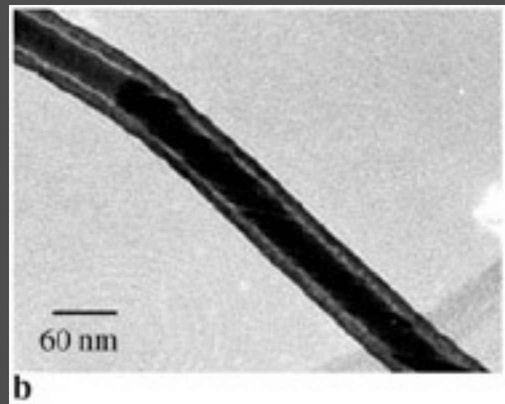
Synthesis of carbon nanotubes with totally hollow channels and/or with totally copper filled nanowires

Q. ZHANG
W.Z. QIAN*
H. YU
F. WEI
Q. WEN

Applied Physics A: Materials Science &Processing 86 (2007) 265

contact angle between Cu and inner carbon wall is 120º~135º





※ **Relatively poor wetting characteristics of Cu on the carbon surface**

Capillary forces may be efficient to drive filling of CNTs by metallic nanoparticles of various transition metals such as Pd, Ni, and Cu.

Capillarity for small droplet

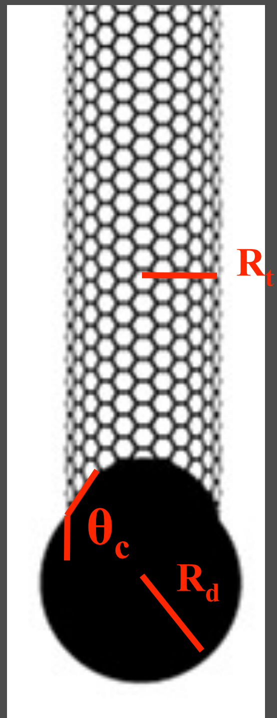
According to Young-Laplace equation:

$$\Delta P = \gamma\left(\frac{1}{R_x}+\frac{1}{R_y}\right)$$

ex: droplet (spherical)

$$R_x = R_y = R$$

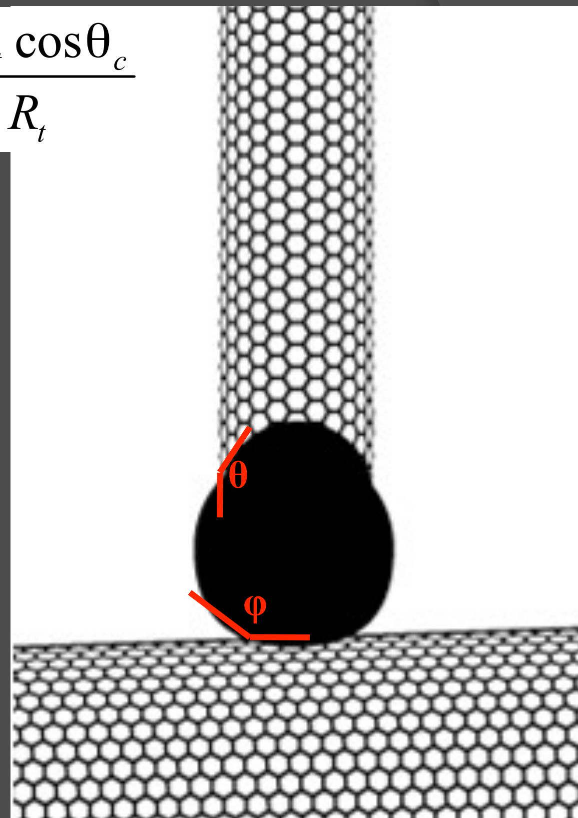
$$\Delta P = \frac{2\gamma}{R}$$



$$\Delta P_t = \frac{2\gamma_{dt}}{R_{meniscus}} = \frac{2\gamma_{dt}\cos\theta_c}{R_t}$$

$$\Delta P_d = \frac{2\gamma_d}{R_d}$$

The droplet is unsupported



For the contact angle θ_c~125° of molten Ag nanodroplet inside the MWNT in our results

$$\Delta P_t = \frac{\gamma_{dt}}{R_t} \qquad \Delta P_d = \frac{2\gamma_d}{R_d}$$

$R_d \downarrow \Rightarrow \Delta P_d \uparrow$

When the droplet is supported, the effect of Laplace pressure will be reduced.

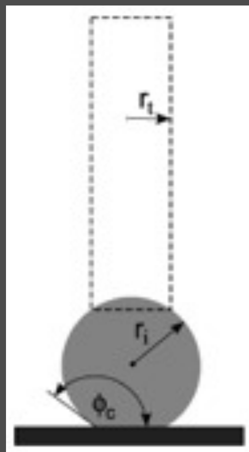
Capillary Absorption of Metal Nanodroplets by Single-Wall Carbon Nanotubes

D. Schebarchov† and S. C. Hendy*,†,‡

Paper : Nano Letter Vol. 8, 2253-2257, 2008

Part A : Present a simple model to demonstrate the capillary absorption for nonwetting liquid nanoparticles by CNT

