



In situ structural manipulation and property measurements of carbon nanotubes

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Nanoscience and Nanotechnology, National Science Council

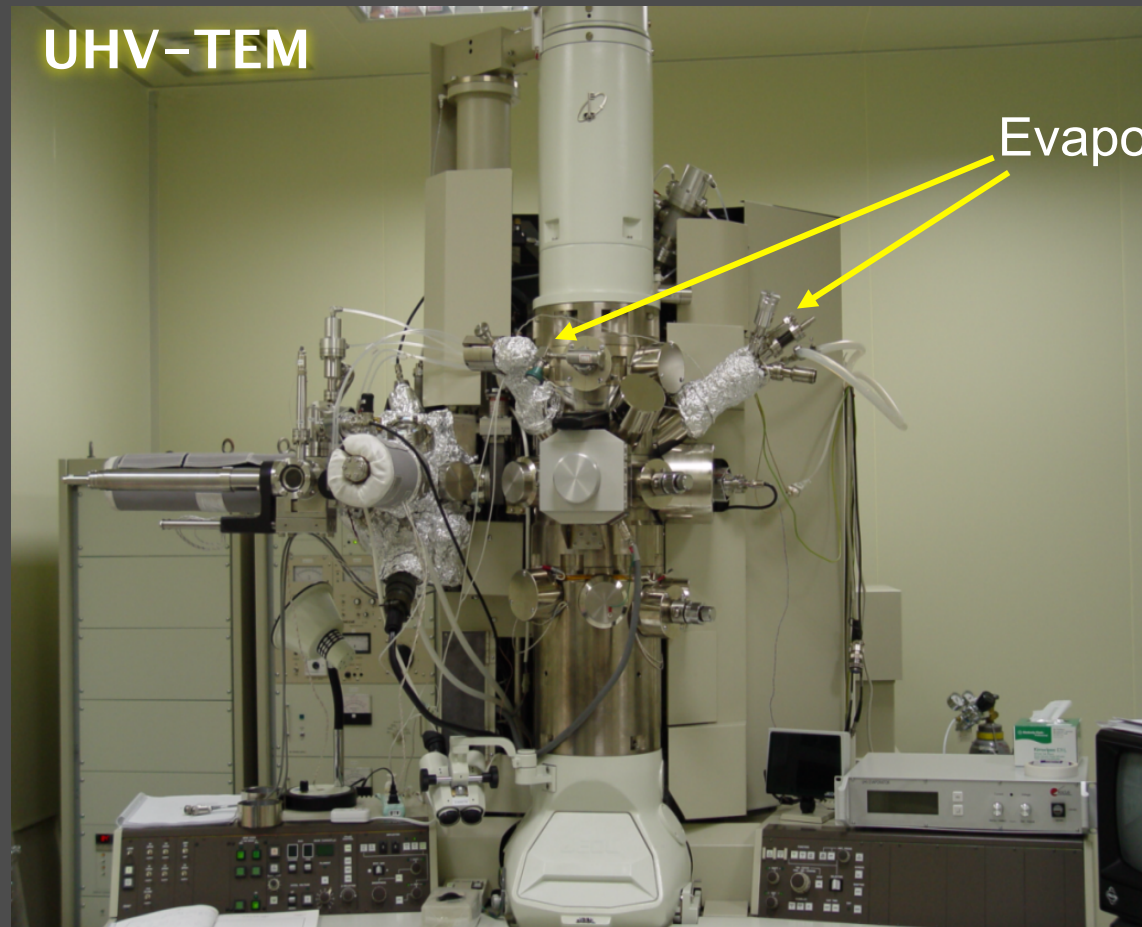


Outline

1. Manipulation of carbon nanotubes
2. Mass detection using CNT as a resonator
3. Capillarity of molten silver droplets

Ultrahigh vacuum HR-TEM

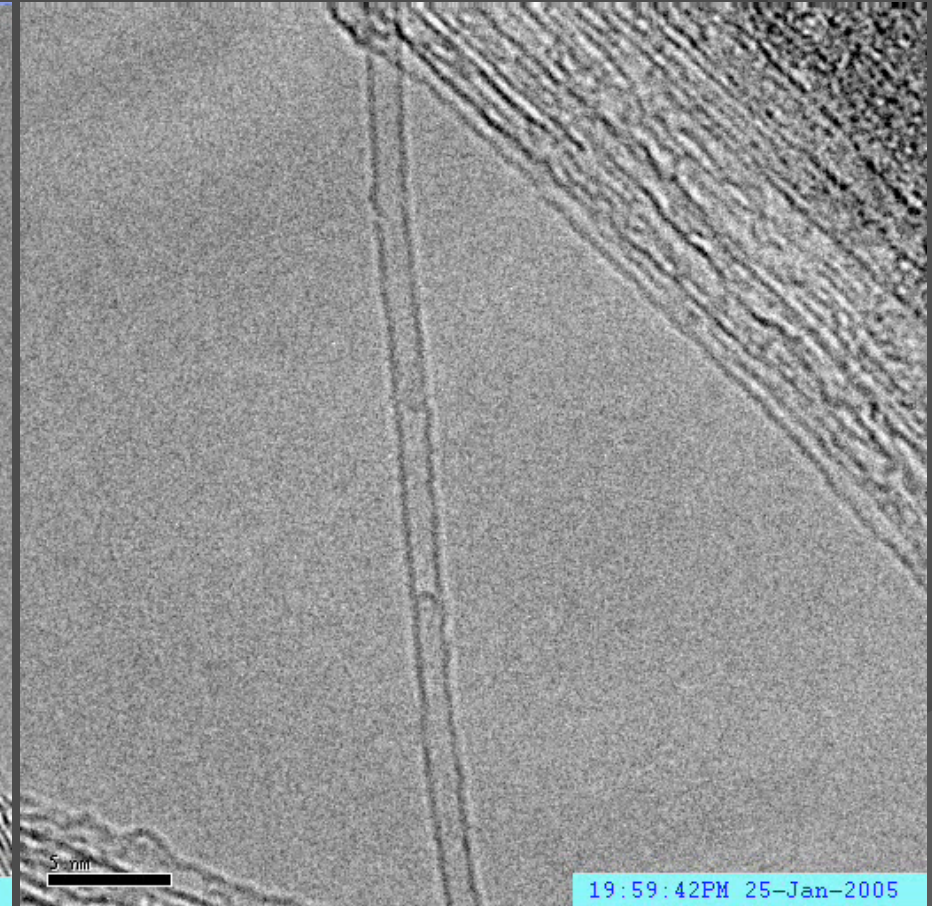
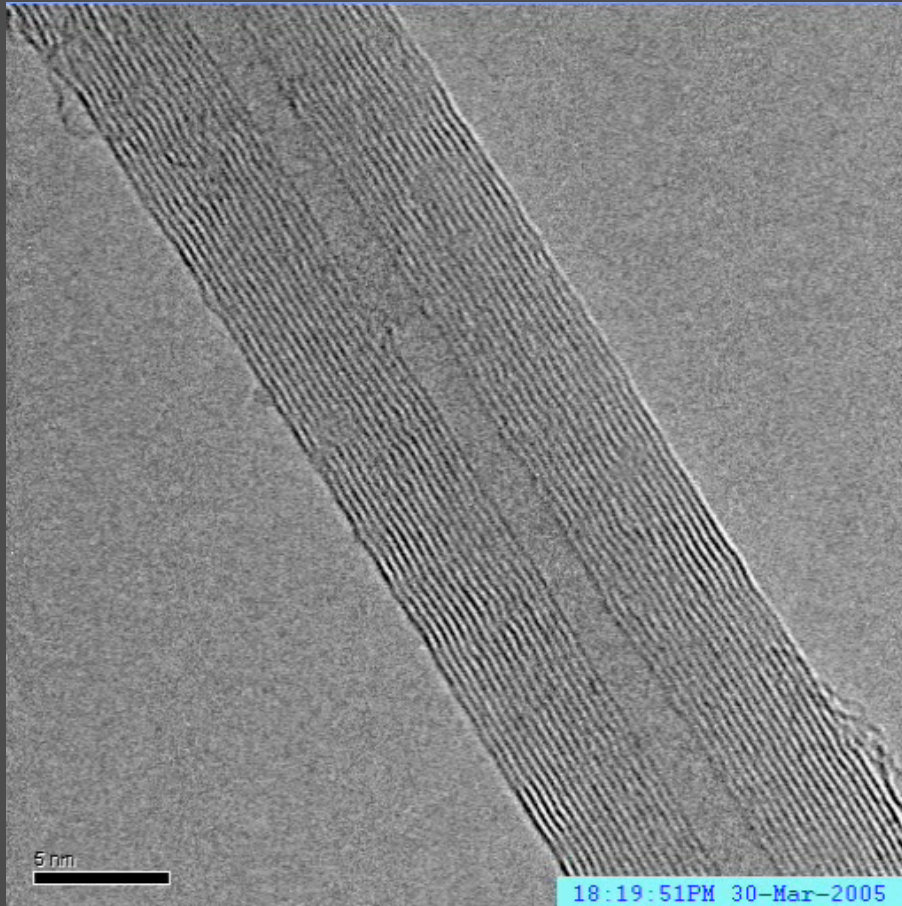
UHV-TEM



Evaporators

Base pressure 2×10^{-10} torr

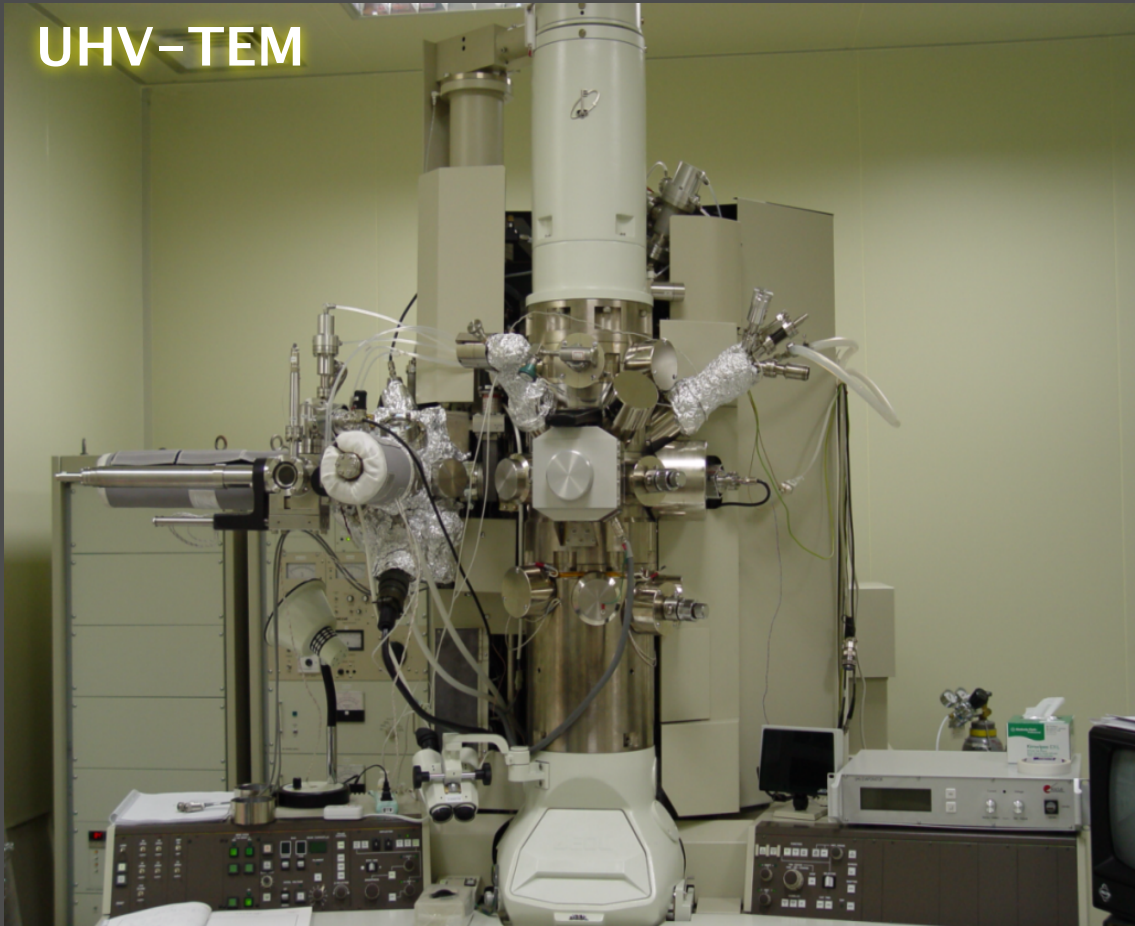
In situ deposition



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

STM@UHV-TEM

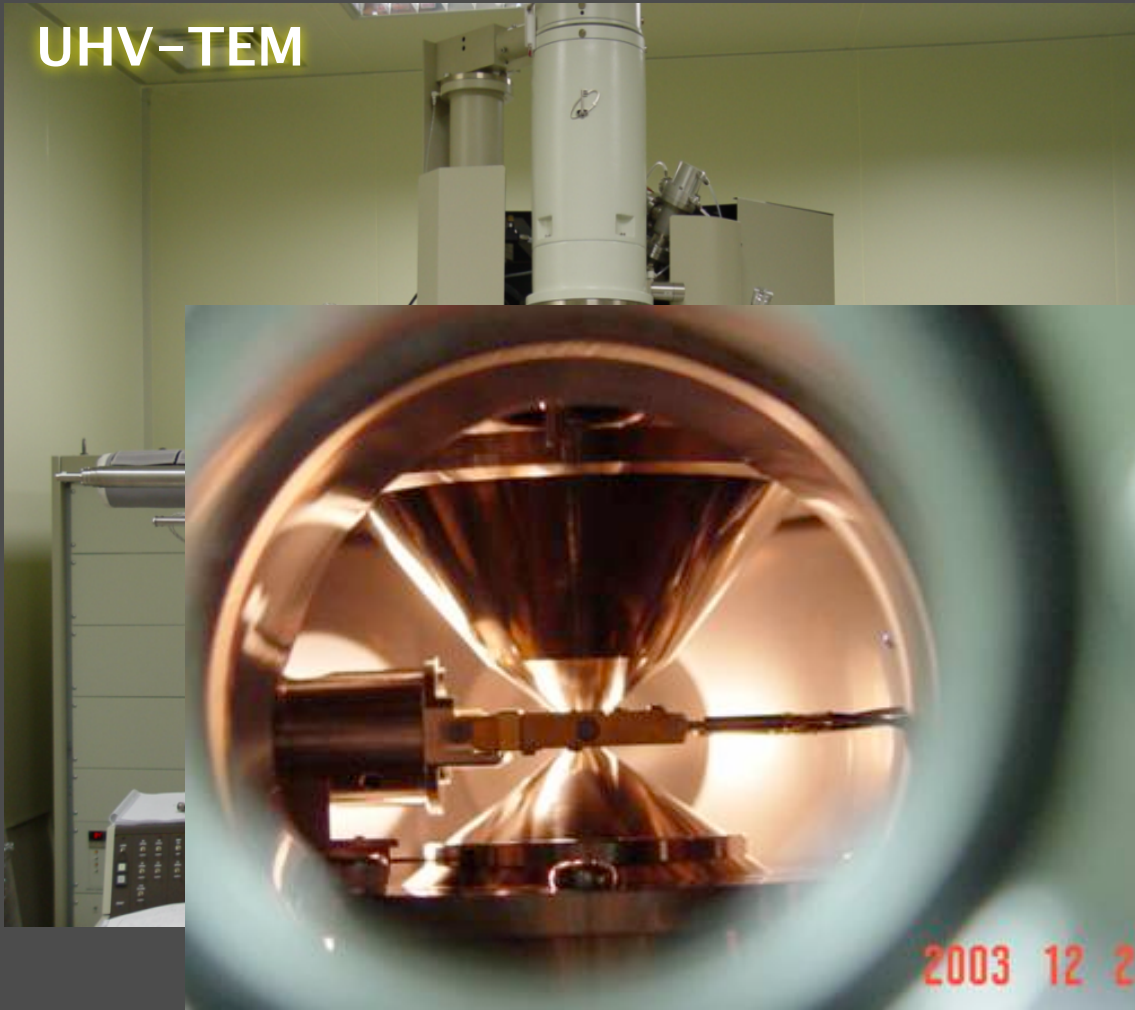
UHV-TEM



Base pressure 2×10^{-10} torr

STM@UHV-TEM

UHV-TEM



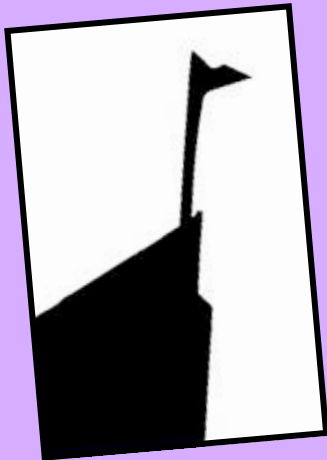
Base pressure 2×10^{-10} torr

STM@UHV-TEM

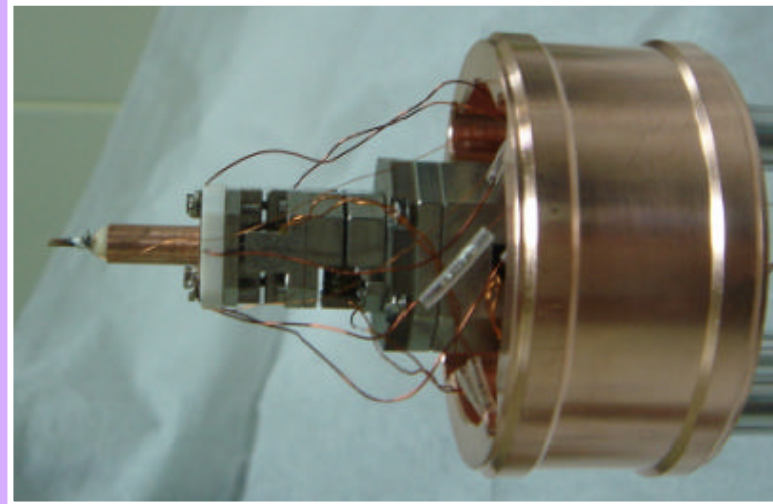
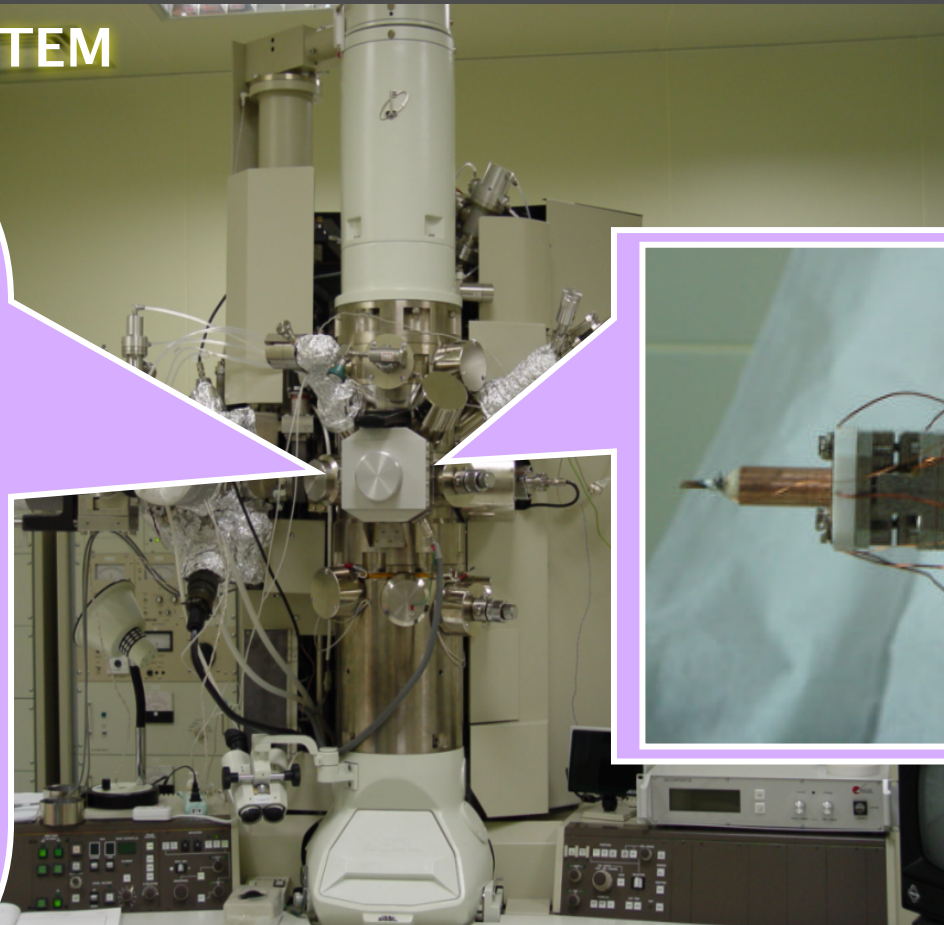
UHV-TEM



