Unraveling the Behavior of Liquids at the Nanoscale

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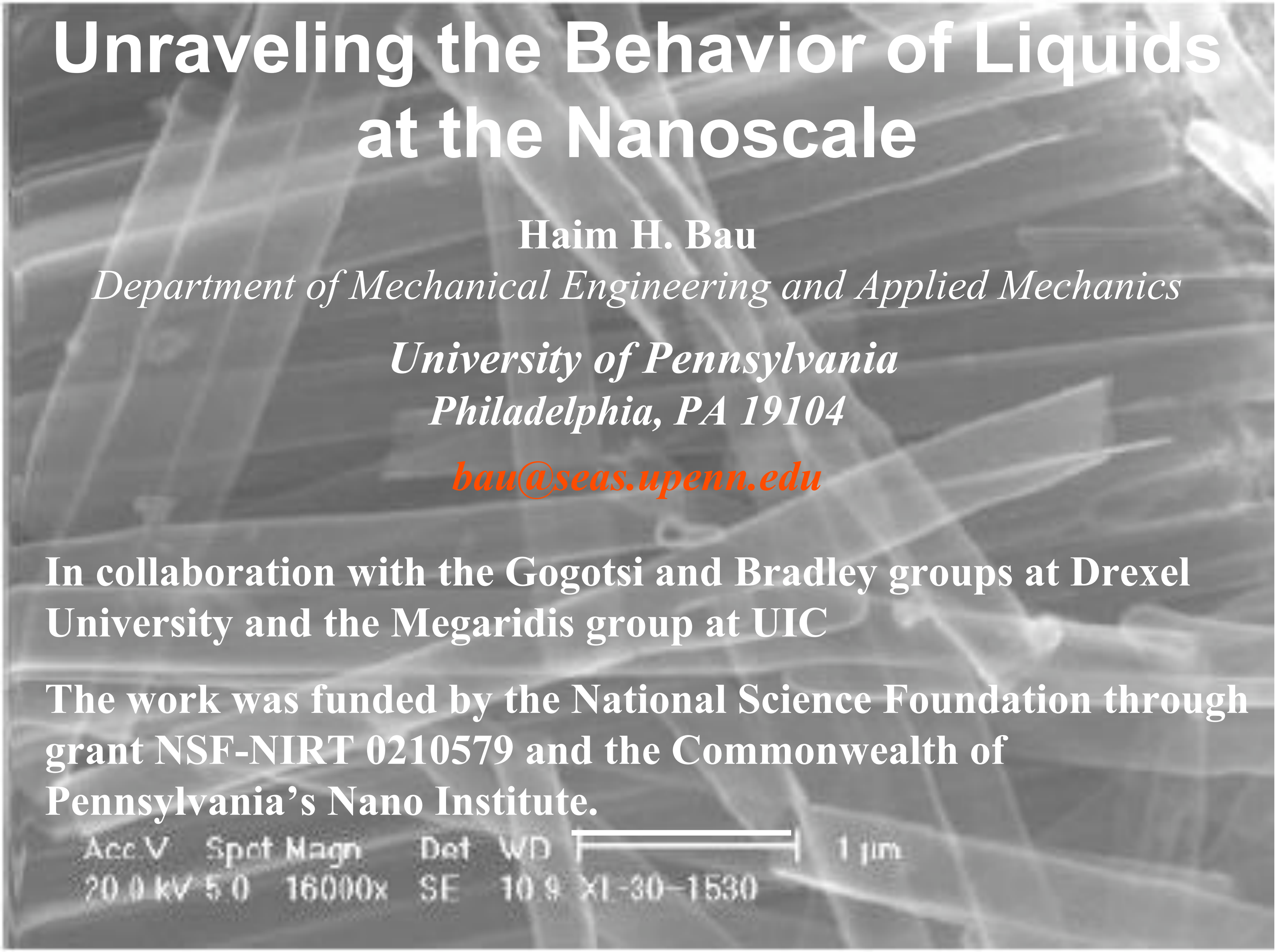
In collaboration with the Gogotsi and Bradley groups at Drexel University and the Megaridis group at UIC

The work was funded by the National Science Foundation through grant NSF-NIRT 0210579 and the Commonwealth of Pennsylvania's Nano Institute.