Initial state



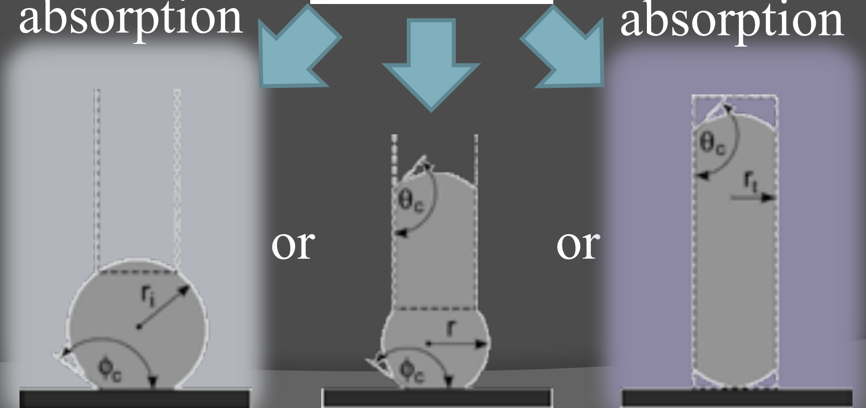
Parameter:

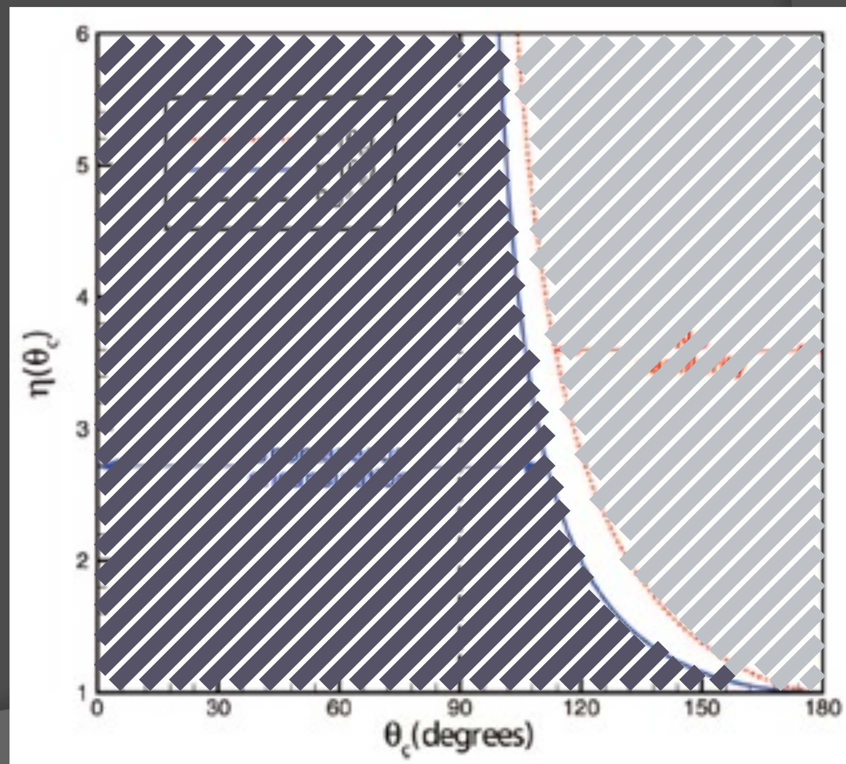
θ_c

$$\eta \equiv r_i / r_t$$

No absorption

Full absorption

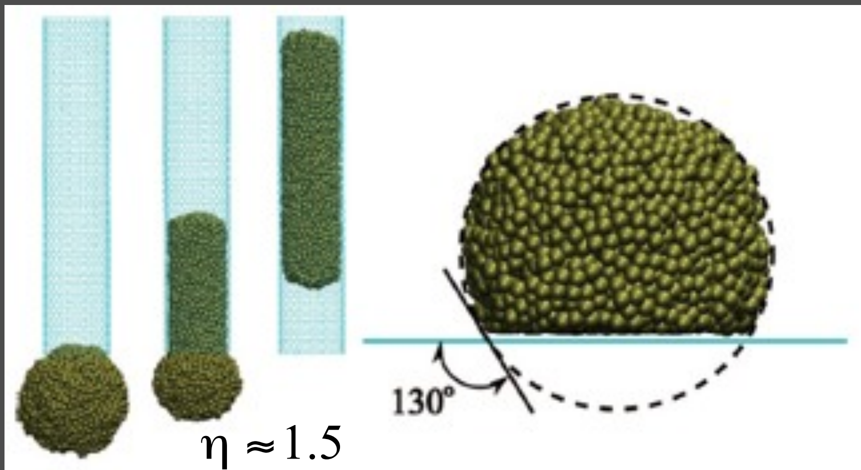




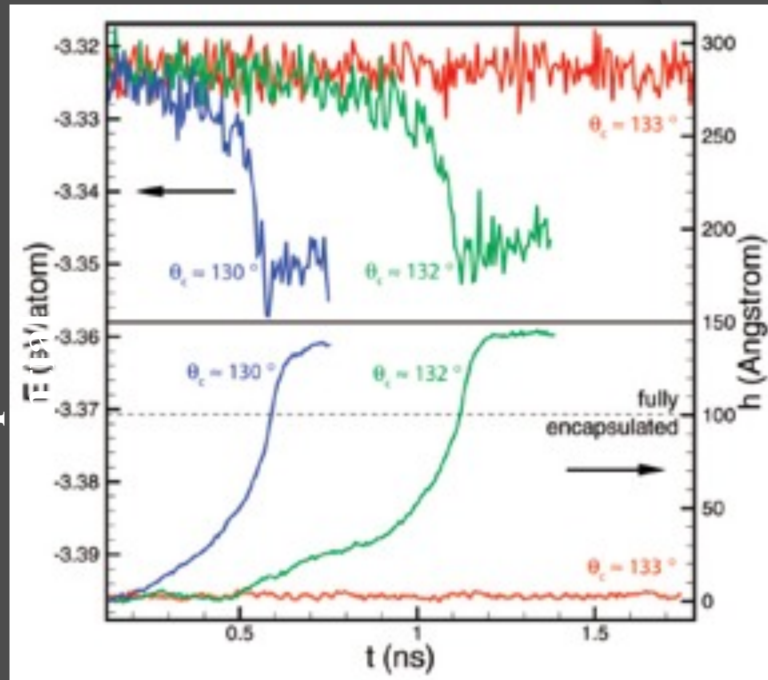
Molecular dynamics simulation