Gold knife



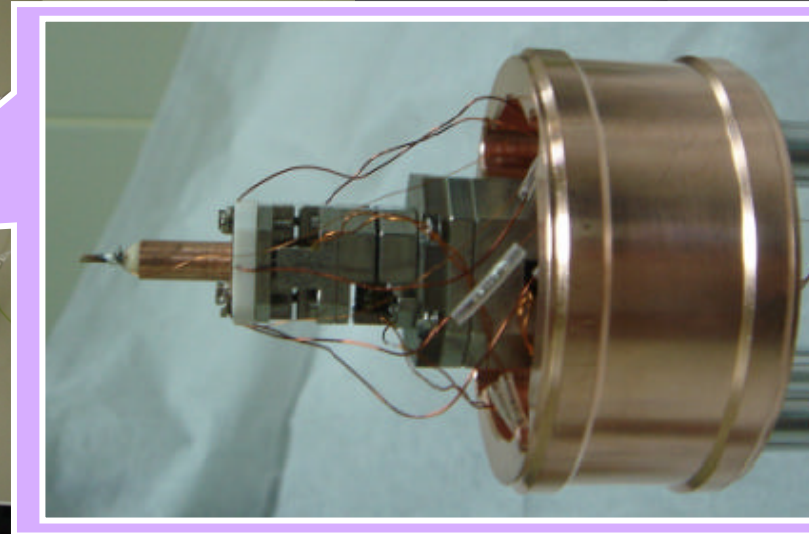
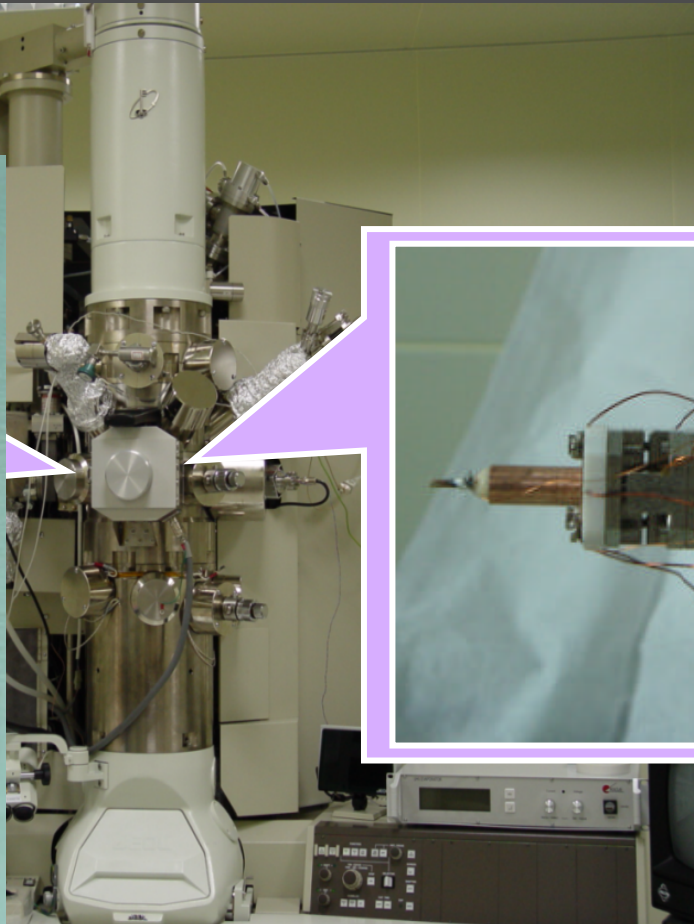
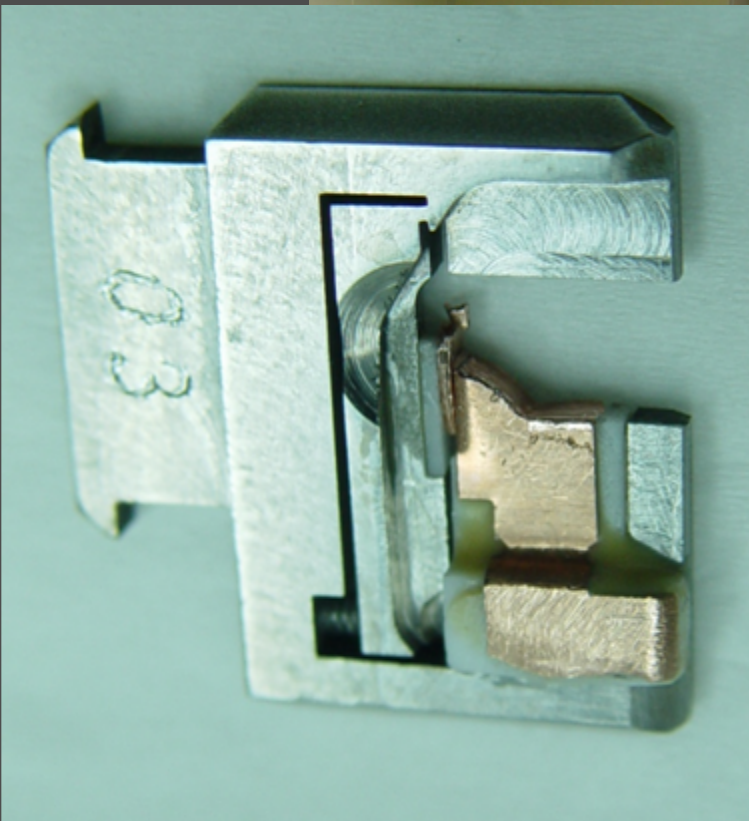
AFM tip



Base pressure 2×10^{-10} torr

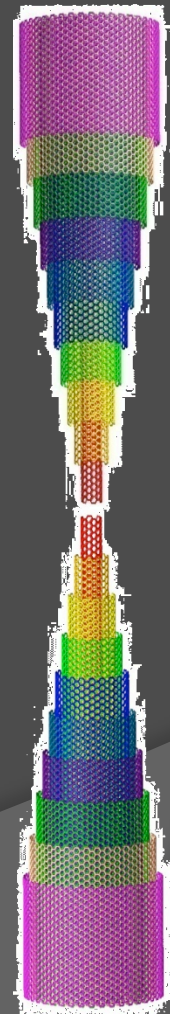
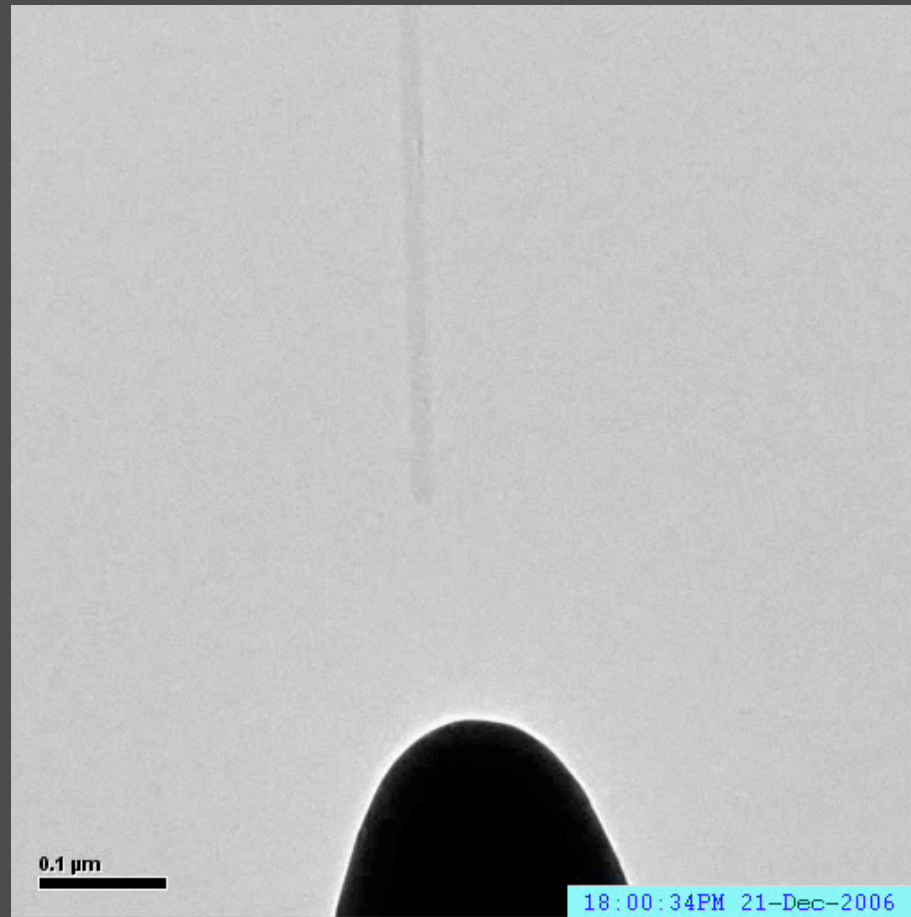
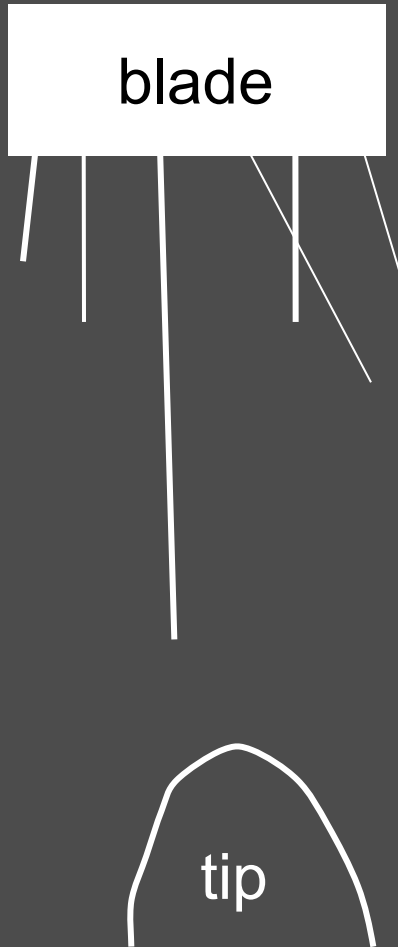
STM@UHV-TEM

UHV-TEM

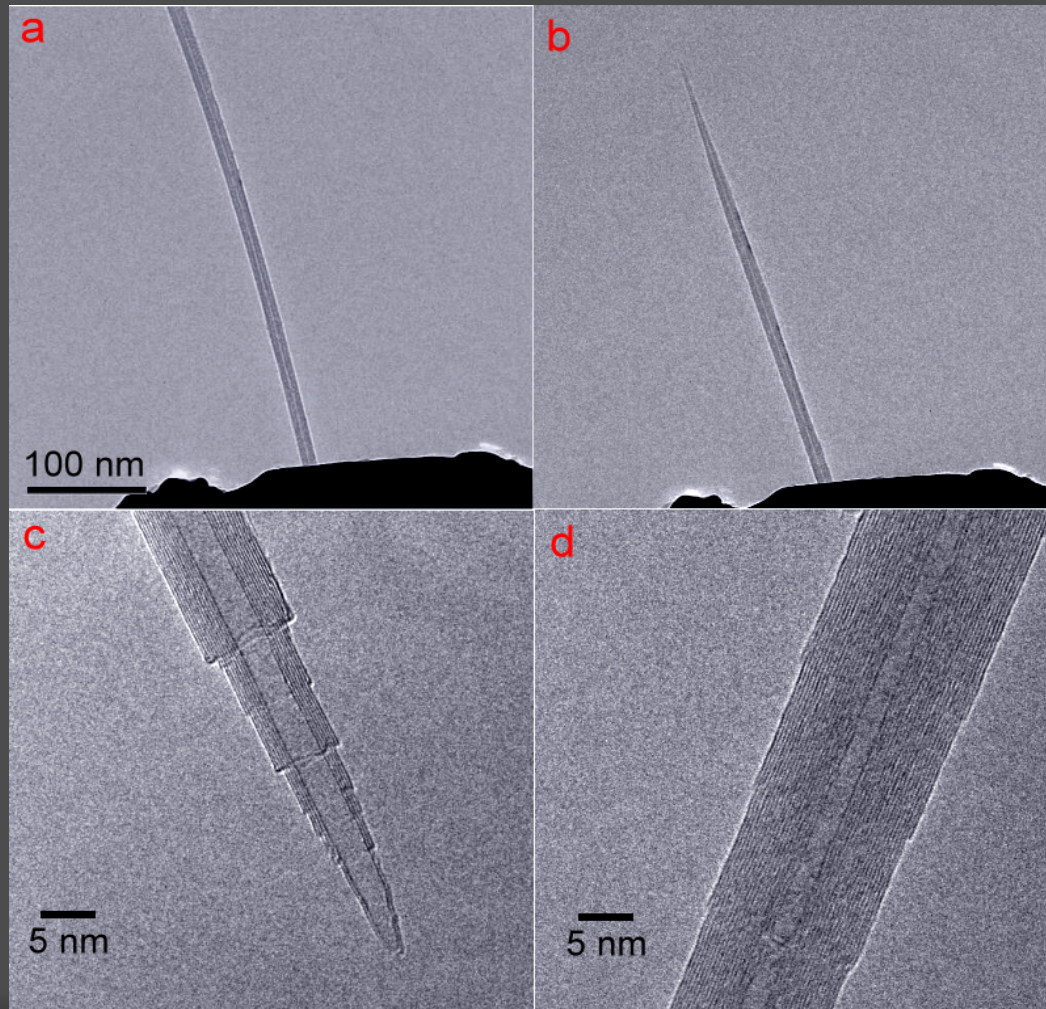


Base pressure 2×10^{-10} torr

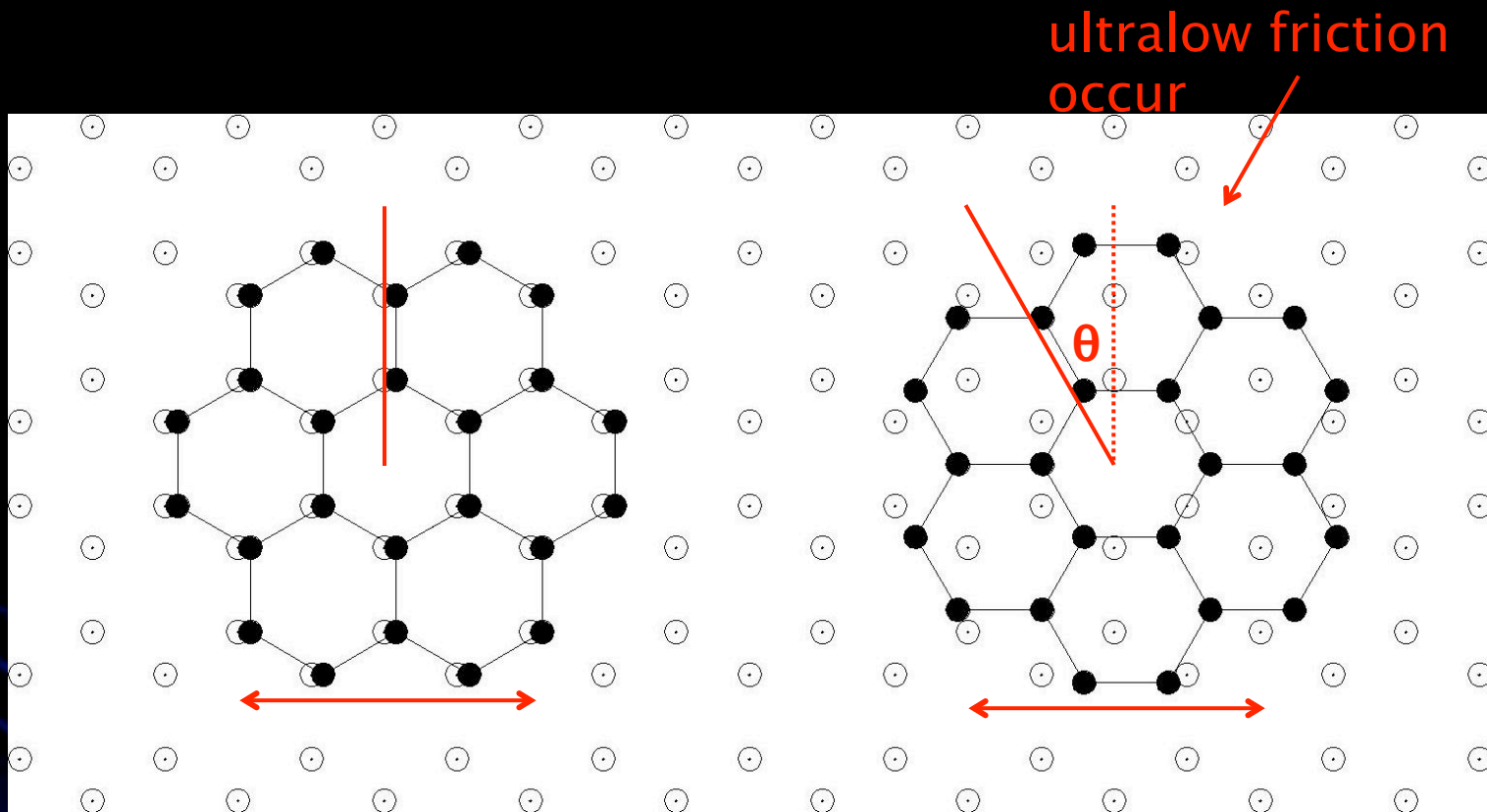
Making CNT tips by STM@TEM



Shaping a nanotube into telescope



superlubricity of graphite



commensurate state

incommensurate state

since M. Hirano and K. Shinjo, Phys. Rev. B 41,
11837 (1990)

Superlubricity of Graphite

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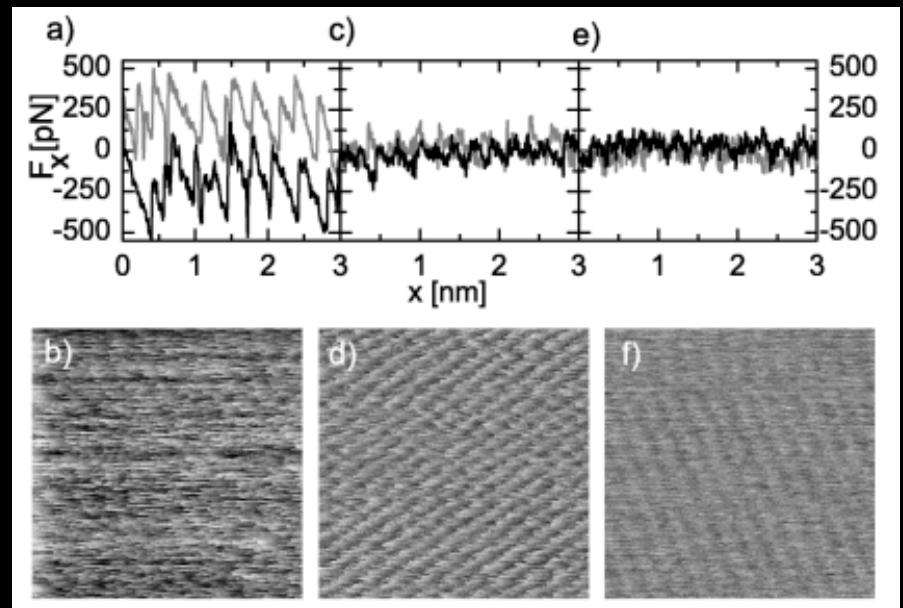
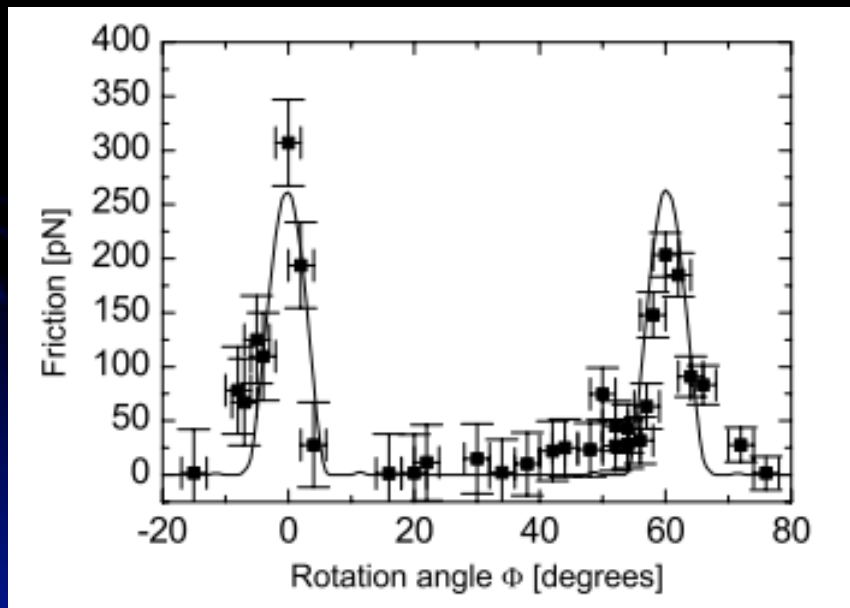
Jennifer A. Heimberg‡

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Laboratory of Materials Science, Delft University of Technology, Rotterdamseweg 137, 2628 AL Delft, The Netherlands

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Phys. Rev. Lett. 92, 126101 (2004)

Design and performance of a high-resolution frictional force microscope with quantitative three-dimensional force sensitivity

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Jennifer A. J. A. Heimberg, D.-J. Spaanderman, and D. Glastra van Loon

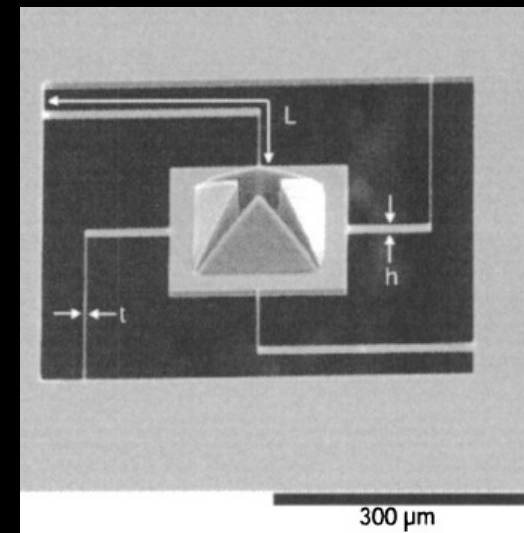
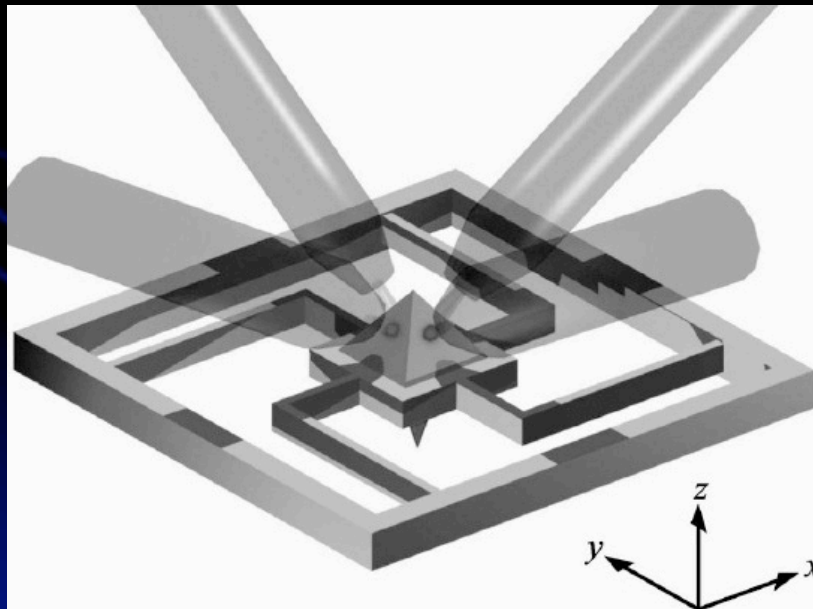
FOM-Institute for Atomic and Molecular Physics, Kruislaan 407, 1098 SJ Amsterdam, The Netherlands

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Delft Institute of Microelectronics and Submicron Technology (DIMES), Delft University of Technology,

P.O. Box 5053, 2600 GB Delft, The Netherlands

(Received 17 March 2004; accepted 22 January 2005; published online 1 April 2005)

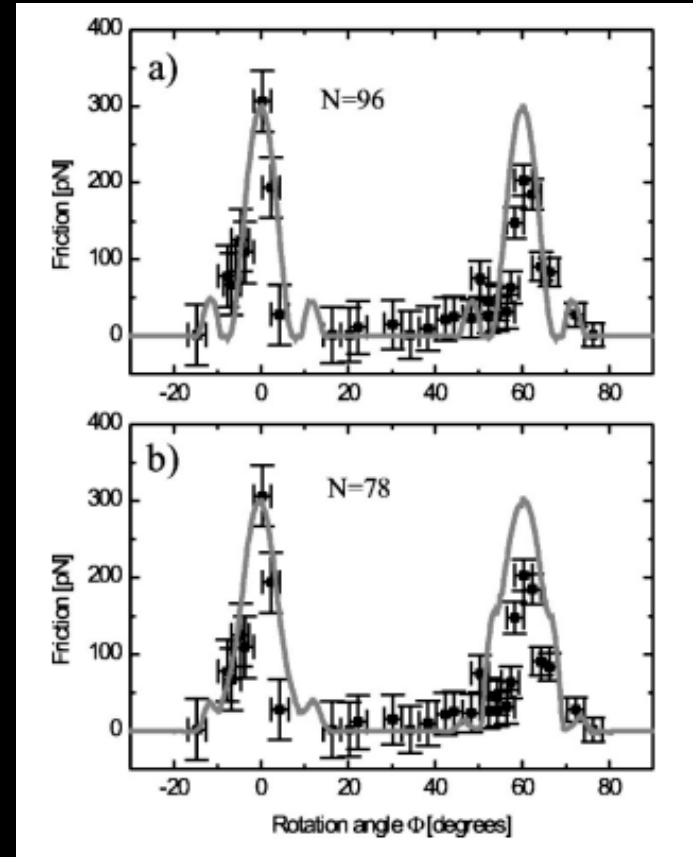
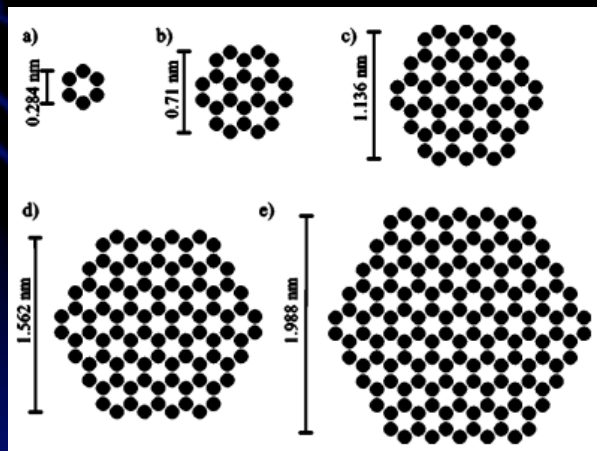
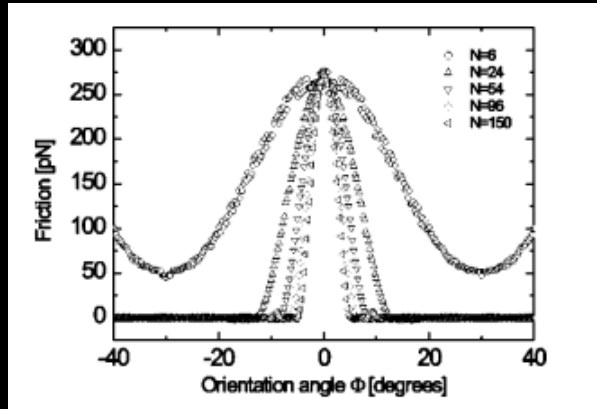