CNT 220 Å long and 30 Å in diameter

Molten Pd cluster with a radius of ~23 Å



Droplet

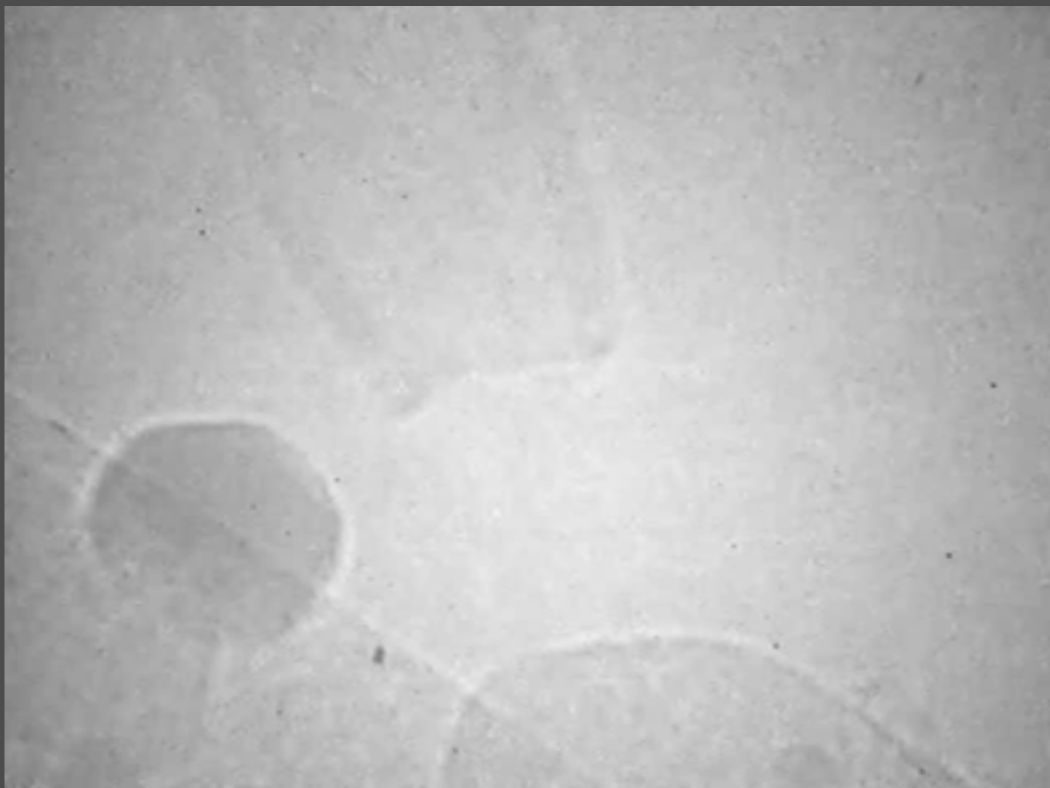


Distance of insertion of Pd cluster

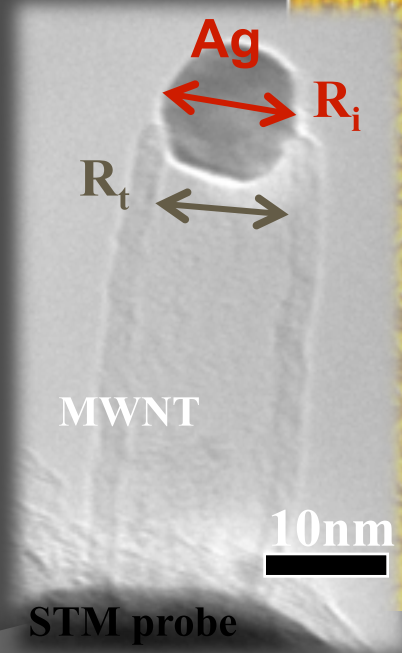
Contact angle θ_c between Pd cluster and inner shell of SWNT

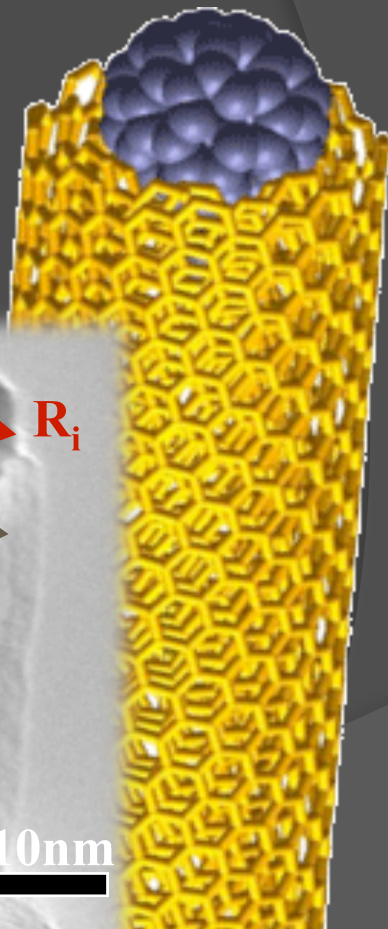
- $\theta_c \le 130°$ Molten nanoparticle were drawn almost immediately.
- $\theta_c \approx 132°$ The presence of a small energy barrier. The absorption is activated.
- $\theta_c > 133°$ did not yield capillary absorption of the droplets.