REVIEW OF SCIENTIFIC INSTRUMENTS 76, 043704
(2005)

Model calculations of superlubricity of graphite

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Kamerlingh Onnes Laboratory, Leiden University, P. O. Box 9504, 2300 RA Leiden, The Netherlands
(Received 26 August 2003; revised manuscript received 12 April 2004; published 26 October 2004)



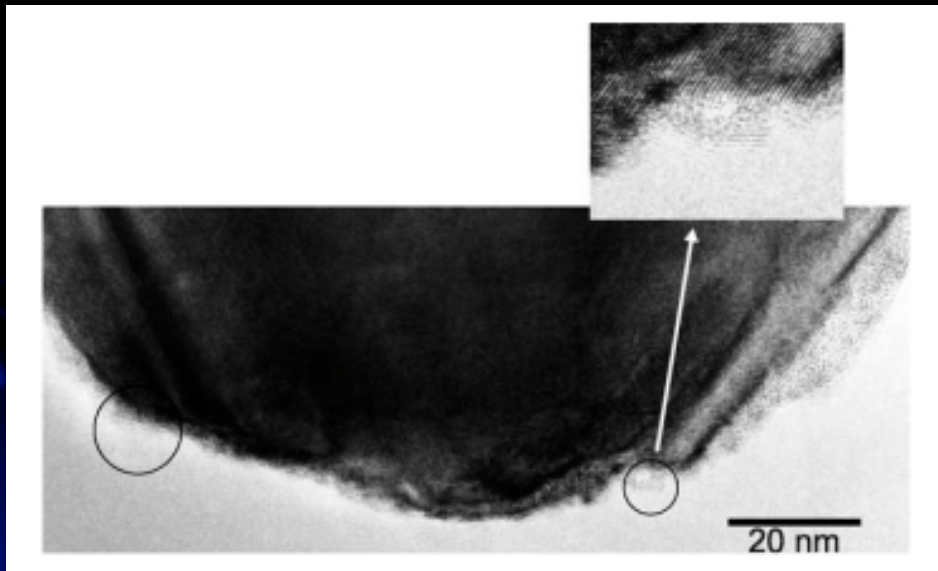
Phys. Rev. B 70, 165418 (2004)

Model calculations of superlubricity of graphite

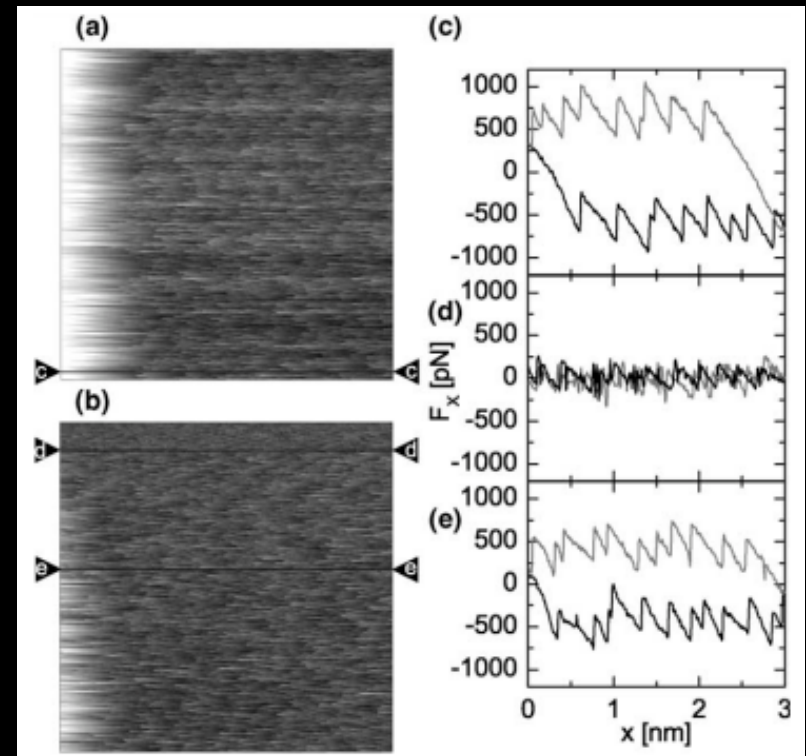
Martin Dienwiebel^{a,*},¹, Namboodiri Pradeep^a, Gertjan S. Verhoeven^a, Henny W. Zandbergen^b, Joost W.M. Frenken^{a,*}

^a Kamerlingh Onnes Laboratory, Leiden University, P.O. Box 9504, 2300 RA Leiden, The Netherlands

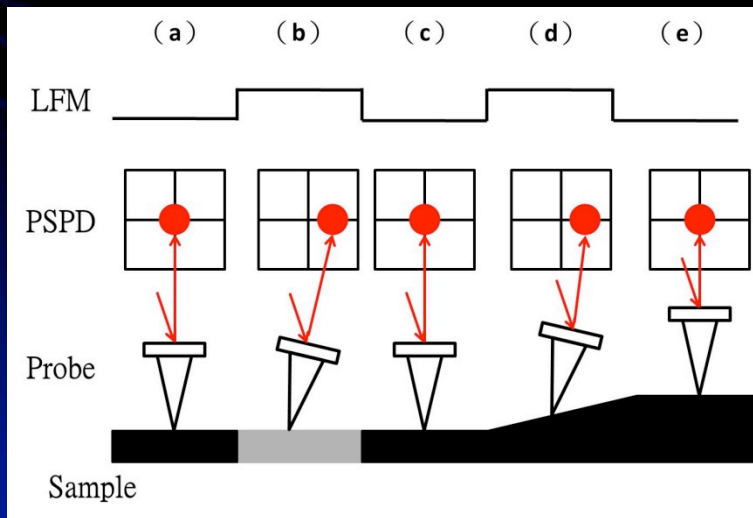
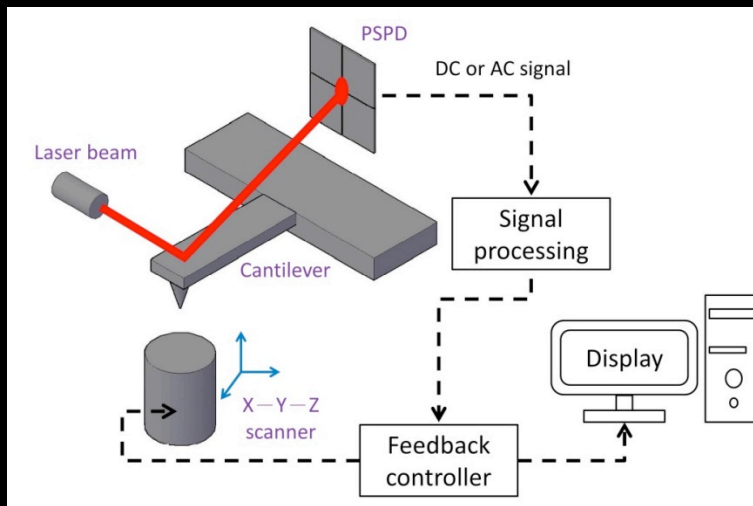
^b Laboratory of Materials Science, Delft University of Technology, Rotterdamseweg 137, 2628 AL Delft, The Netherlands



Surface Science 576 (2004) 197–211



lateral force microscopy (LFM)

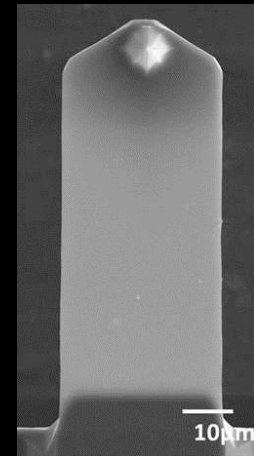
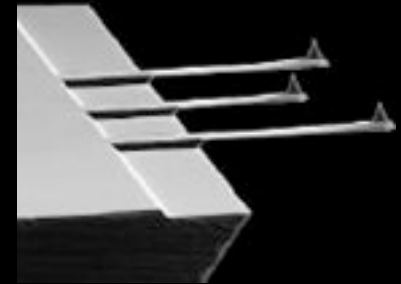
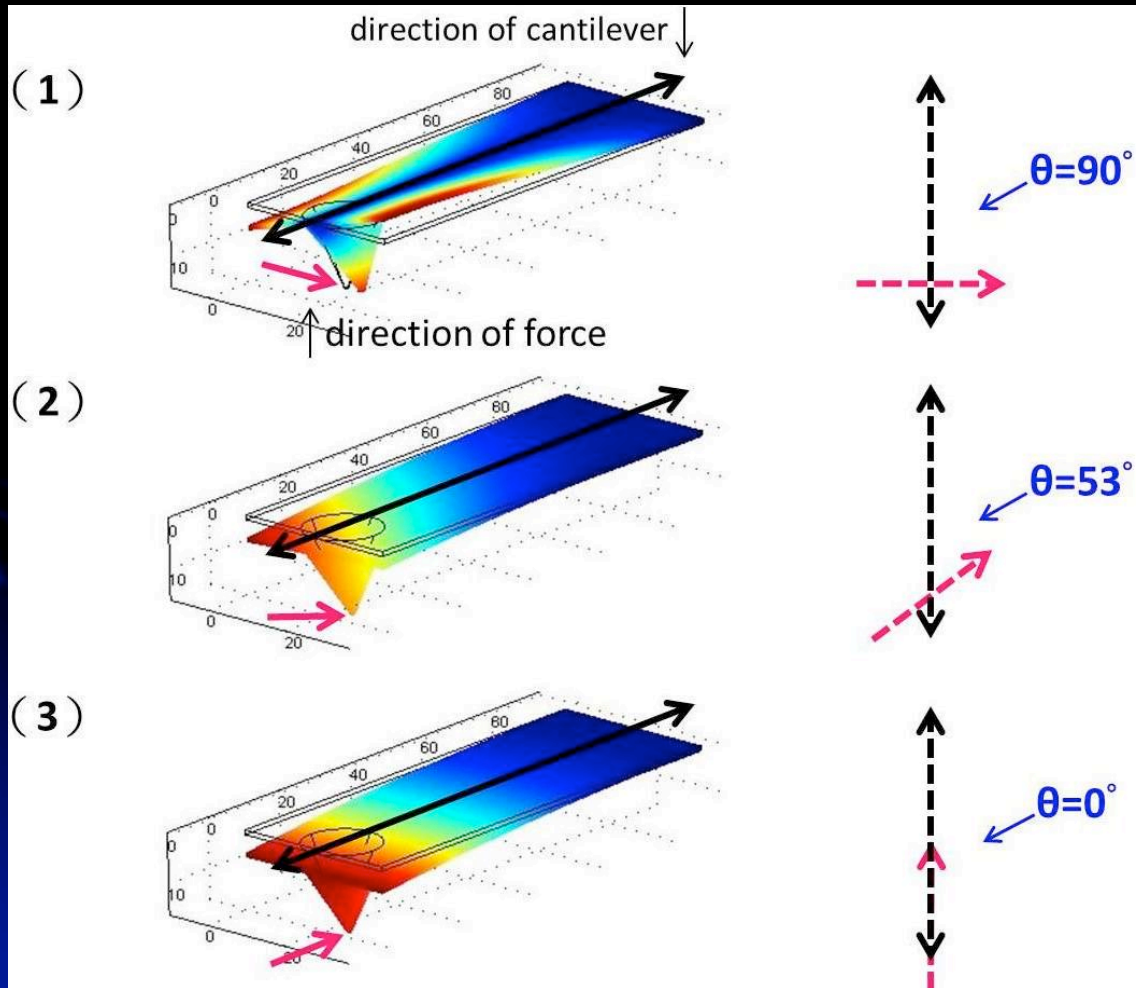


Veeco DI Innova SPM

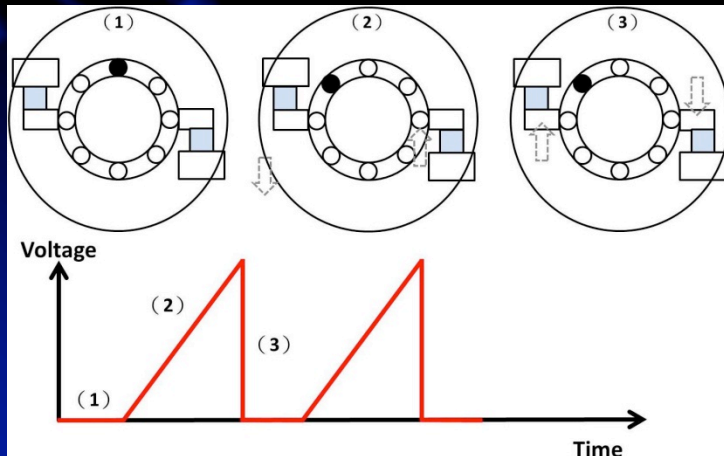
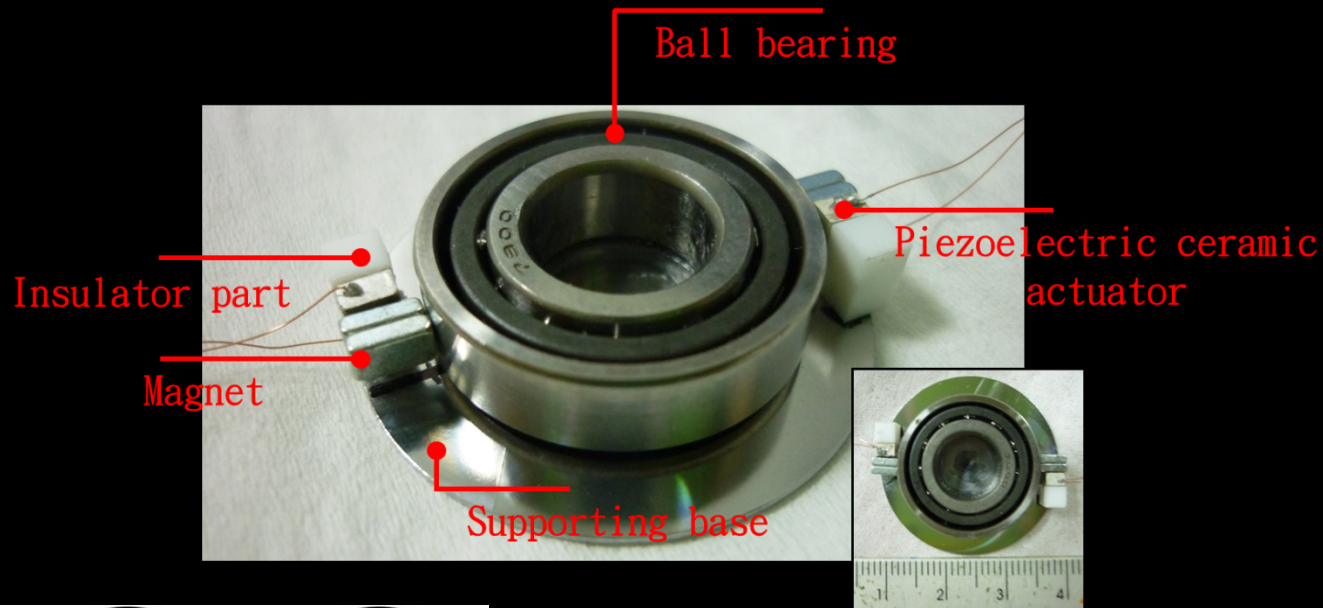
$100 \times 100 \times 7.6 (\mu m)$

$5 \times 5 \times 1 (\mu m)$

anisotropic rectangular cantilever beam



inertial rotational stepper



minimum drive voltage : 20V
average step : 0.069 degree/step

visual measurement method

pattern matching technique

(1)

AFM Cantilever

Tracking Pattern

70 μ m

(2)

AFM Cantilever

θ

70 μ m

0°

10°

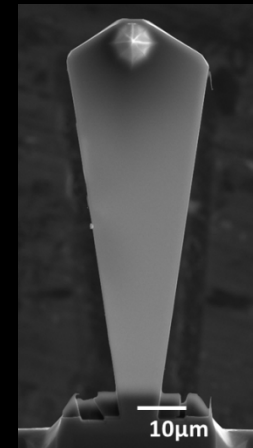
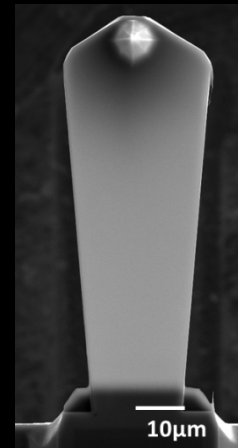
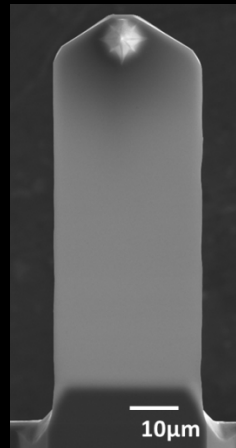
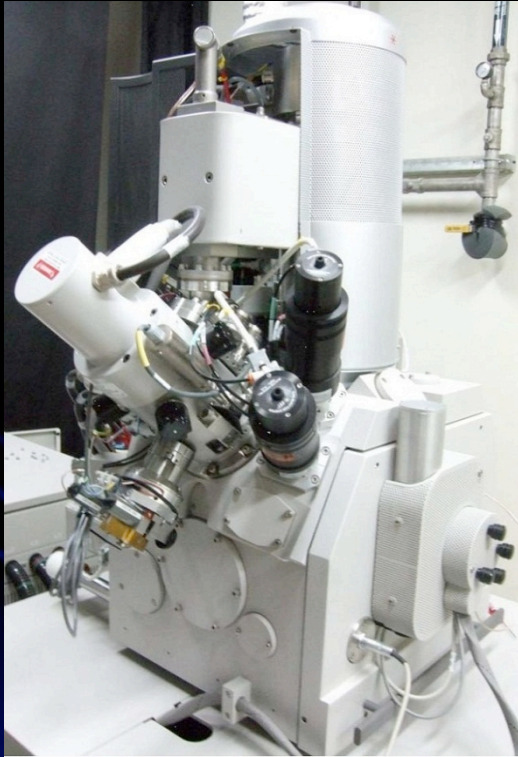
155°

300°

10°

angle deviation < 0.035
degree

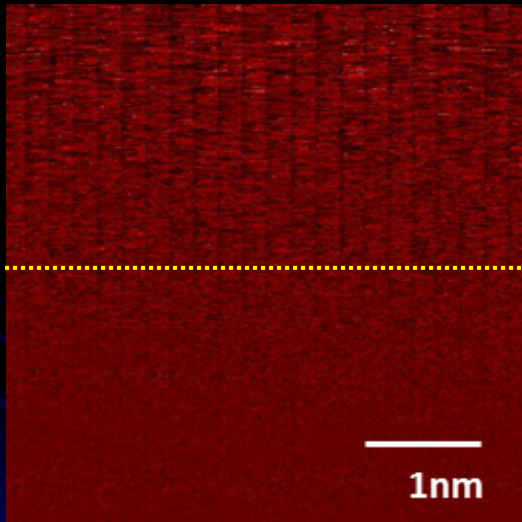
increase the torsional sensitivity



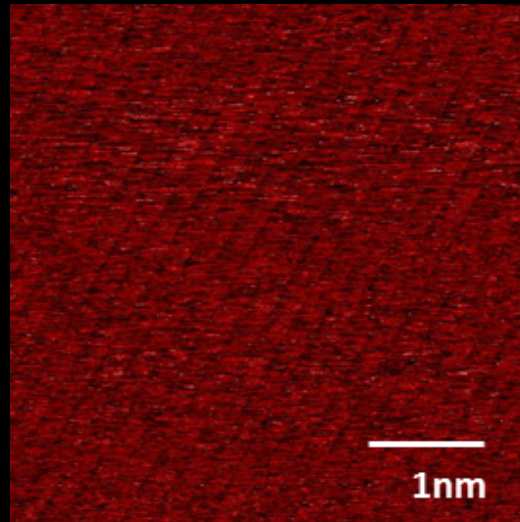
dual-beam focused ion beam (DB-FIB)
system