Approaching Ag nanoparticle with open-ended MWCNT

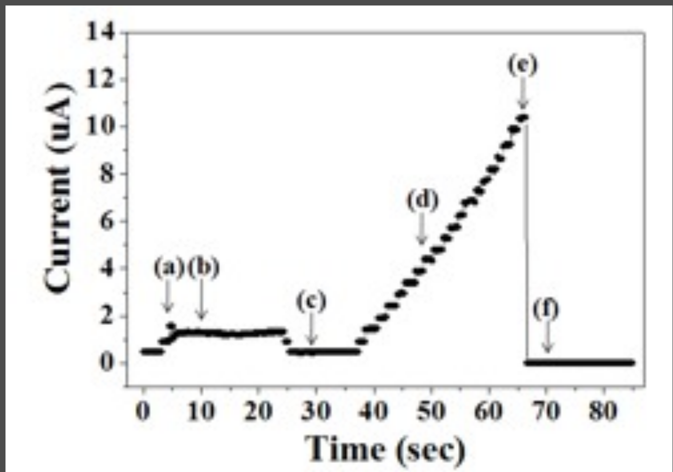


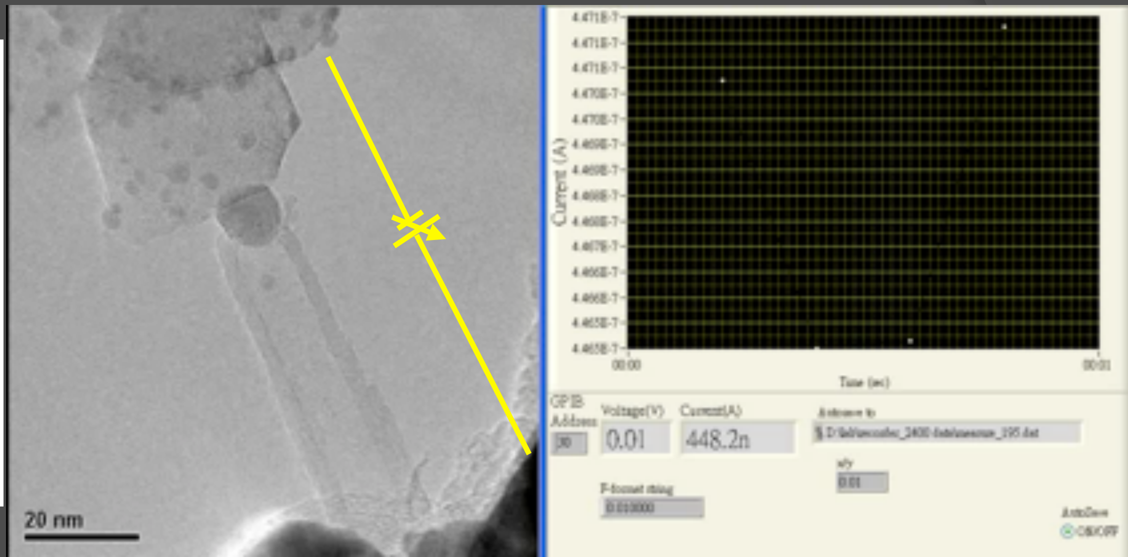
$$\eta \equiv R_i / R_t$$

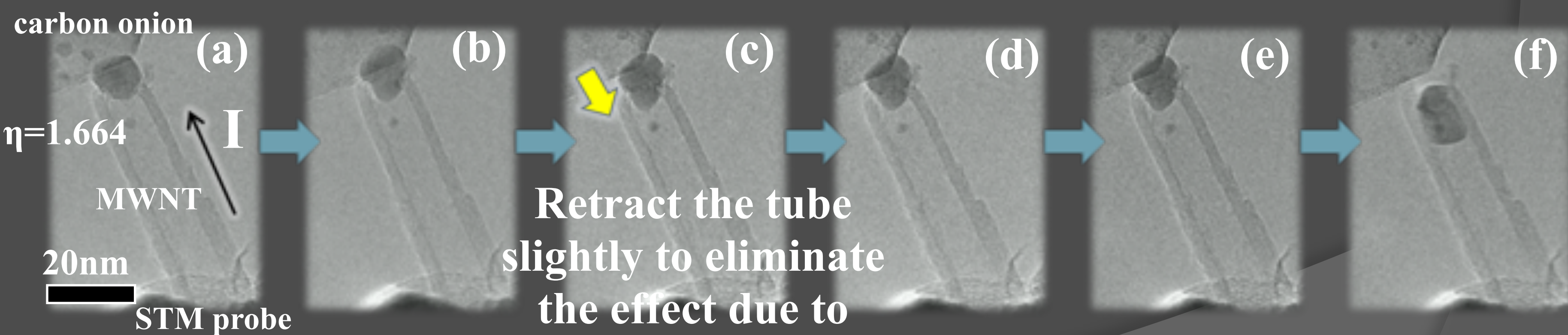




Capillary absorption of Ag droplet







Retract the tube slightly to eliminate the effect due to compression

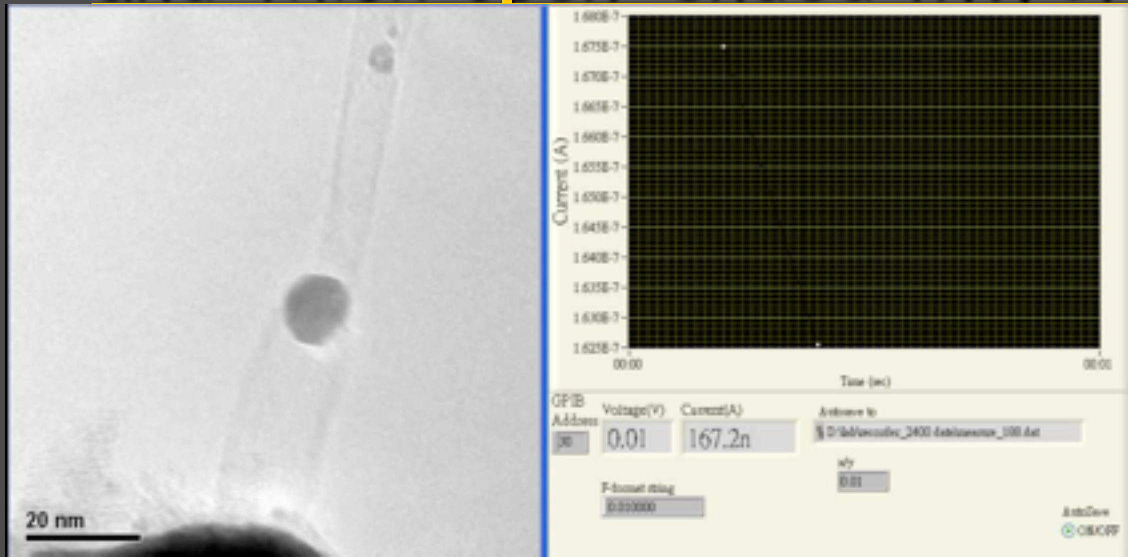
Capillary absorption at TV rate

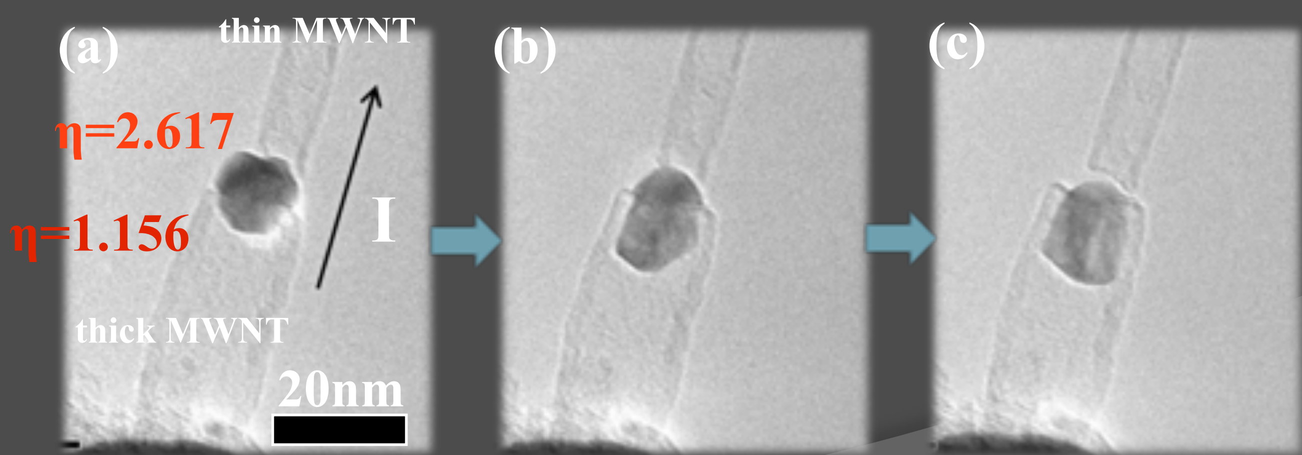
Current-induced joule heat caused the state change of Ag nanodroplet to melt and then triggered the capillary absorption

CCD record: two frames per second

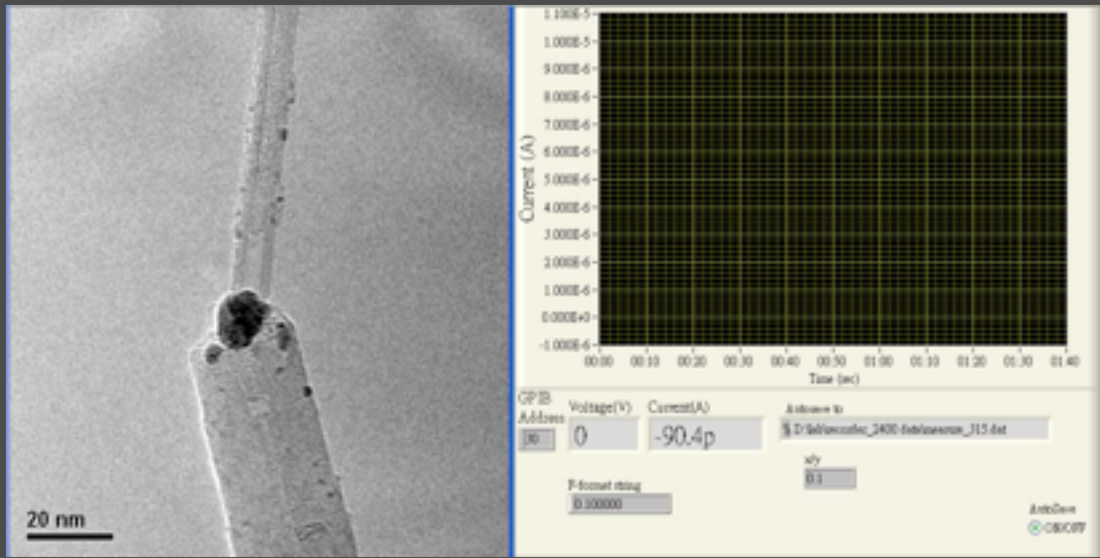
TV record: ~30 frames per second

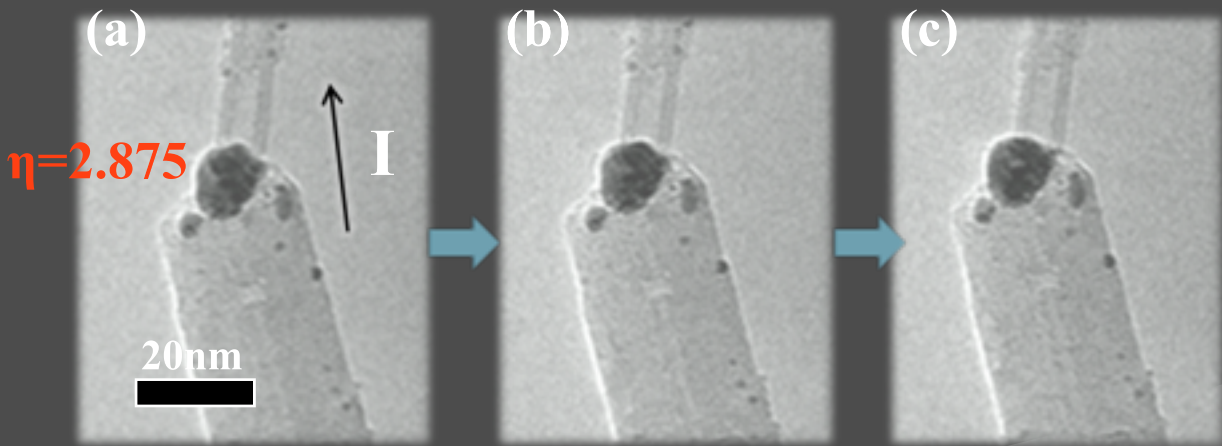
Ag nanoparticle between a thin and thick open-ended MWCNT