graphite flake-attached tip

Normal force
80–100nN

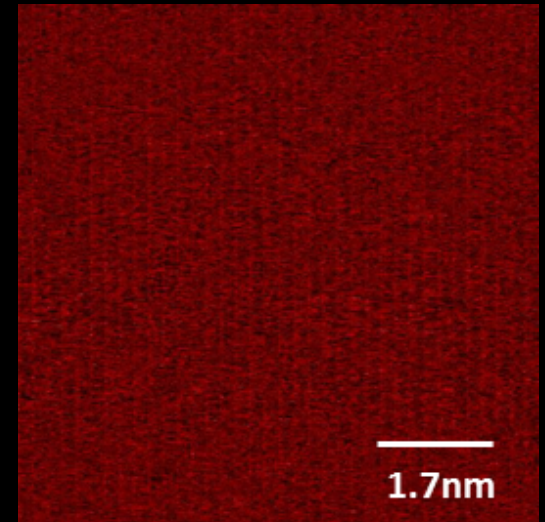


pick up a graphite flake

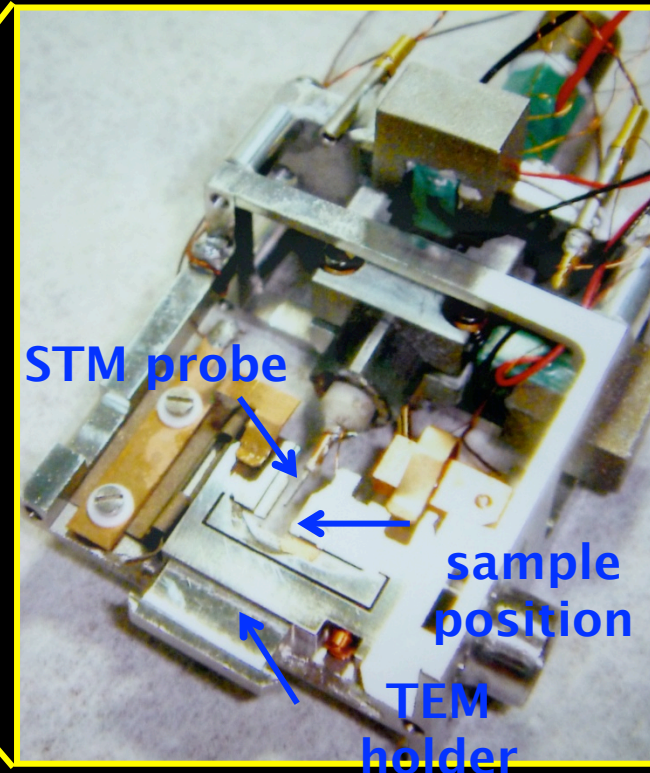
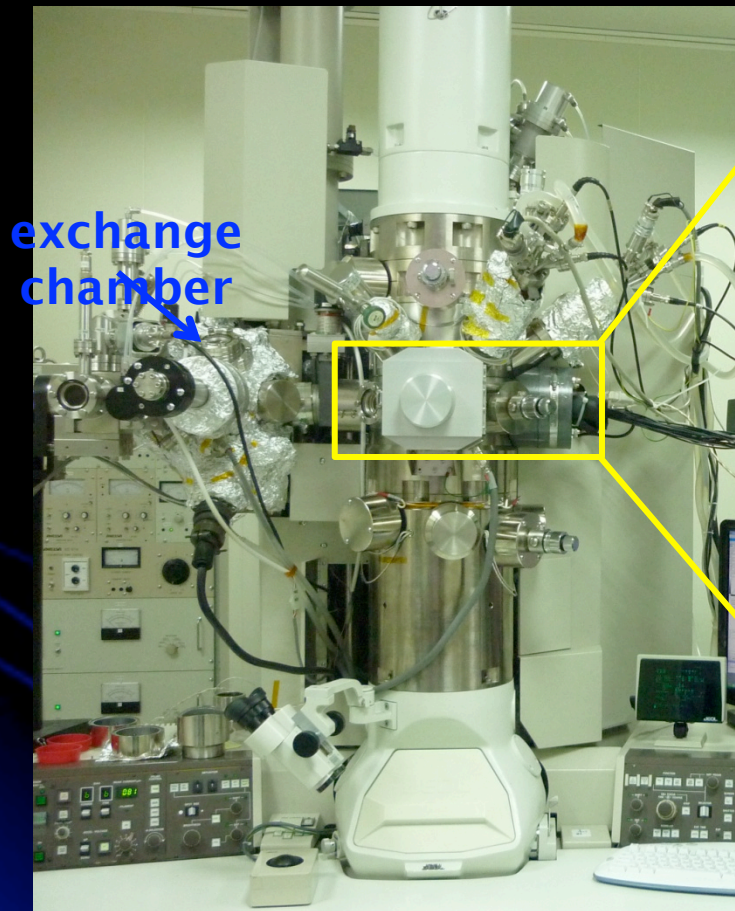


move to another flat
area

reset the normal force $\sim$
20nN

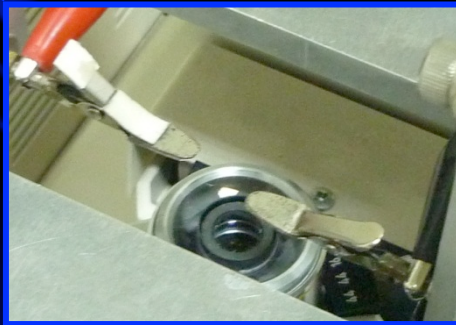
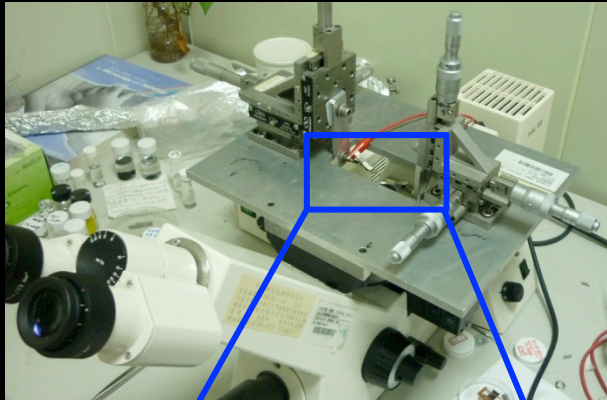


carbon nanotube tip

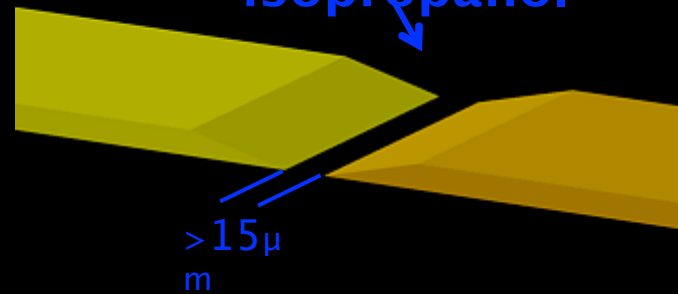


Y.S. Huang, C.S. Chang, T.T. Tsong
National Nano Project & Evaluation Conference
(2006)

STM@UHV-TEM
system

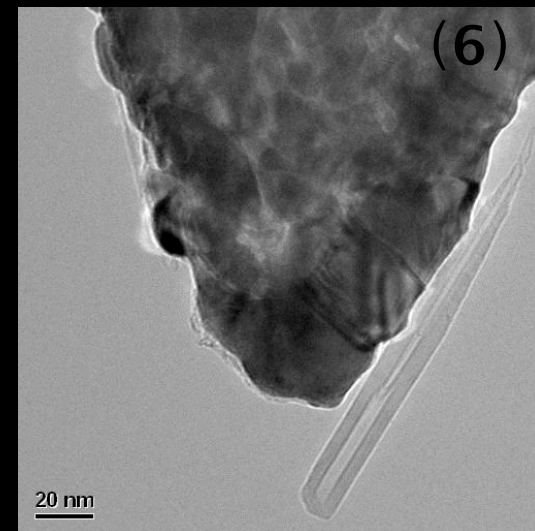
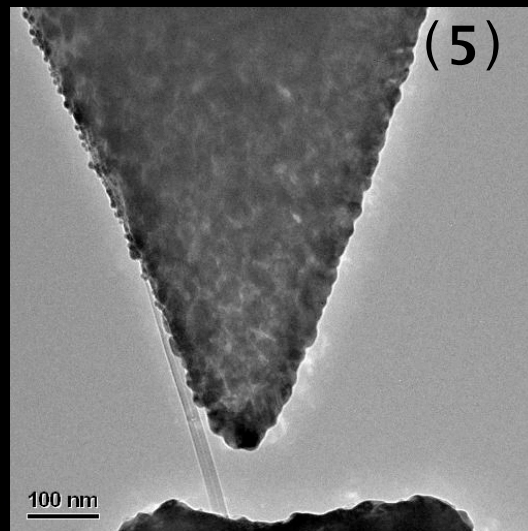
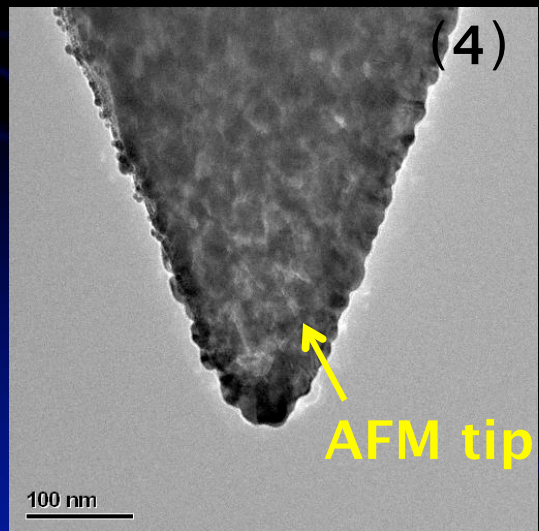
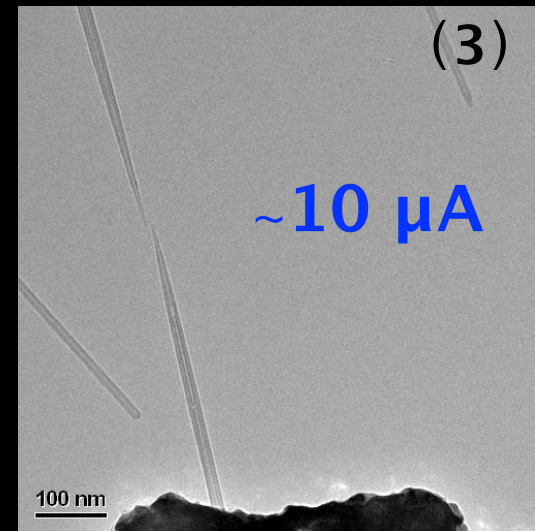
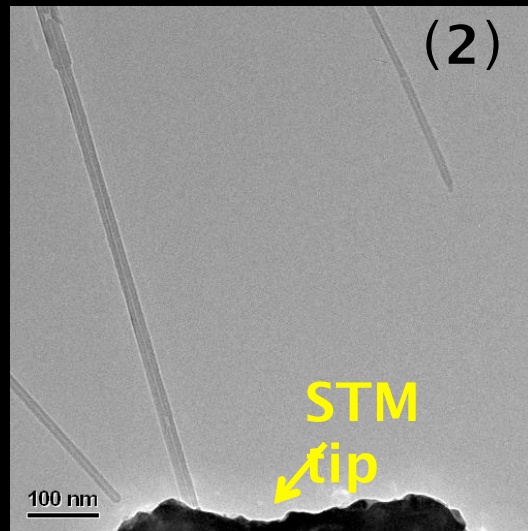
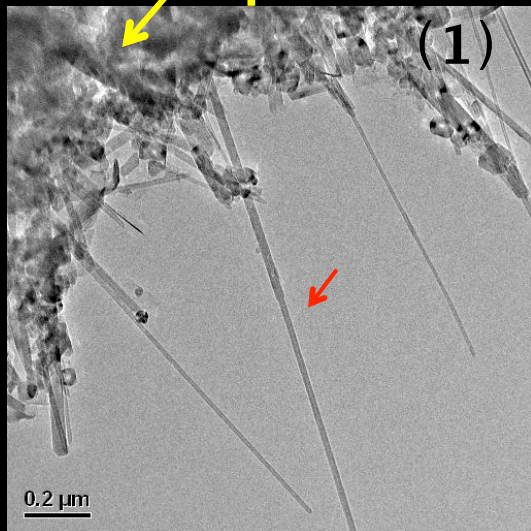


carbon nanotubes +
isopropanol

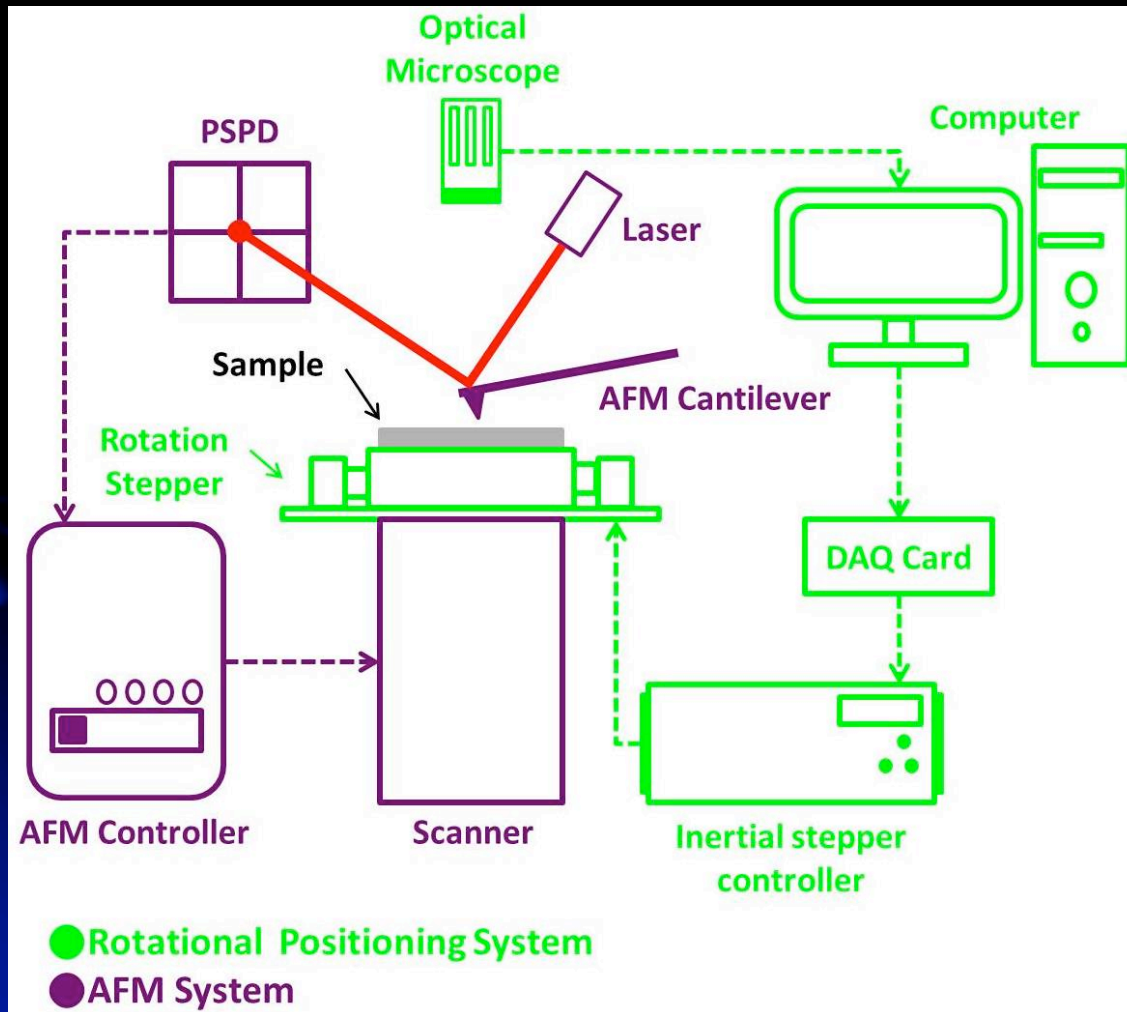


dielectrophoresis conditions
AC : 7 ~ 9V / 5 ~ 7MHz

CNT array by electrophoresis

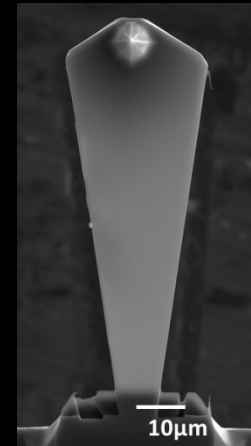
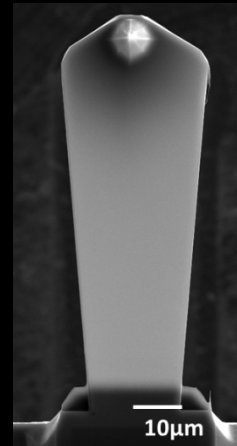
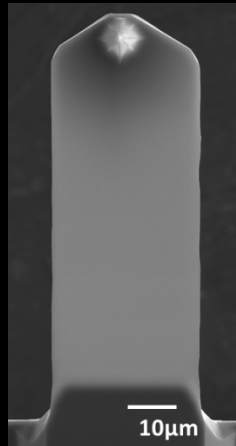


instrument configuration



temperature-
controlled
~21 °C
relative humidity
~(1-10)±1%

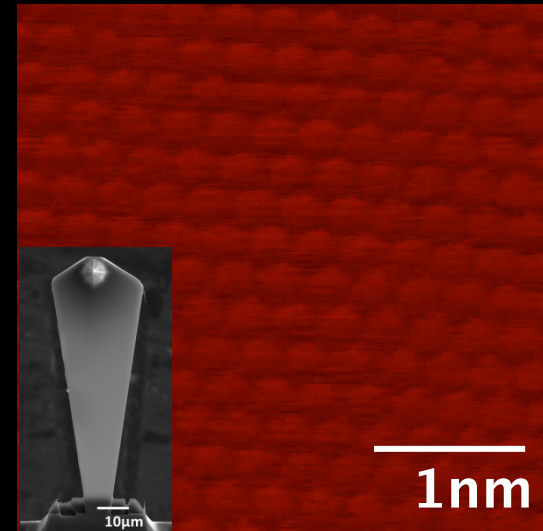
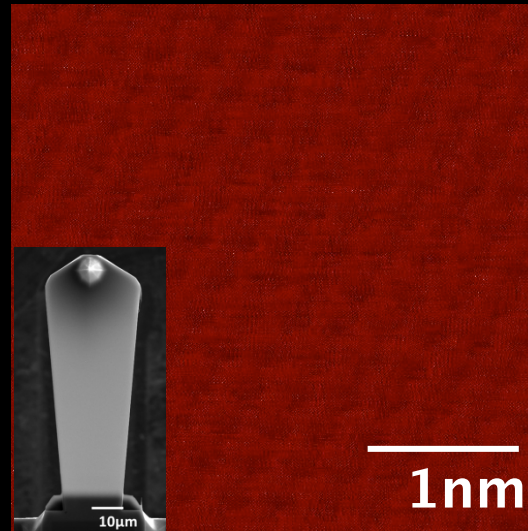
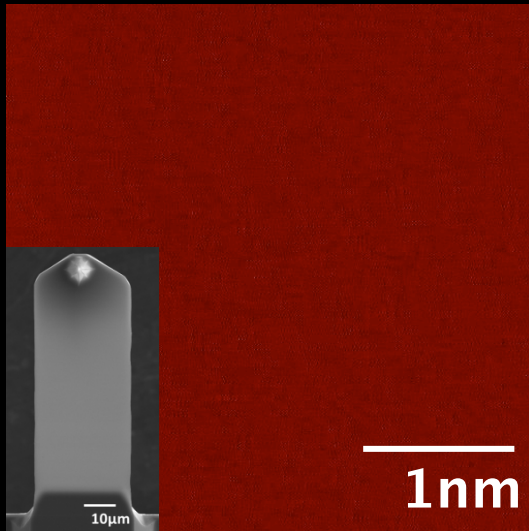
higher torsional sensitivity



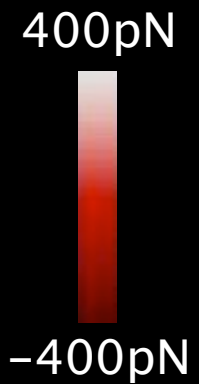
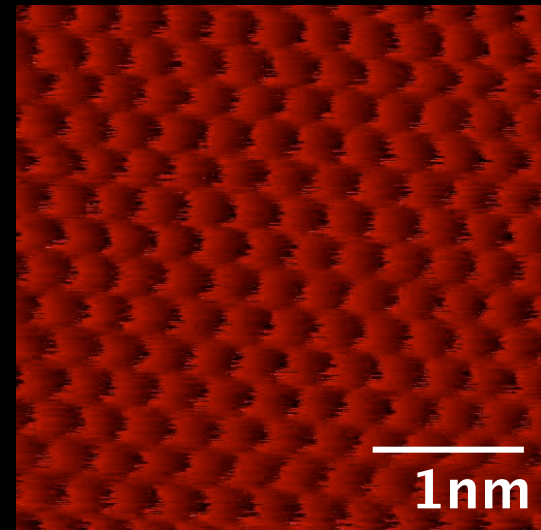
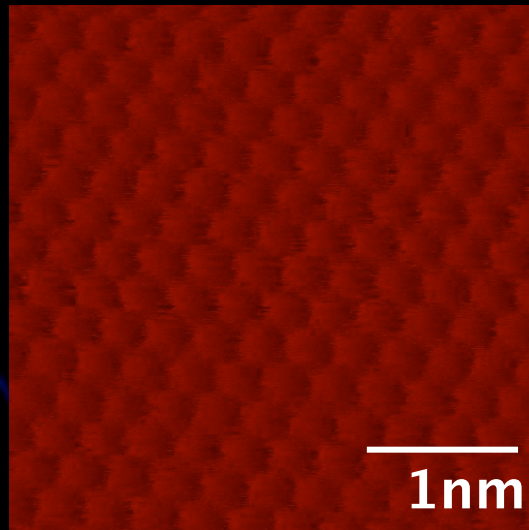
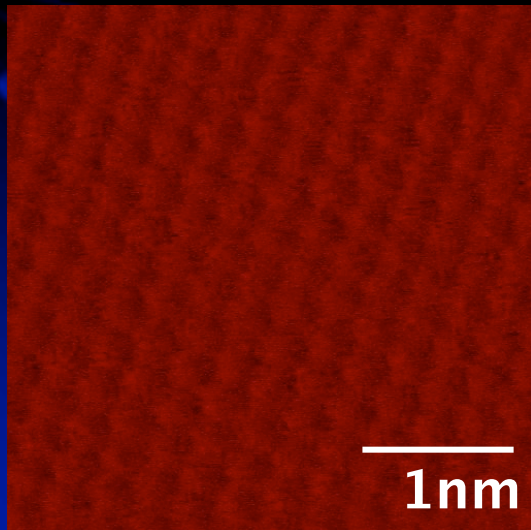
	Original	Modified (1)	Modified (2)
Flexural spring constant(N/ m)	1.638	1.417	0.1231
Lateral spring constant(N/ m)	13.25	3.417	1.437