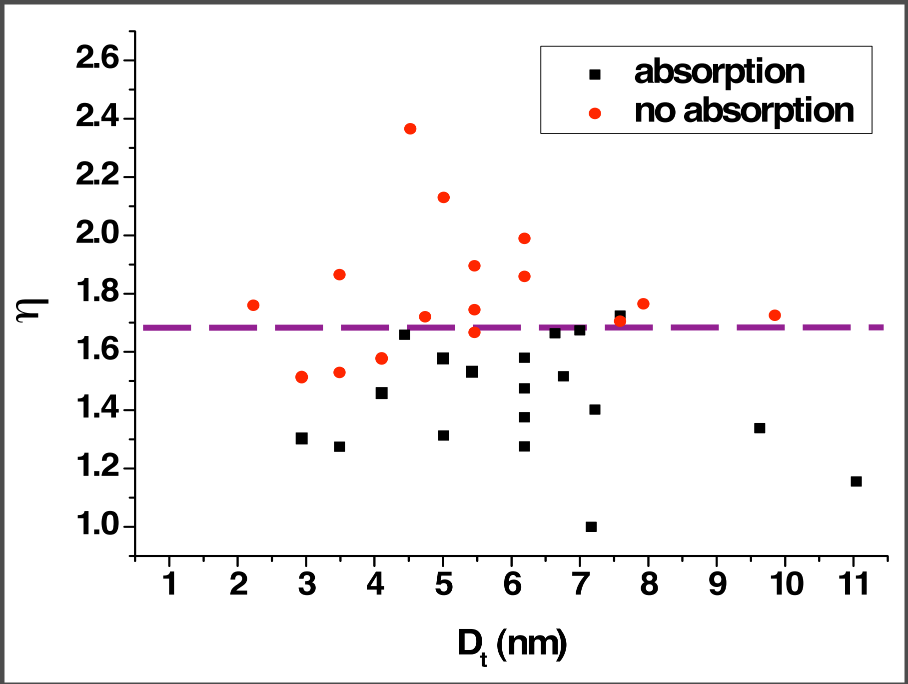
No absorption for large η

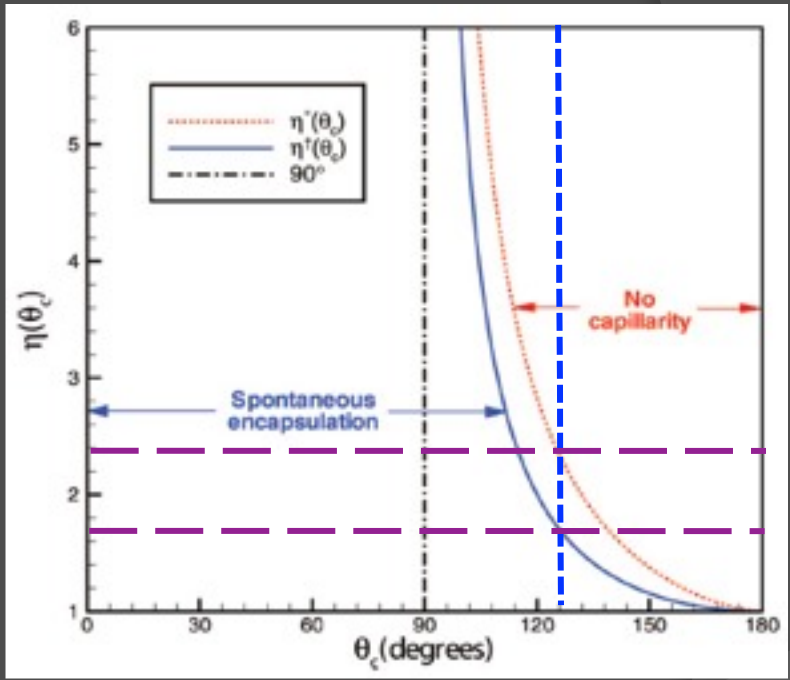




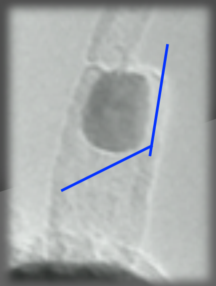
The Ag nanodroplet drained out gradually from the hollow core of MWNT as the passing current increased

Capillary absorption as function of η





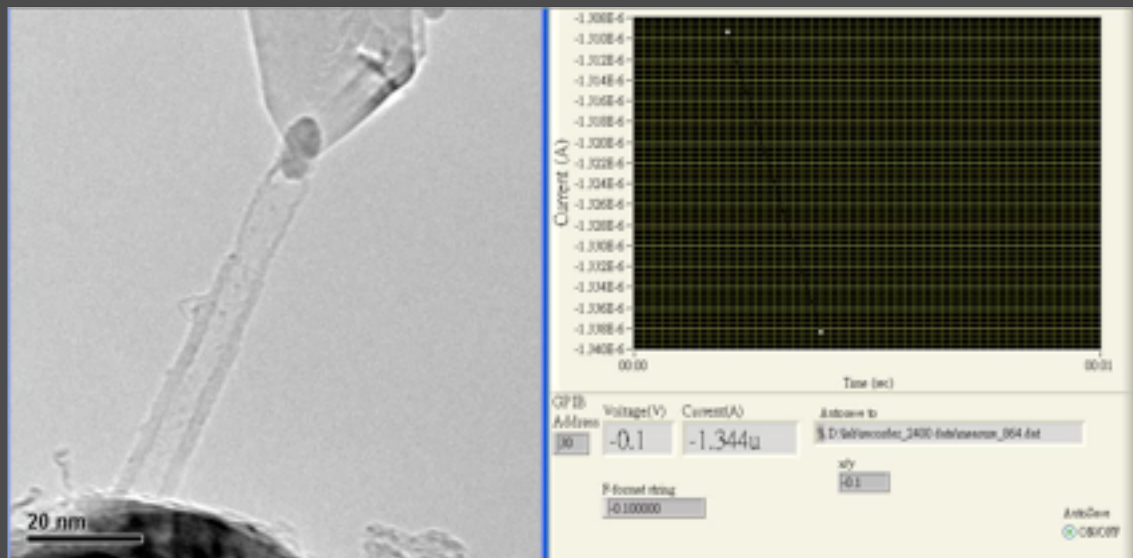
The critical η~1.7 for capillary absorption in our experiment agrees well with the calculated result for tube's diameter > 5nm.