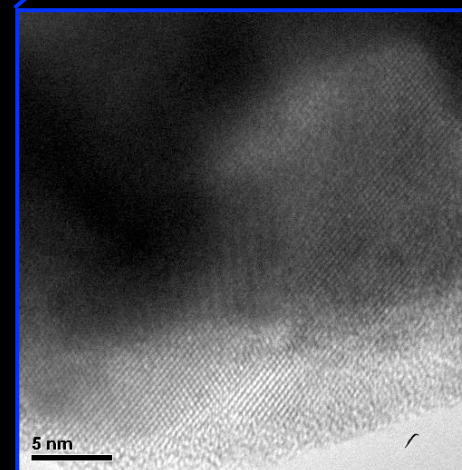
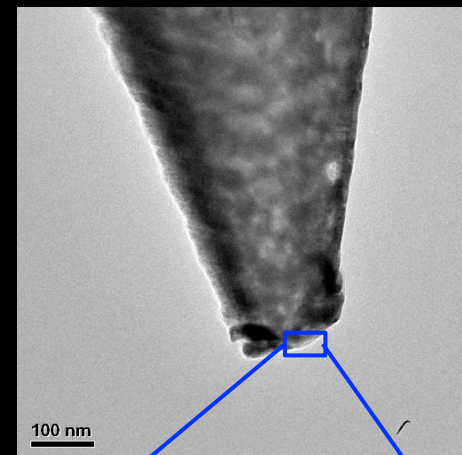
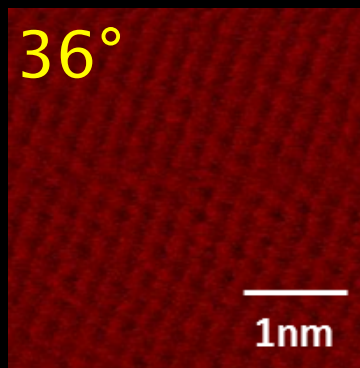
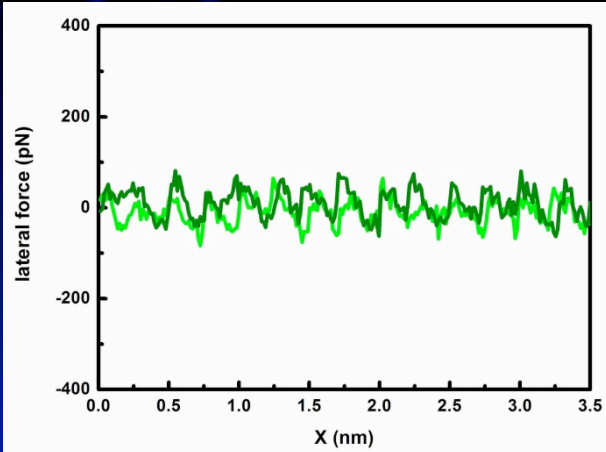
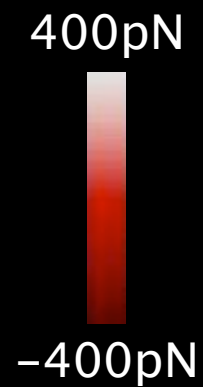
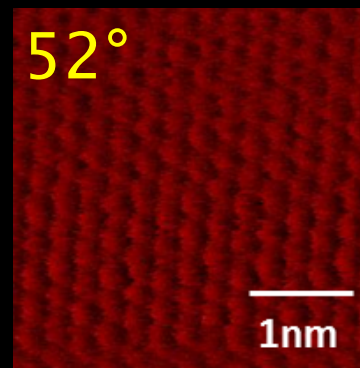
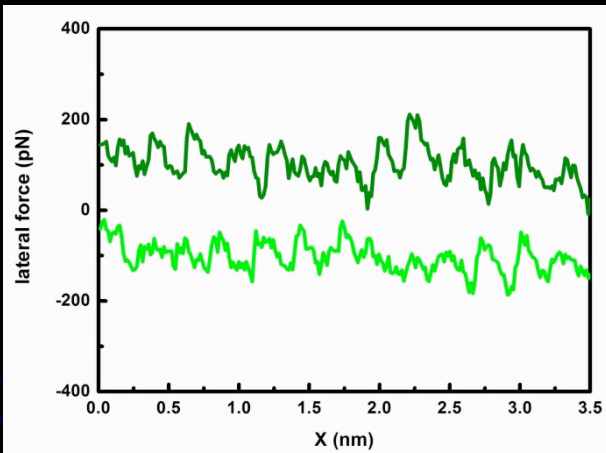
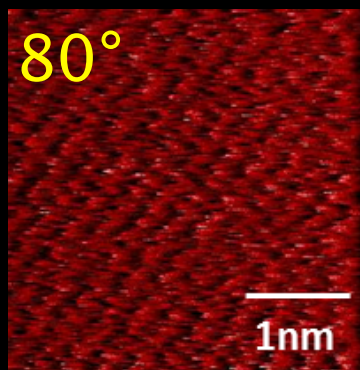
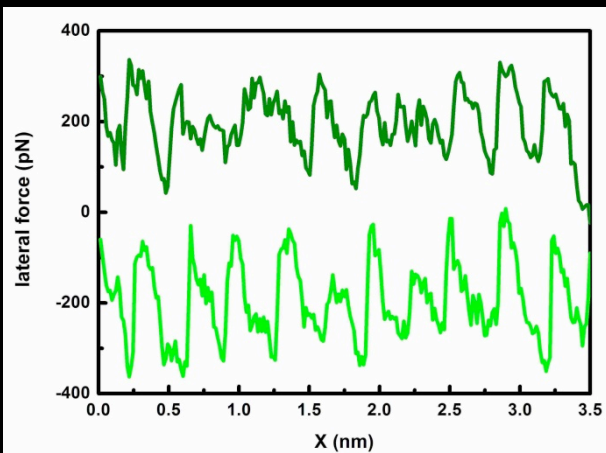
lateral force resolution down to several
pN

AFM images



LFM images

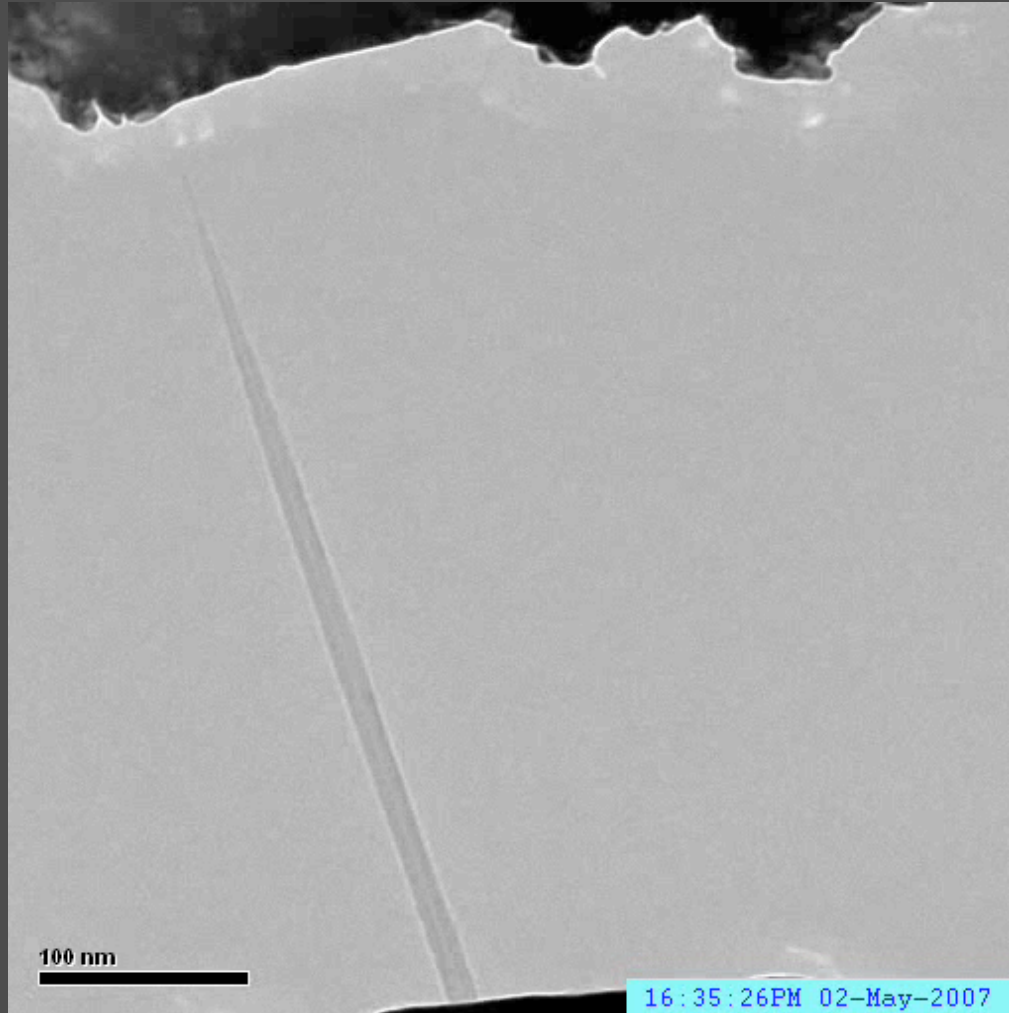




Peeling the nanotube from inside



Peeling the nanotube from inside



Nano electromechanical oscillator

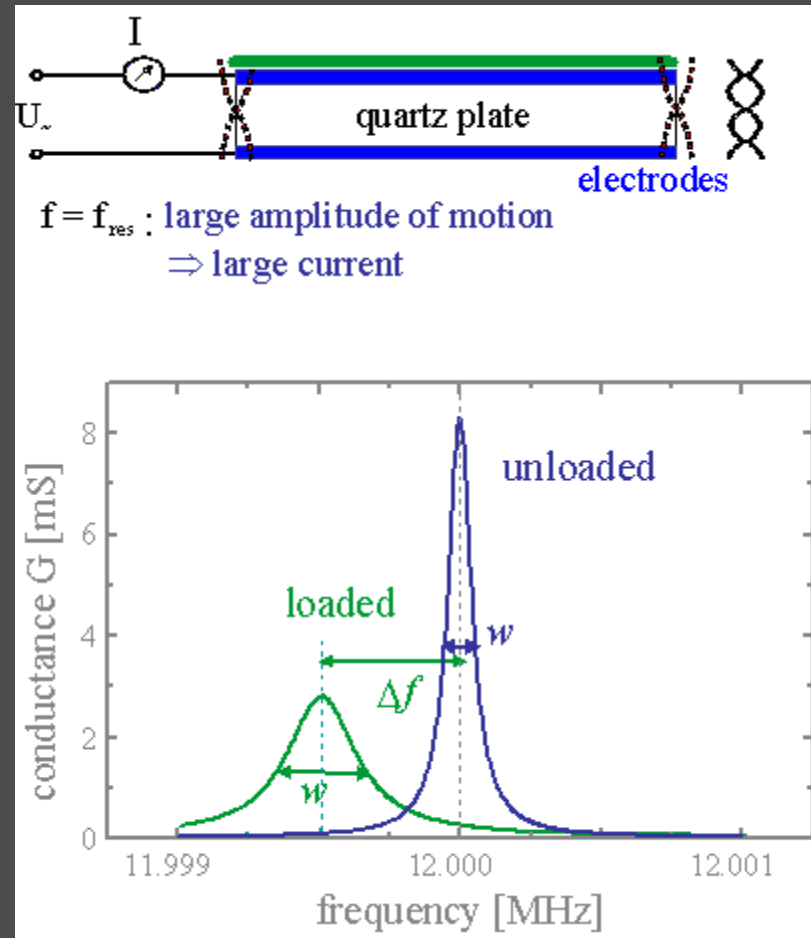
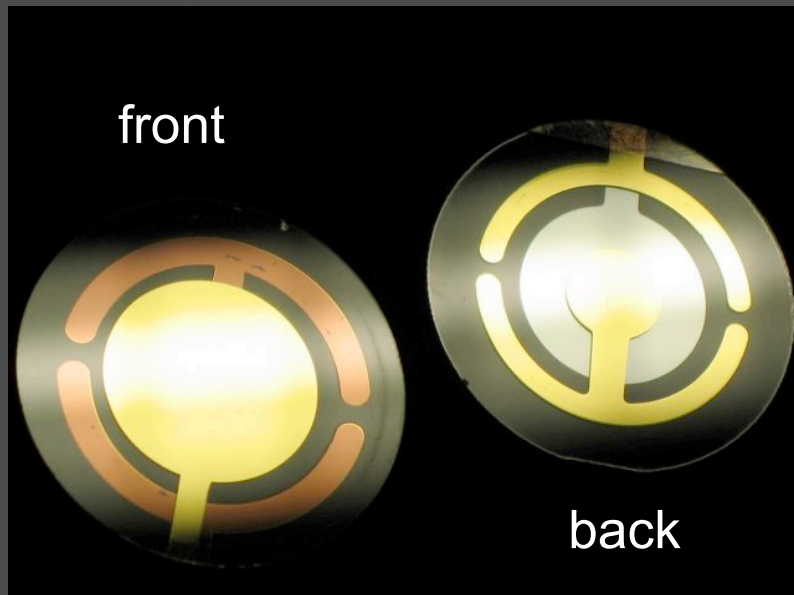


Nano electromechanical oscillator

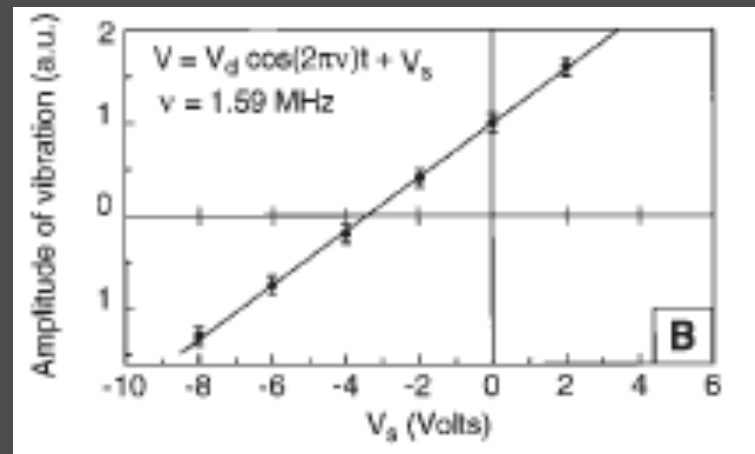
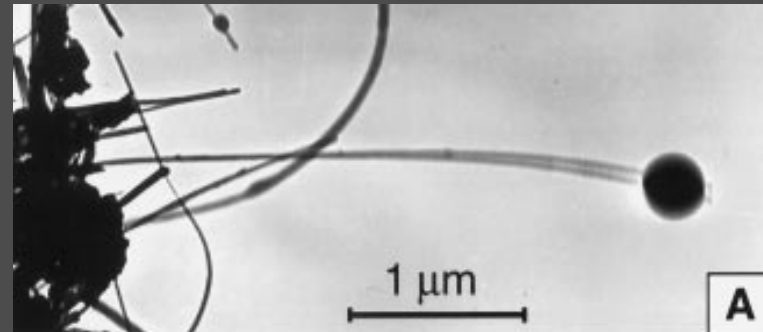
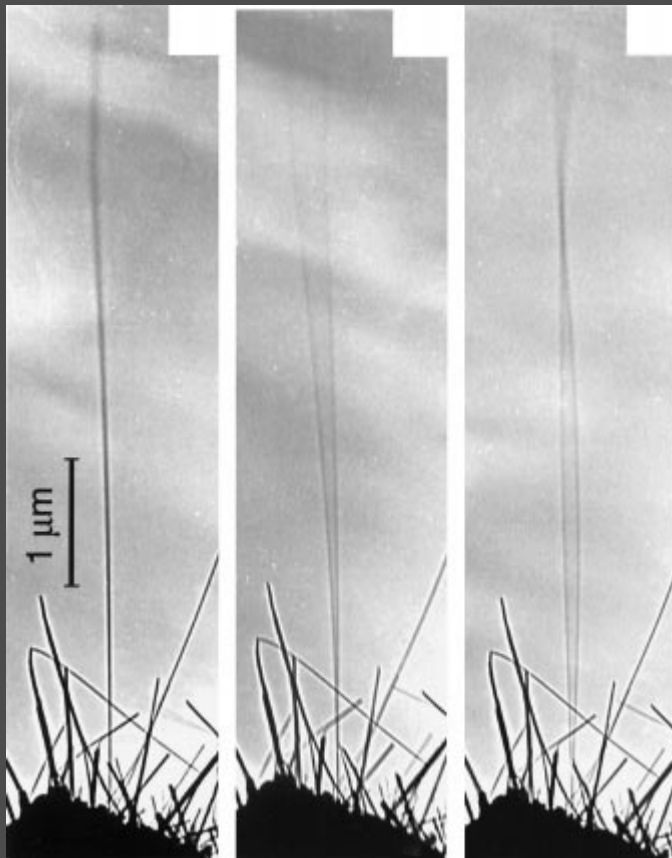


$$v_i = \frac{\beta_i^2}{8\pi} \frac{1}{L^2} \sqrt{\frac{(D^2 + D_i^2)E_\beta}{\rho}}$$

Quartz crystal microbalance

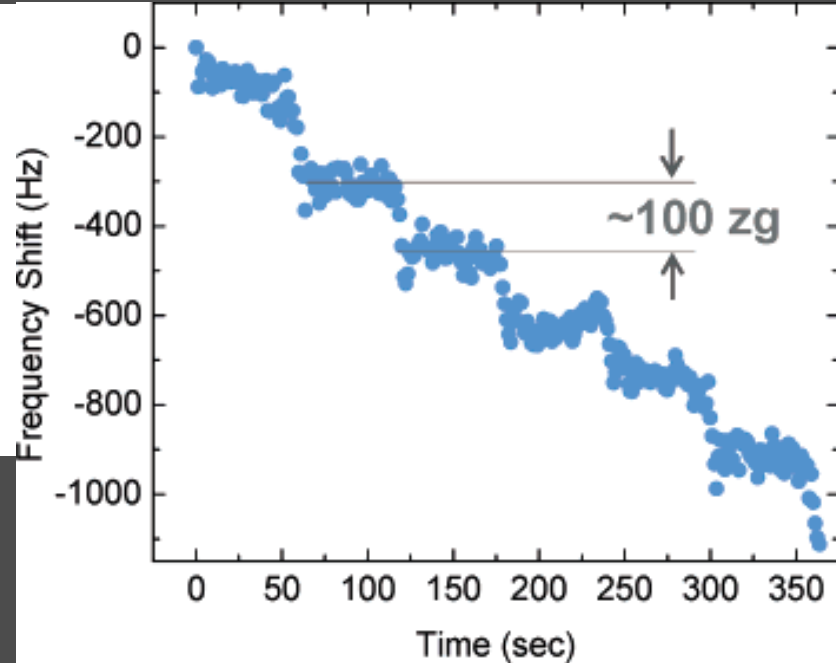
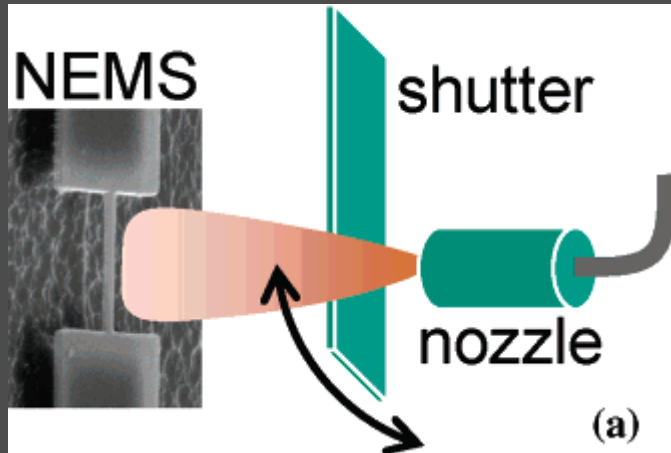


Electromechanical Resonances of Carbon Nanotubes



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

Zeptogram Nanomechanical Sensing



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

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

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

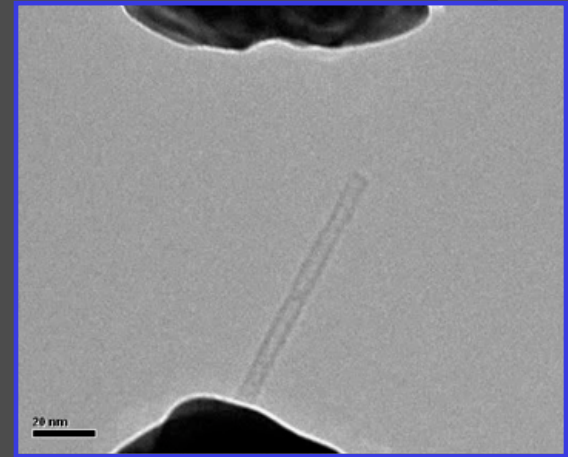
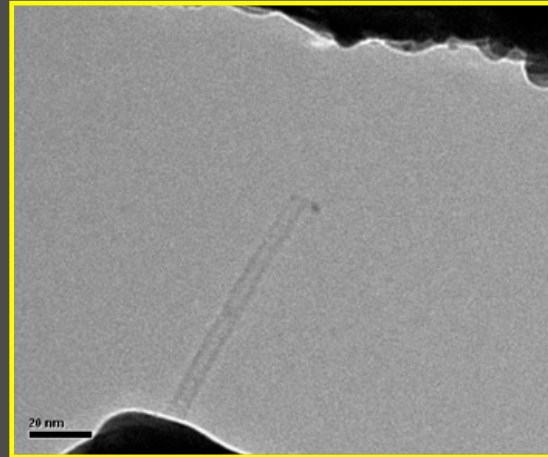
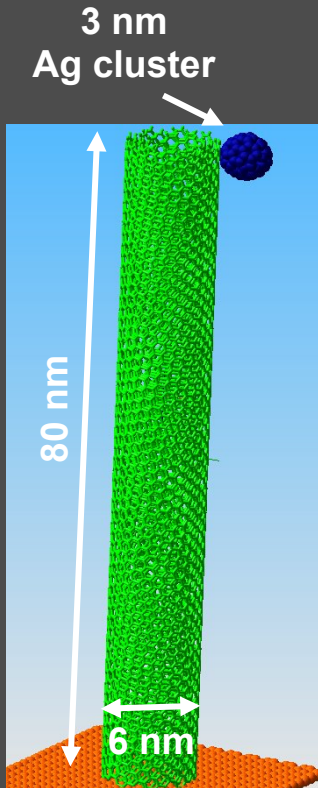


Criteria for an atom balance

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

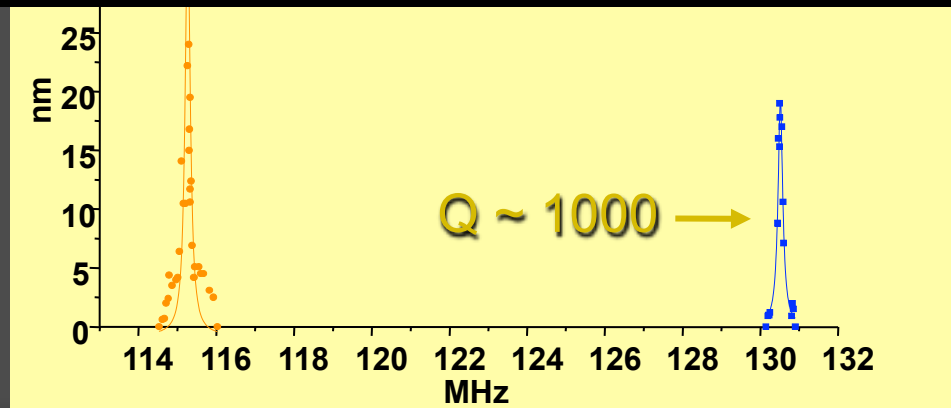
- Small balance mass
- Sensitive detection mechanism
 - Minimal thermal effects
- Well-controlled environment

"Atom" balance



$$m \sim -m_0(\Delta f/2f_0) \sim 1.8 \times 10^{-19} \text{ g (mass of 1000 Ag atoms)}$$