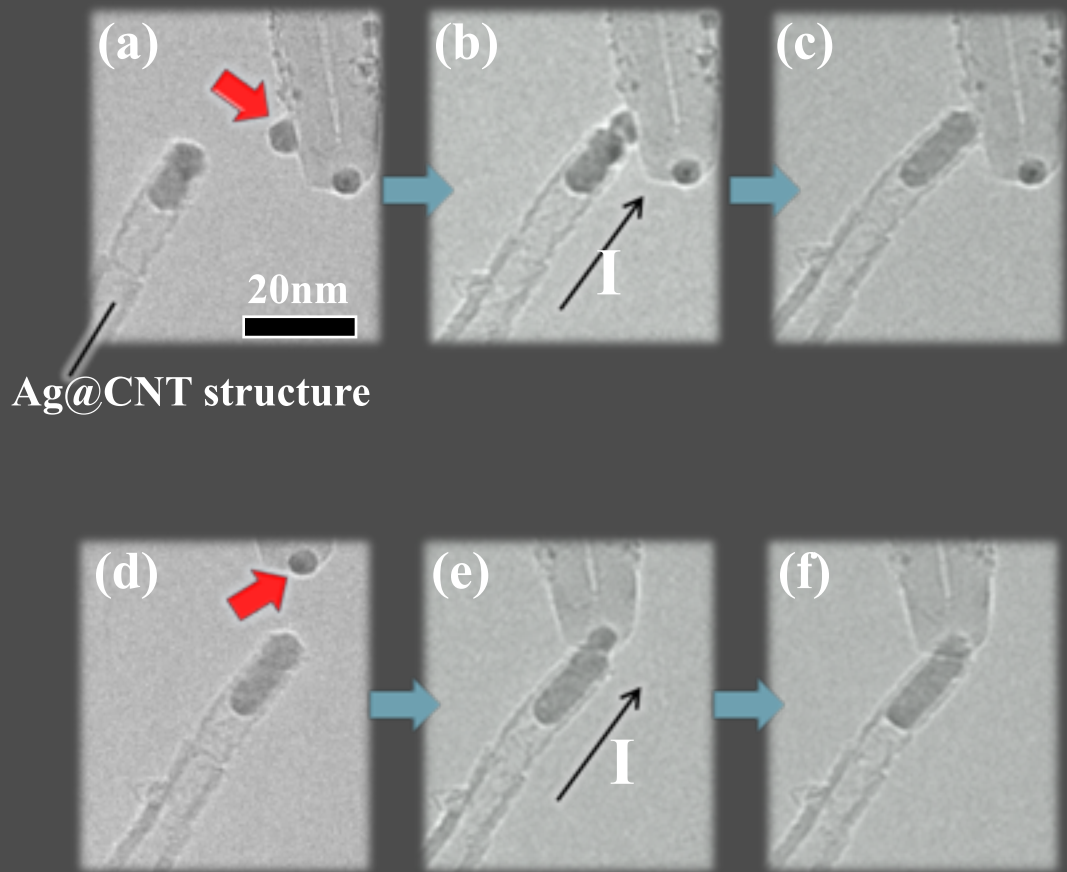
Contact angle ~ 125°

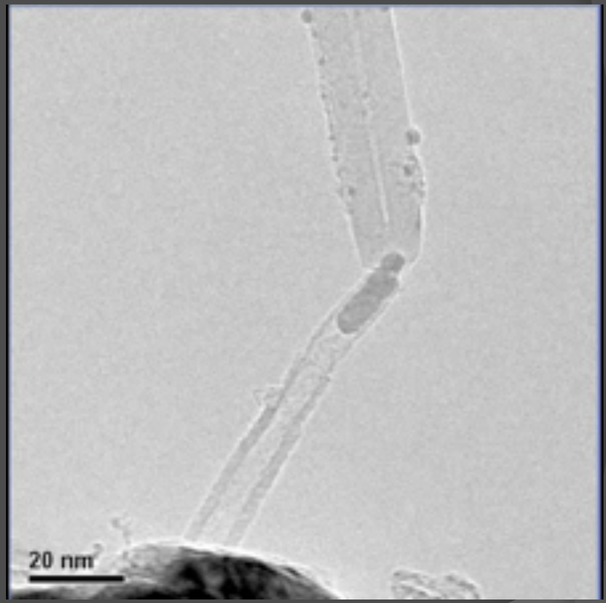
Exclusion of electromigration effect

Capillary absorption occurs independent of the current direction



Fabrication of Ag nanowire in a CNT





Summary

1. *The dynamic process of capillary absorption of nonwetting Ag nanodroplets by the MWCNT was in-situ observed.*
2. *The electromigration effect is not the main attribute for absorption of Ag nanodroplet.*
3. *For a large ratio of $\eta = R_i/R_t$, the Ag nanodroplet tends to cohere to itself and drains out from the hollow core of MWCNT. Therefore, the η value for the occurrence of capillary absorption must be below a critical value ~ 1.7.*
4. *The one-dimensional Ag nanowire with a specific length can be fabricated inside a MWCNT by capillary absorption for NEMS electronics or other applications.*