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 : $m_0 = 3.1 \text{ ag}$

Thermal energy: $kT = 26 \text{ meV}$

Drive energy: $E_c \sim 200 \text{ meV}$

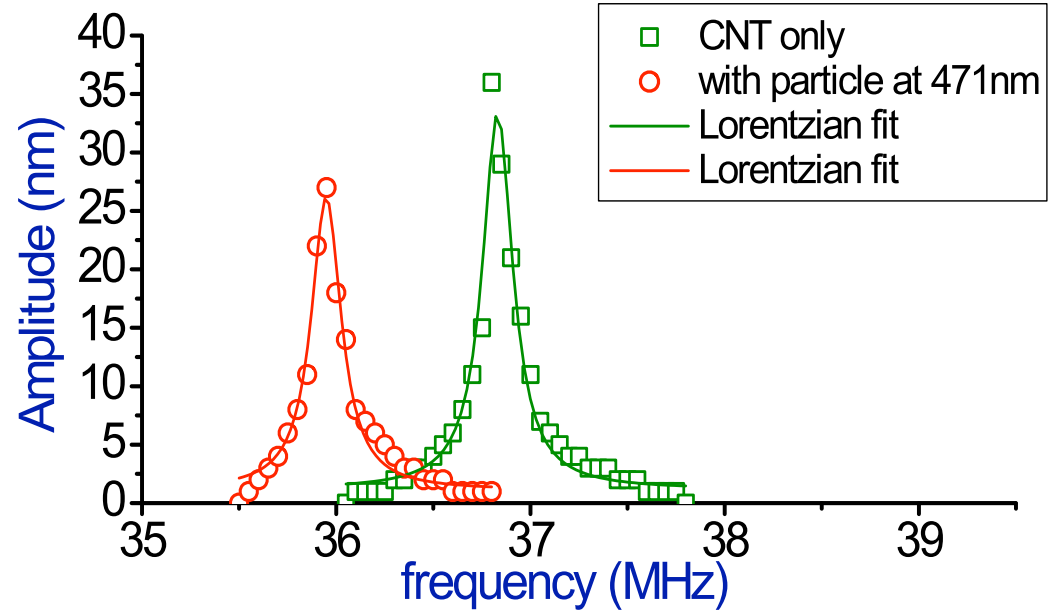
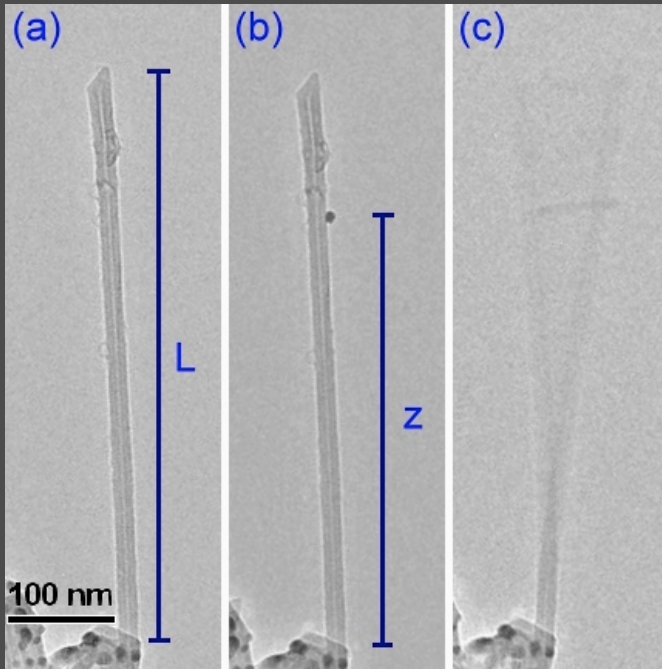
Measurement bandwidth: $\delta f \sim 100 \text{ Hz}$

Quality factor: $Q \sim 1000$

Resonance freq: $f_0 \sim 130 \text{ MHz}$

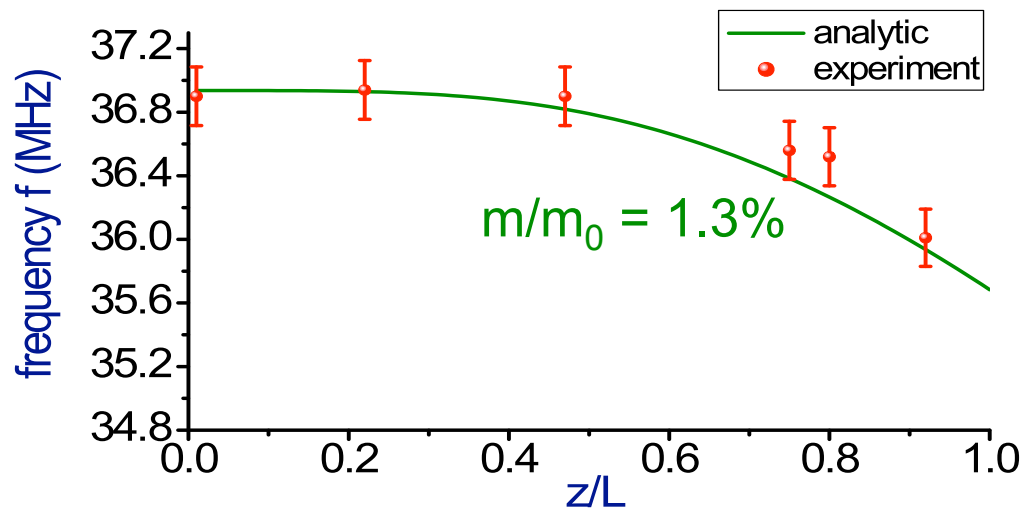
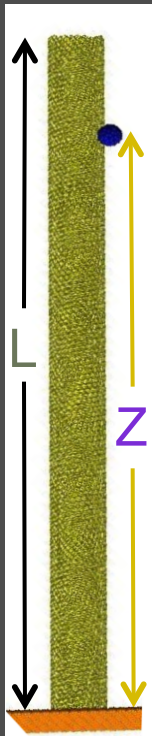
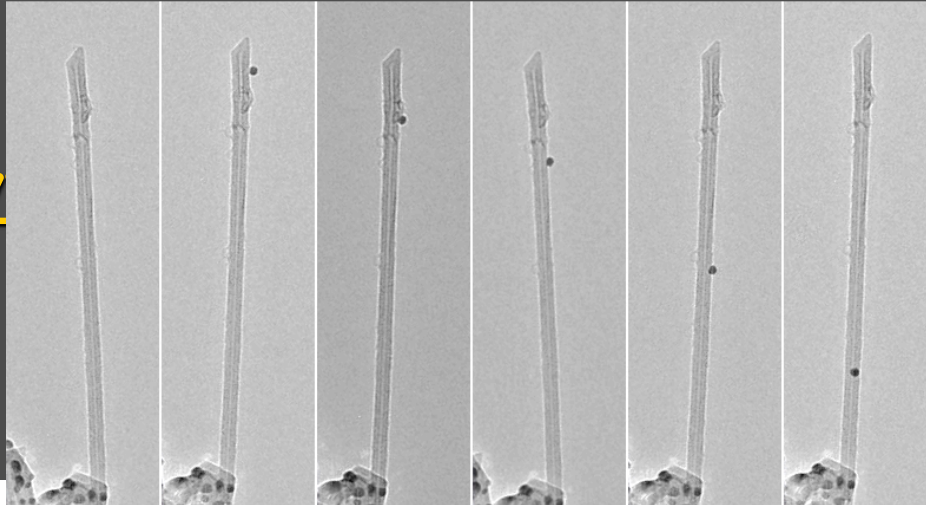
$$\delta m \sim 0.1 \text{ zg} < 0.18 \text{ zg (mass of Ag atom)}$$

Shift of resonance frequency



Analysis

Results

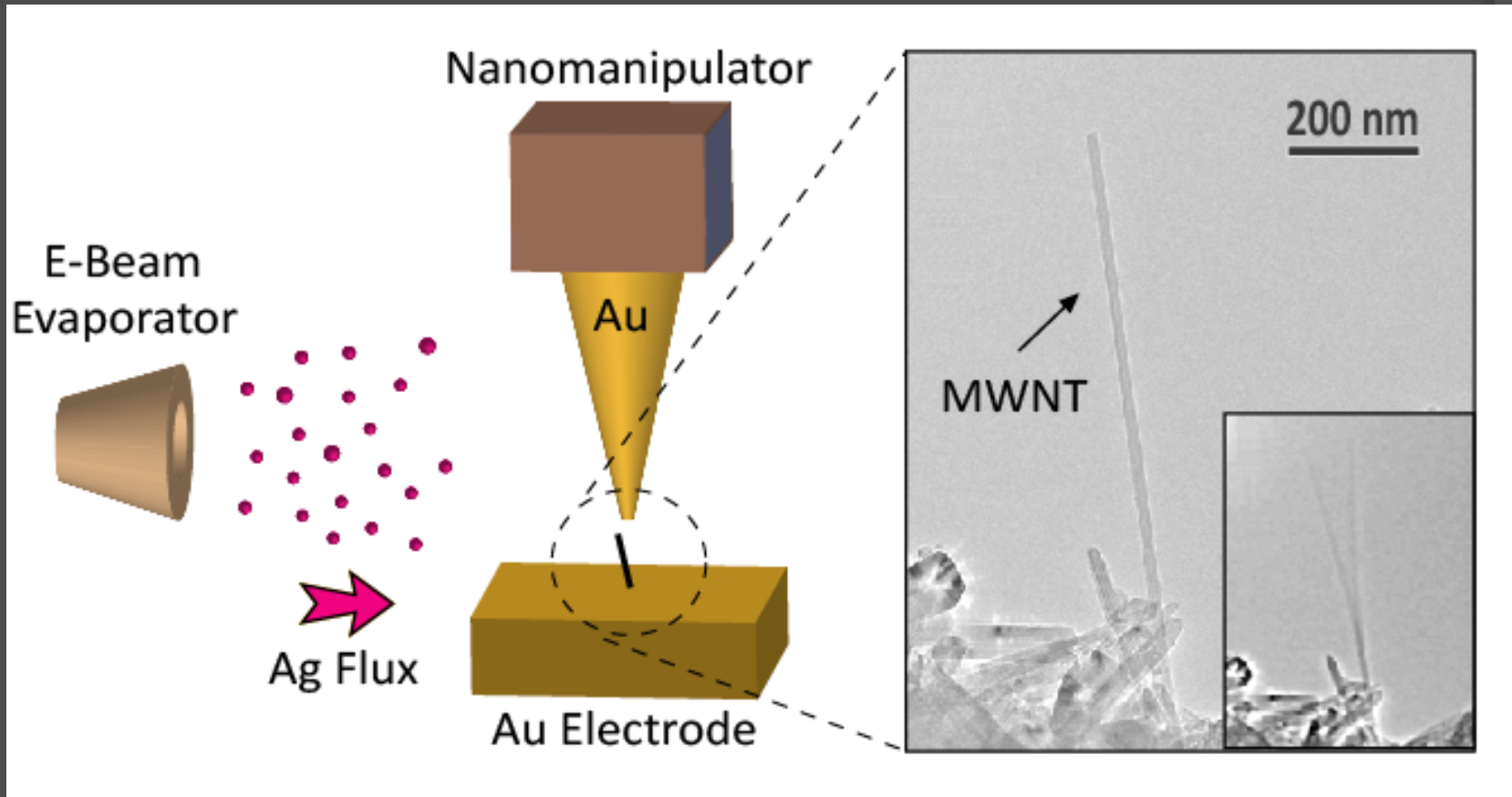


$$f^2 = f_0^2 \left(1 + \frac{m}{m_0} U^2(z) \right)^{-1}$$

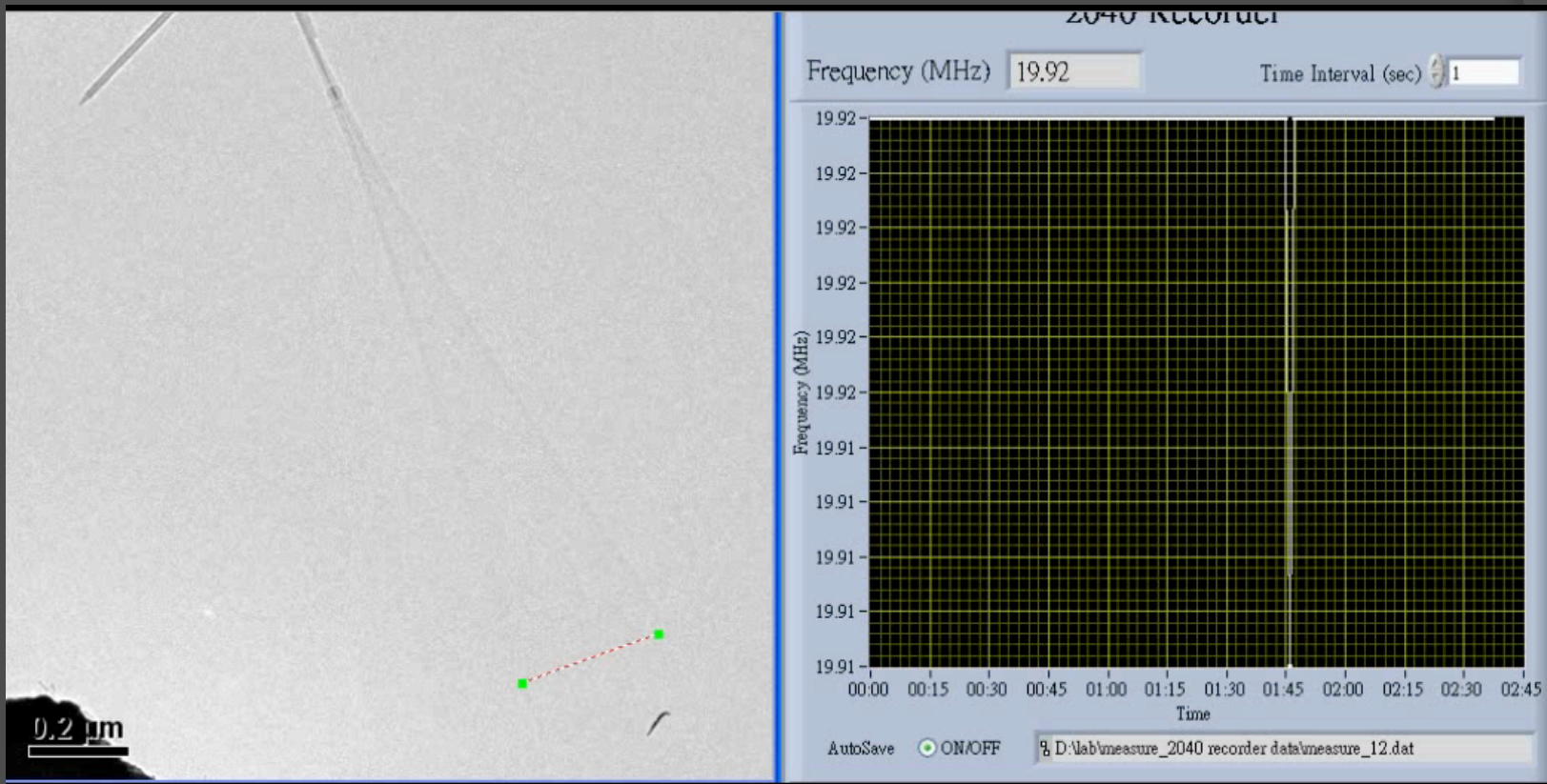
$$f_0 = \frac{3.516}{8\pi L^2} \sqrt{(D^2 + D_i^2) \frac{E_b}{\rho}}$$

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

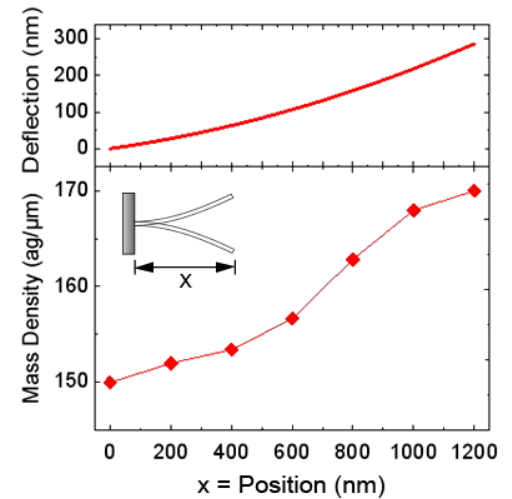
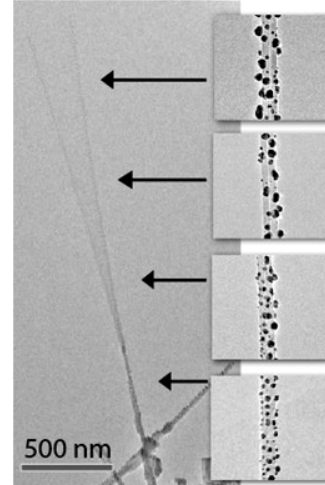
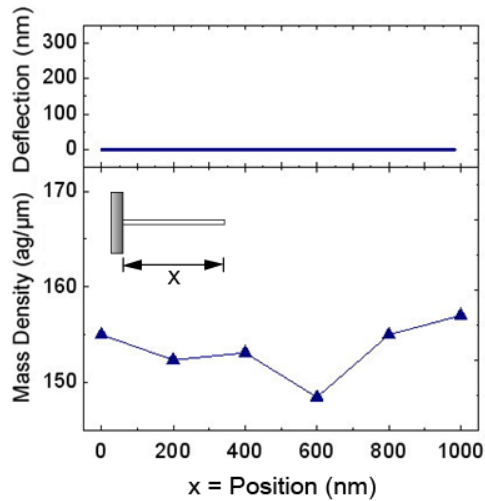
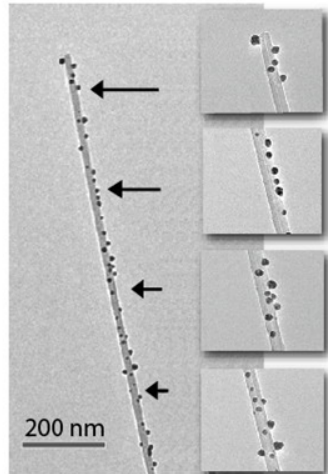
Nanotube resonator as mass sensor



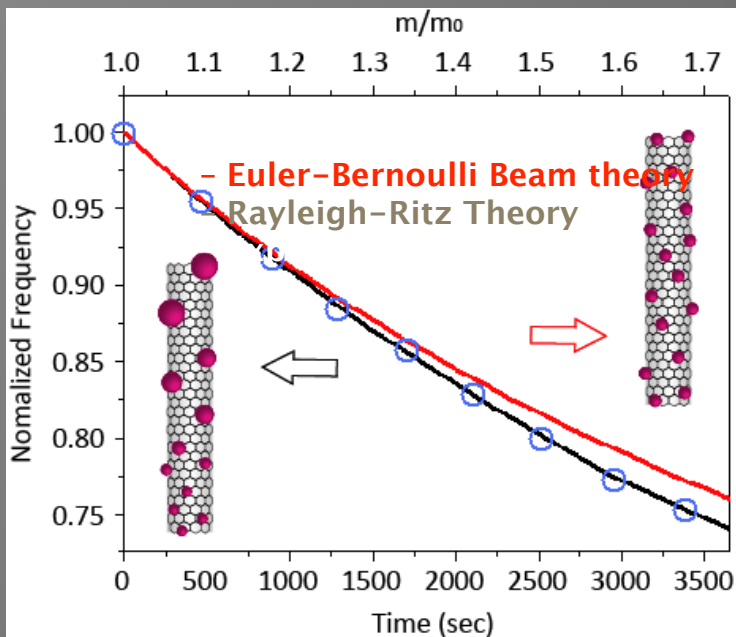
In situ measurement of freq. shift



Gradient Coating Effect of Vibrating CNTs



Self-weighting ability

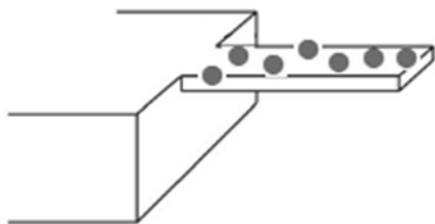


Euler-Bernoulli Beam theory

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

(Δm must be uniformly distributed on the cantilever)

Rayleigh-Ritz Theory



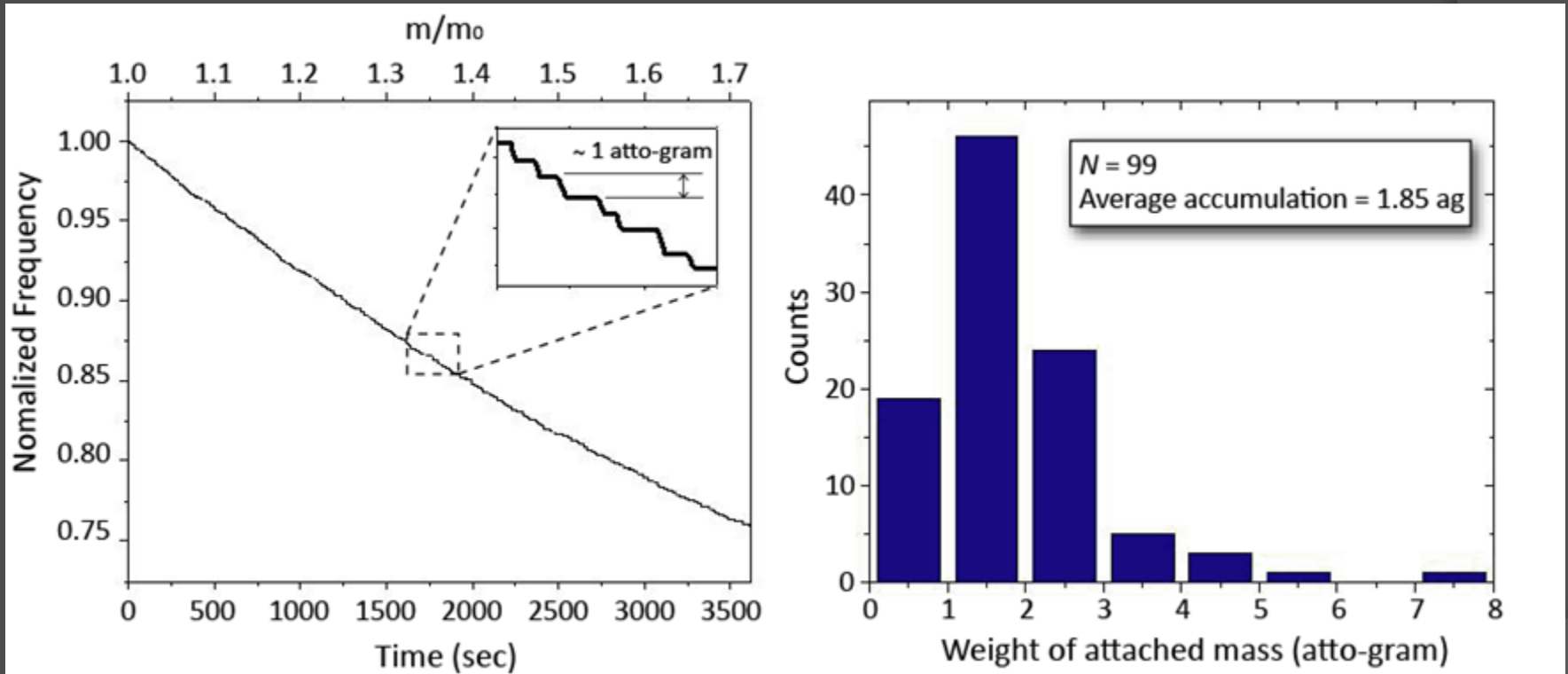
$$E_{\text{strain}} = E_{\text{kin}} + E_{\text{kin}, \Delta m1} + E_{\text{kin}, \Delta m2} + E_{\text{kin}, \Delta m3} \dots$$

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

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

$$\lambda(z) = a_0 z + a_1 \quad (\text{Linear mass density})$$

Weighting resolution



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



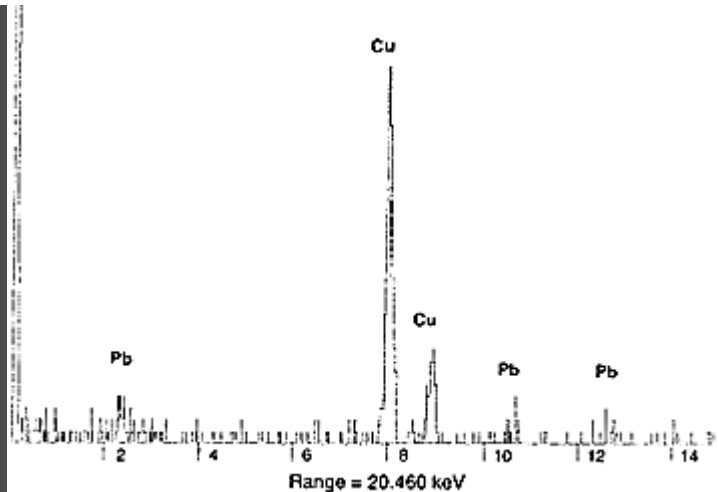
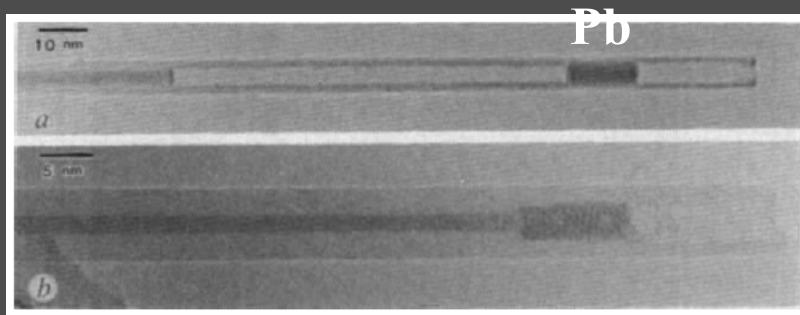
Summary

- *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.*

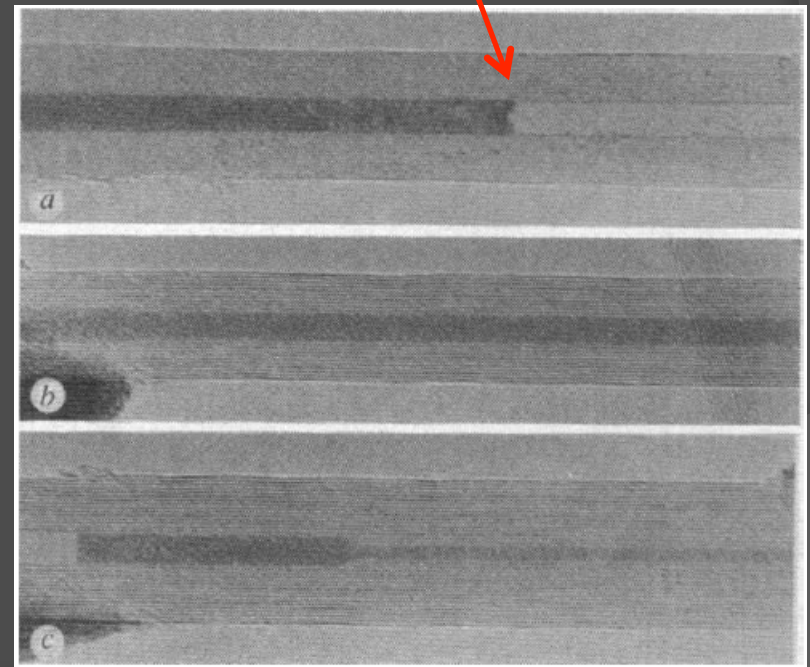
Capillarity-induced filling of carbon nanotubes

P. M. Ajayan & Sumio Iijima

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

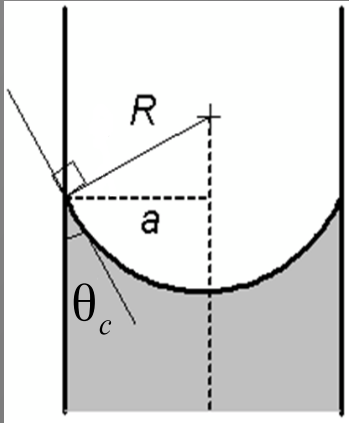


Pb seems to wet CNT



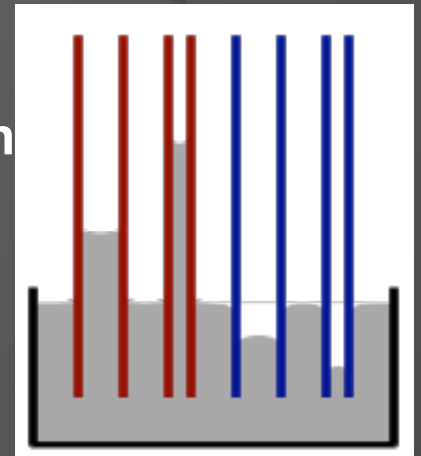
Macroscopic capillarity

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



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

$\theta_c < 90^\circ \rightarrow$ resulting in spontaneous absorption of the liquid into the capillary tube
 $\theta_c > 90^\circ \rightarrow$ 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 $\gamma < 200$ mN/m.

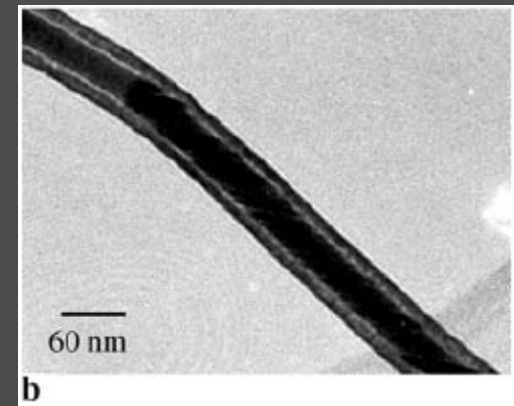
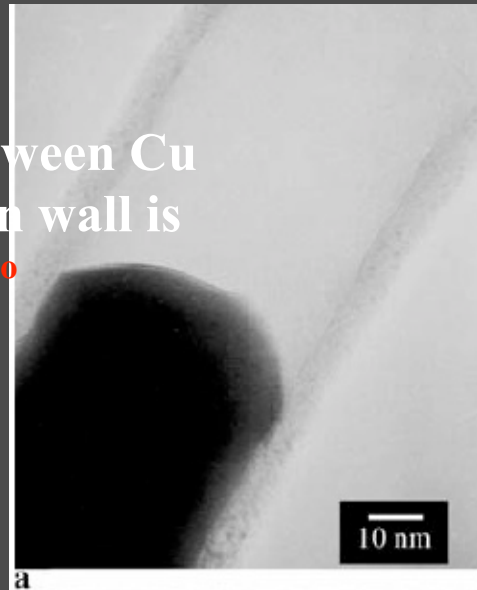
Surface tension (γ) for Ag ~ 900 mN/m

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
120°~135°



※ 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

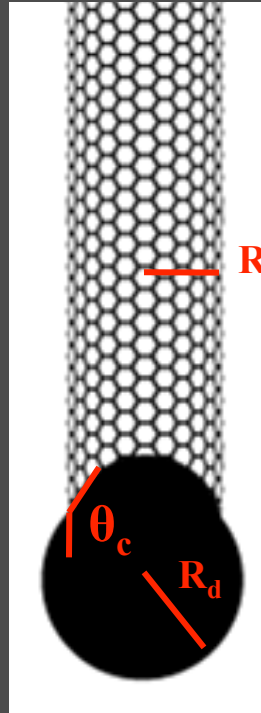
According to Young-Laplace equation:

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

ex: droplet (spherical)

$$R_x = R_y = R$$

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



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

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

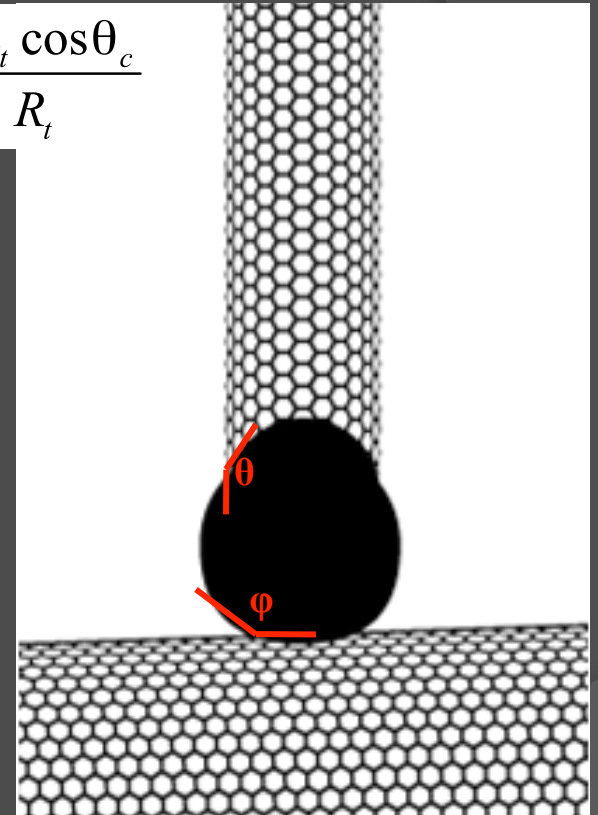
The droplet is unsupported

For the contact angle $\theta_c \sim 125^\circ$ of molten Ag nanodroplet inside the MWNT in our results

$$\Delta P_t = \frac{\gamma_{dt}}{R_t}$$

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

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



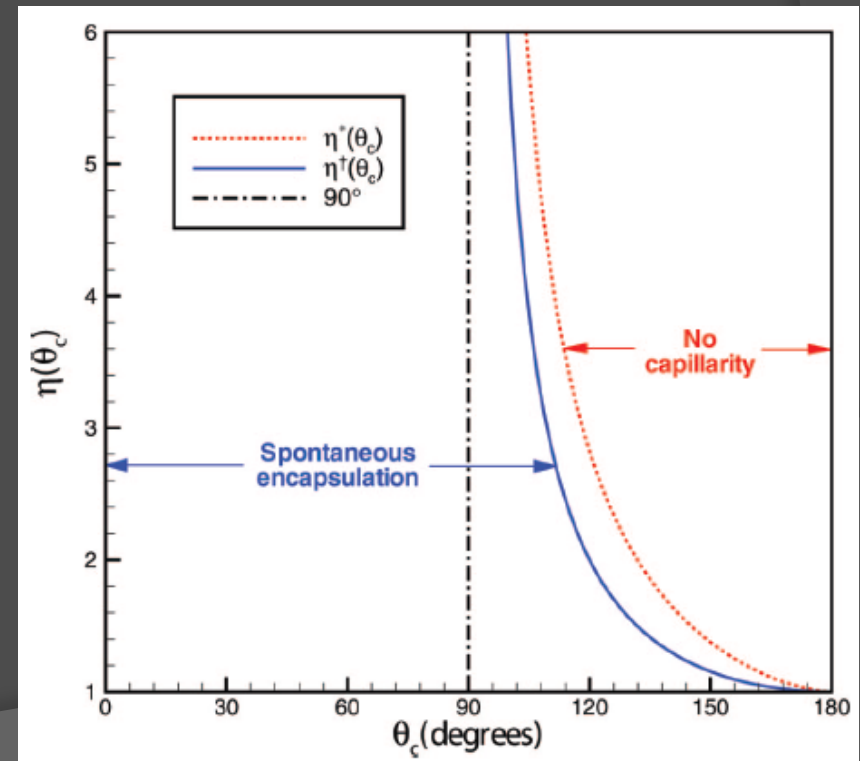
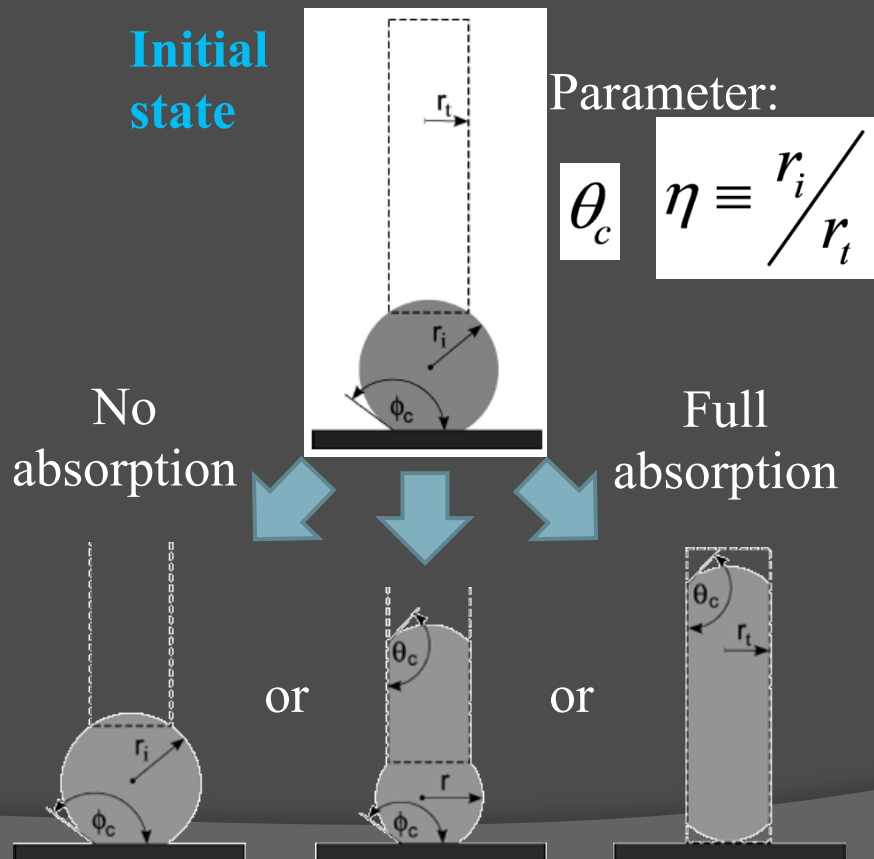
When the droplet is supported, the effect of Laplace pressure will be reduced.

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

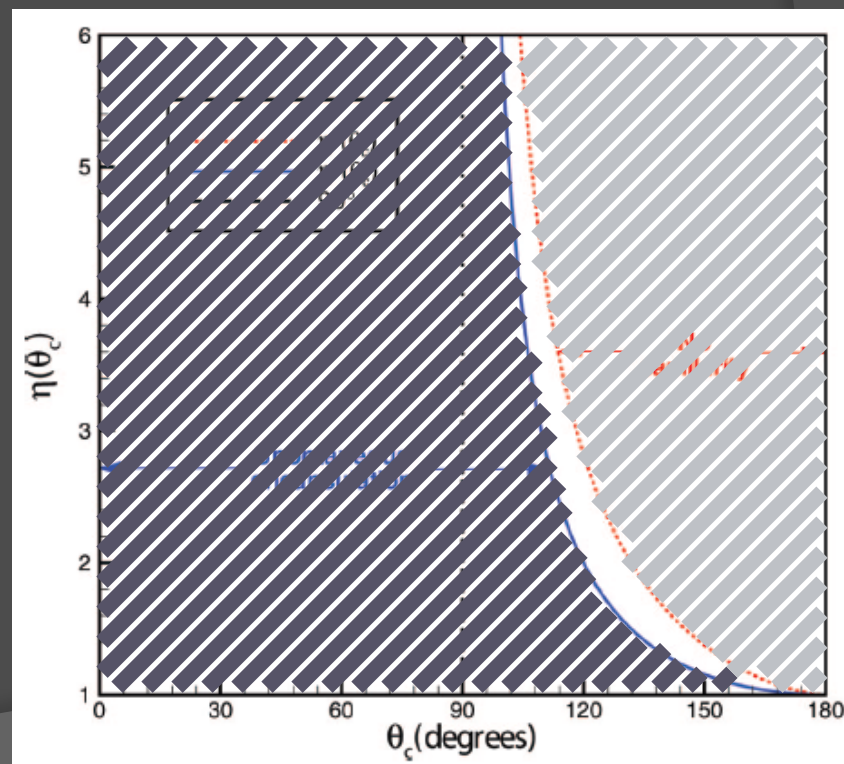
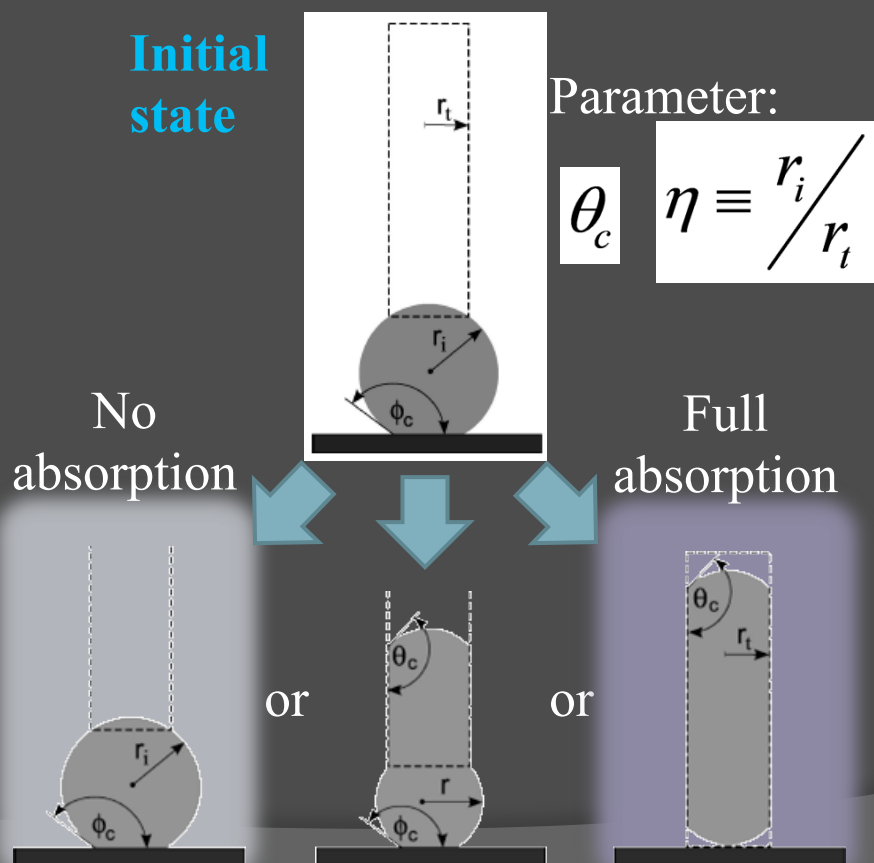


Capillary Absorption of Metal Nanodroplets by Single-Wall Carbon Nanotubes

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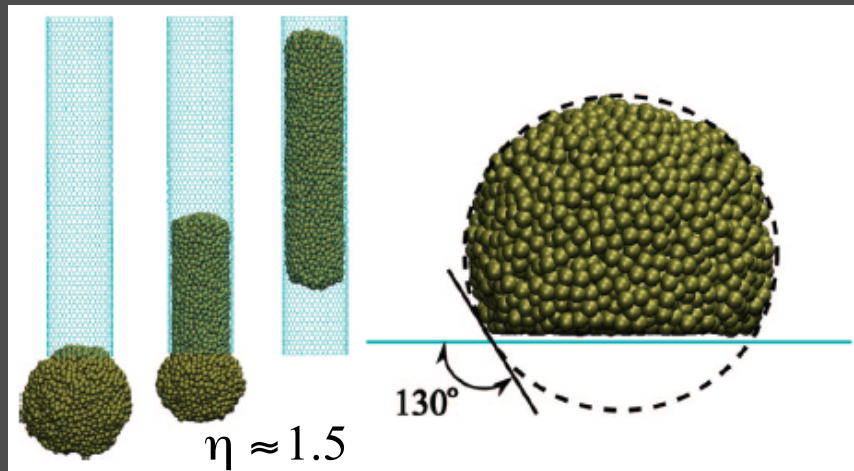
Part A : Present a simple model to demonstrate the capillary absorption for nonwetting liquid nanoparticles by CNT



Molecular dynamics simulation

CNT 220 Å long and 30 Å in diameter

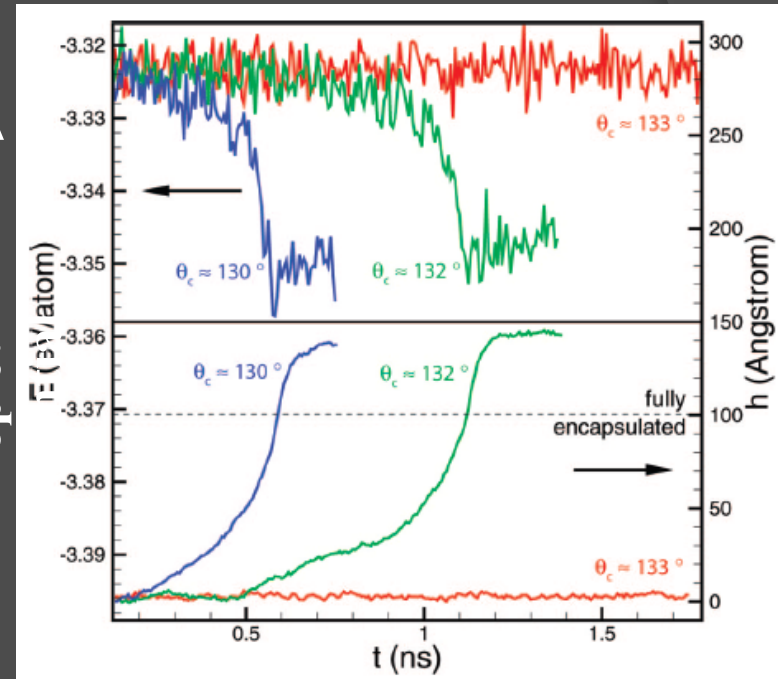
Molten Pd cluster with a radius of ~23 Å



Contact angle θ_c
between Pd cluster
and inner shell of
SWNT

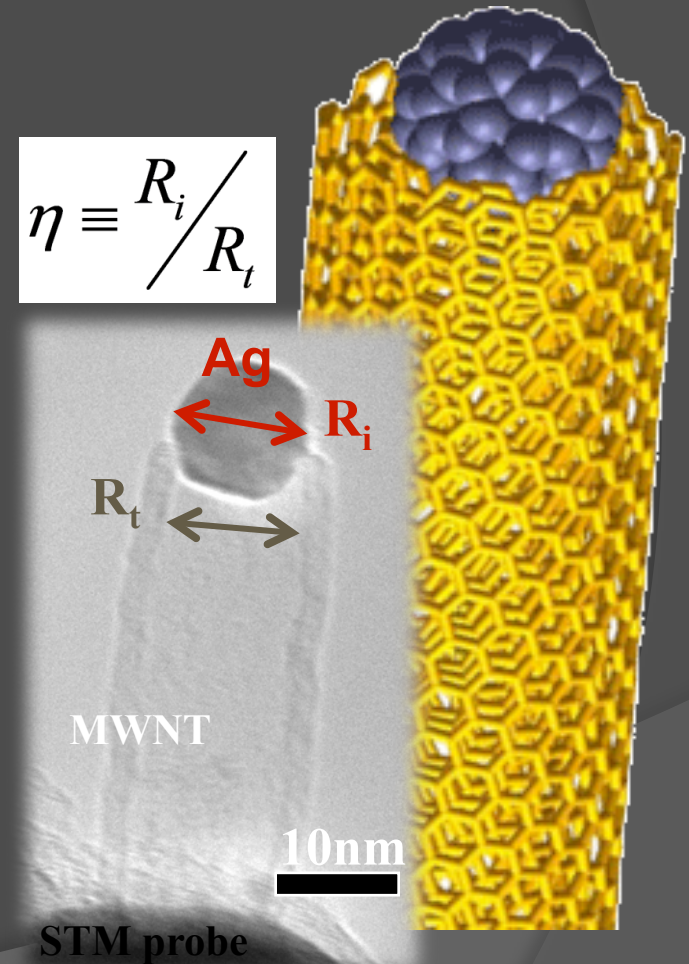
- $\theta_c \leq 130^\circ$ Molten nanoparticle were drawn almost immediately.
- $\theta_c \approx 132^\circ$ The presence of a small energy barrier. The absorption is activated.
- $\theta_c > 133^\circ$ did not yield capillary absorption of the droplets.

Droplet

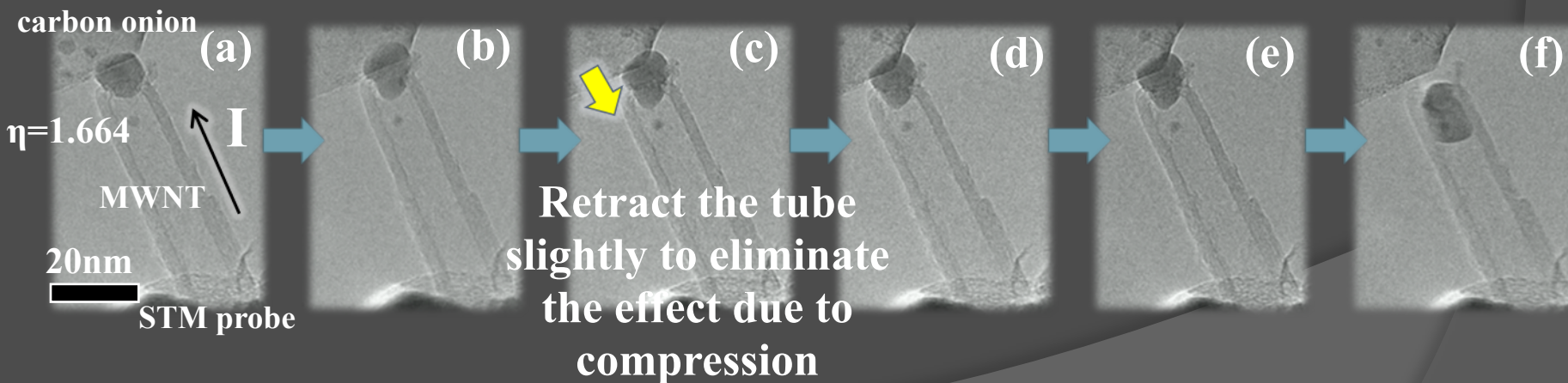
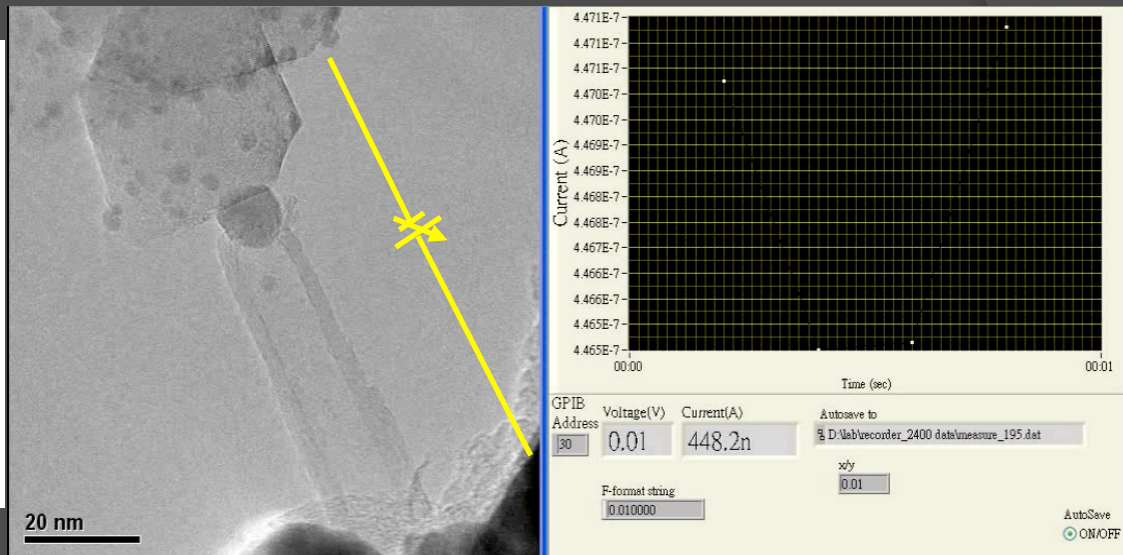
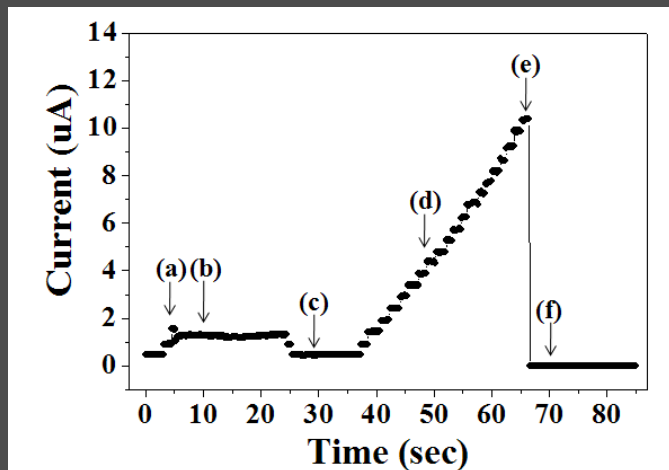


Distance of insertion of Pd cluster

Approaching Ag nanoparticle with open-ended MWCNT



Capillary absorption of Ag droplet



Capillary absorption at TV rate

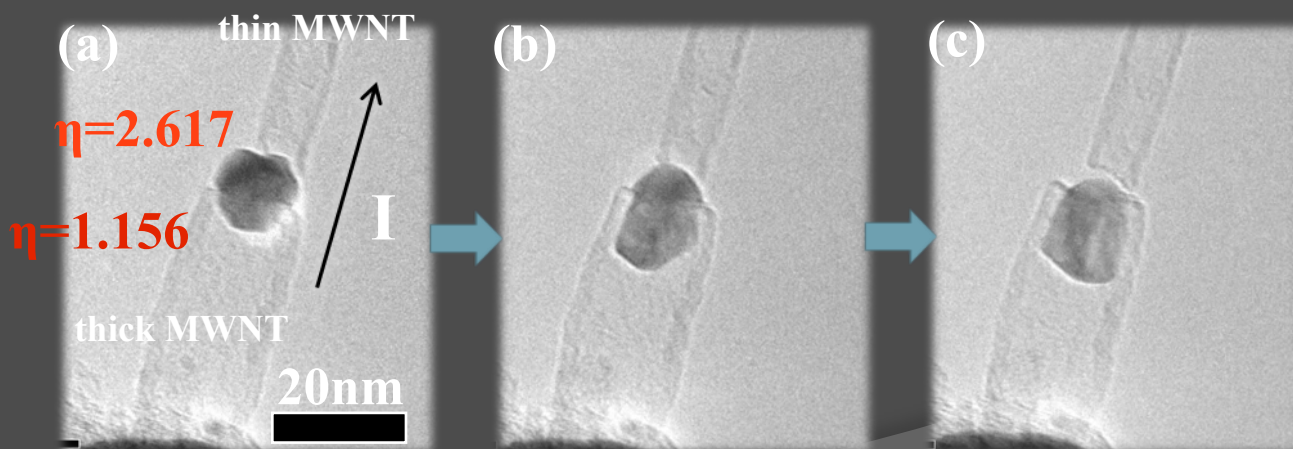
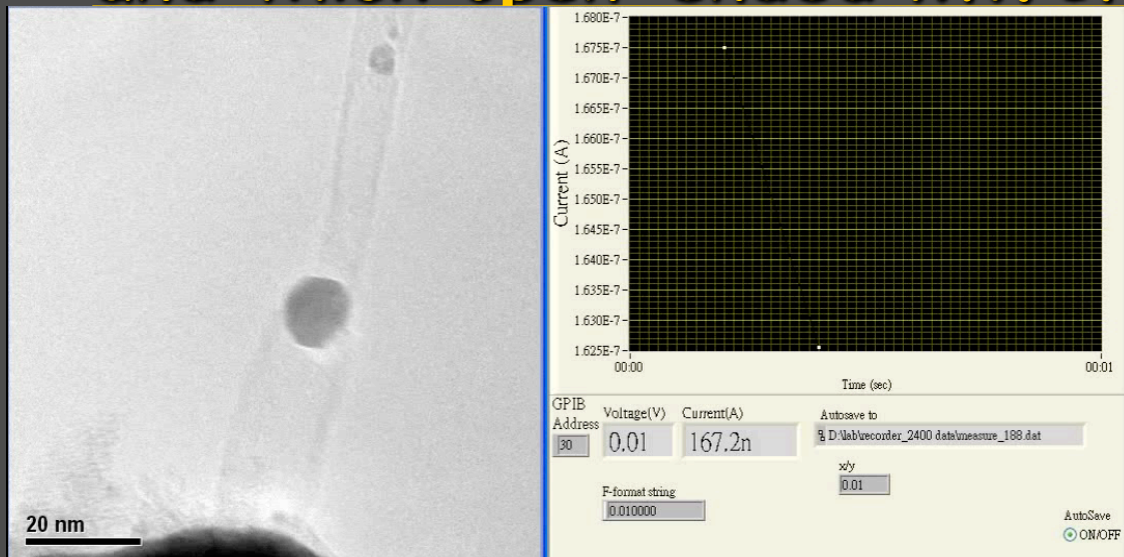
Current-induced joule heat caused the state change of Ag nanodroplet to **melt** and then triggered the capillary absorption



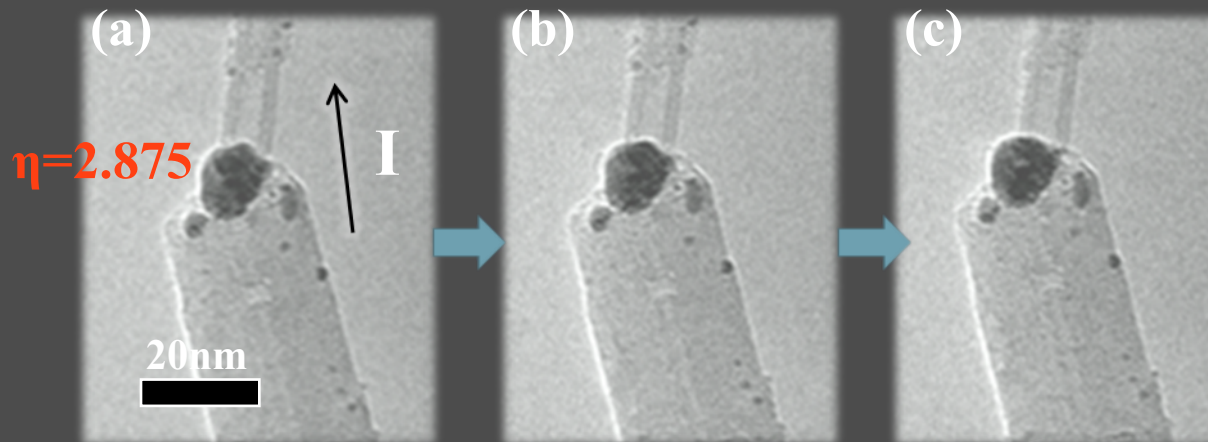
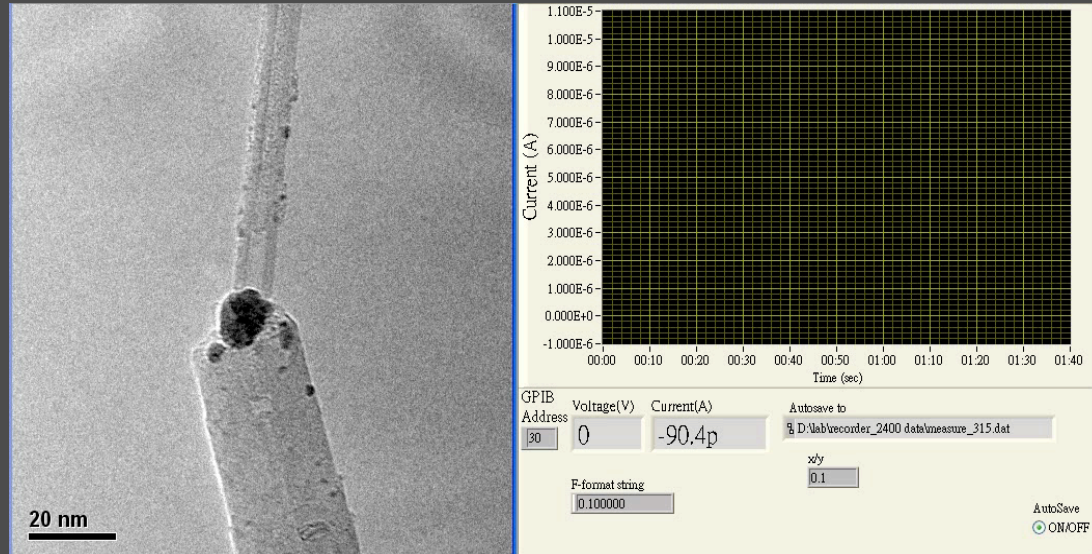
CCD record: two frames per second

TV record: ~30 frames per second

Ag nanoparticle between a thin and thick open-ended MWCNT

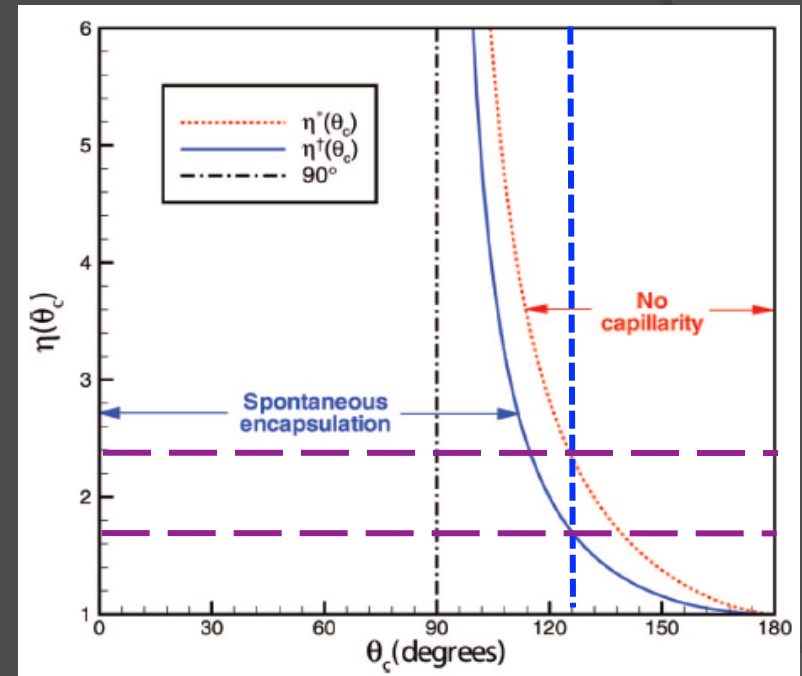
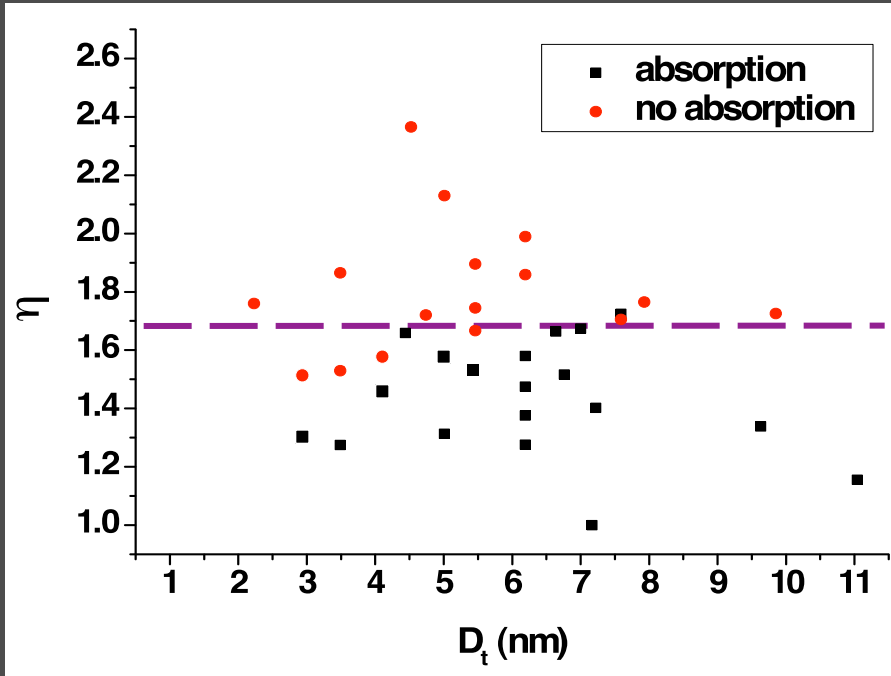


No absorption for large η

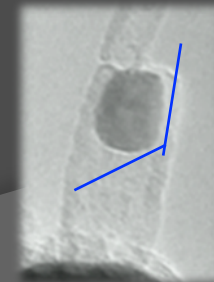


The Ag nanodroplet drained out gradually from the hollow core of MWNT as the passing current increased

Capillary absorption as function of η



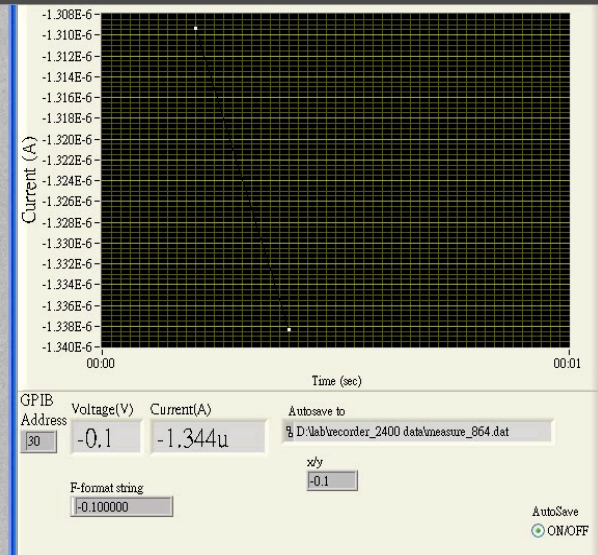
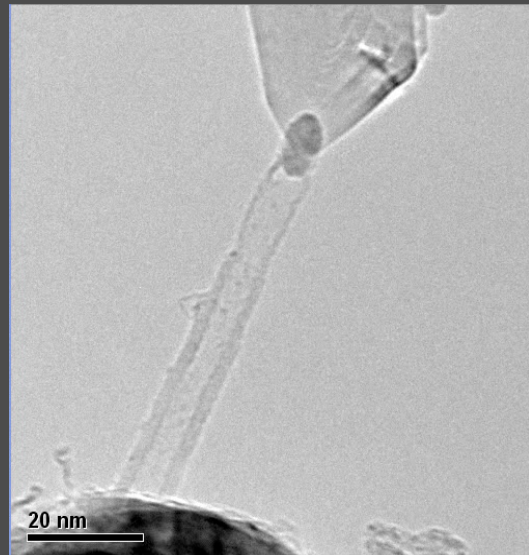
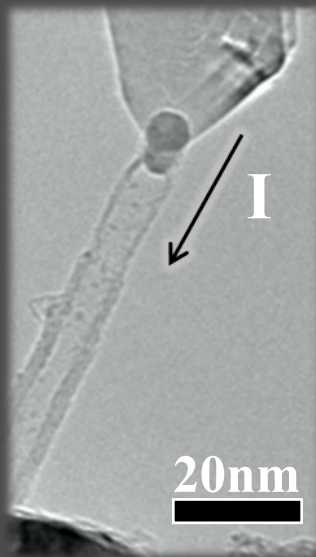
The critical $\eta \sim 1.7$ for capillary absorption in our experiment agrees well with the calculated result for tube's diameter $> 5\text{nm}$.



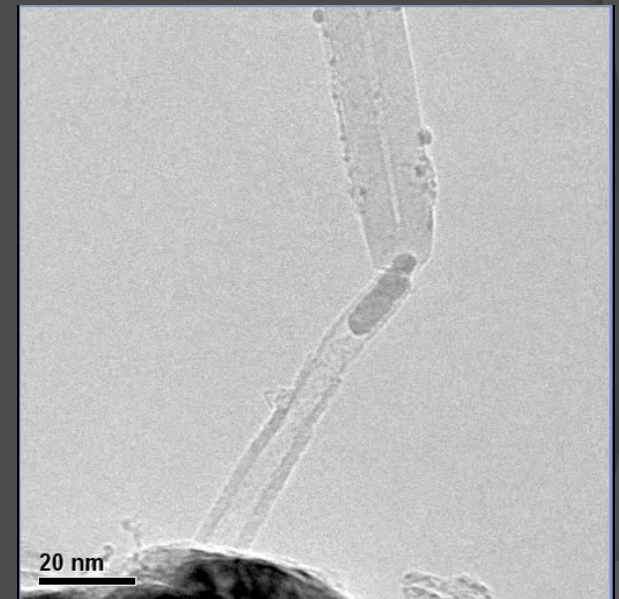
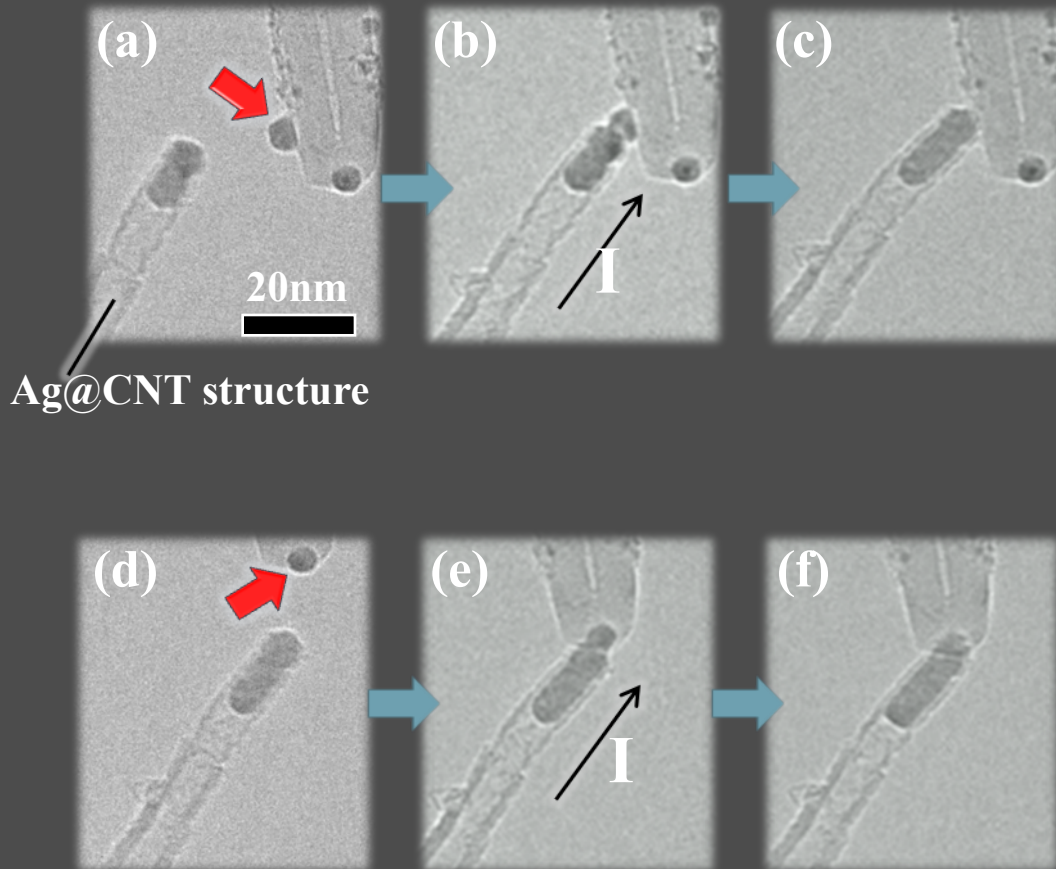
Contact angle
 $\sim 125^\circ$

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.*