The MICRO and NANO FLUIDICS GROUP at UPenn

Nanotechnology

Byong Kim (Postdoc), Shashank Sinha (Postdoc), Michael Schrlau (PhD), Tom Murray (UG), Greg Friedman (UG)

Collaborators: UPenn MSE, Drexel Univ., and Univ. Illinois Chicago

Microfluidics & LOC

Michael Mauk (Postdoc), Z. Chen (Postdoc), Jim Wang (Postdoc), Hui Liu (PhD), Shizhi Qian (PhD), Junting Zheng (MS)

Collaborators: Penn Dental School, Leiden University Medical Center, OraSure Technologies, and Drexel University Medical School

Molecular Motors

Mike Riegelman (PhD), Mark Arsenault (PhD), Joe Grogan (PhD)

Collaborators: UPenn Muscle Institute (Yale Goldman and Henry Shuman) and NIH

Flow Control

Hui Zhao (PhD), Marcel Remillieux (Engineering Diploma)

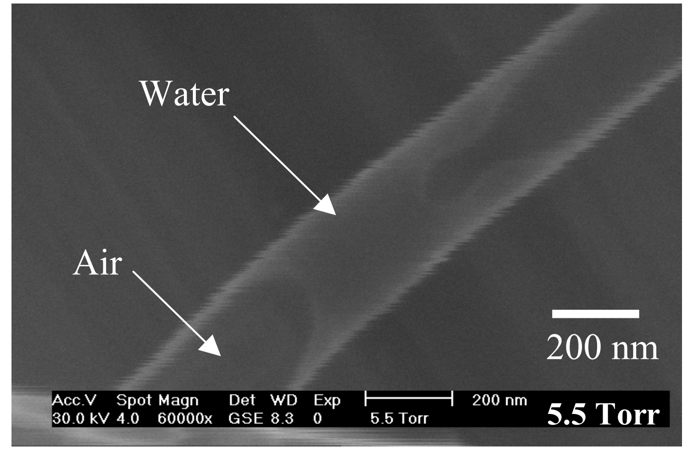
OBJECTIVES

- **Develop experimental techniques to investigate the behavior of liquids at the nano-scale**
- **Overcome the limitations of visible light. New paradigm in Fluid Physics: electron microscopy of liquid flow with sub nanometer resolution**
- **Facilitate electron microscope observations of "live" macro molecules (without cryo-cooling)**

Carbon Nanotube-Based Devices

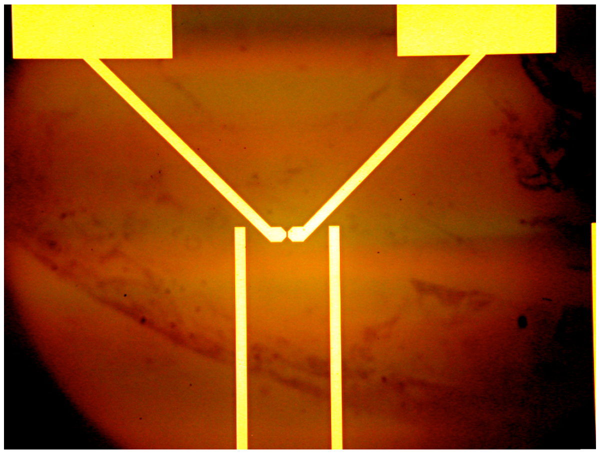
Why carbon nanotubes?

1. Carbon nanotubes can be fabricated with diameters ranging from a fraction of a nanometer to several hundred nanometers, allowing one to conduct experiments with various tube sizes.
2. The tubes are straight and open and have uniform diameter
3. The tubes' surface properties can be modified with heat and/or chemical treatments to facilitate behaviors ranging from hydrophilic to hydrophobic, allowing one to probe the effect of surface properties on the liquids' behaviors.
4. The tubes' walls are sufficiently thin to be transparent to light and electrons.
5. The tubes can contain high-pressure fluids for an extended time even in the vacuum environment of the electron microscope

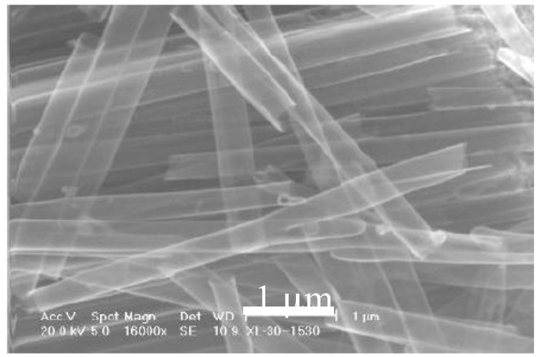


An Environmental Scanning Electron Microscope study of the CNTs, performed by Gogotsi's group at Drexel, shows that the tube is hydrophilic.

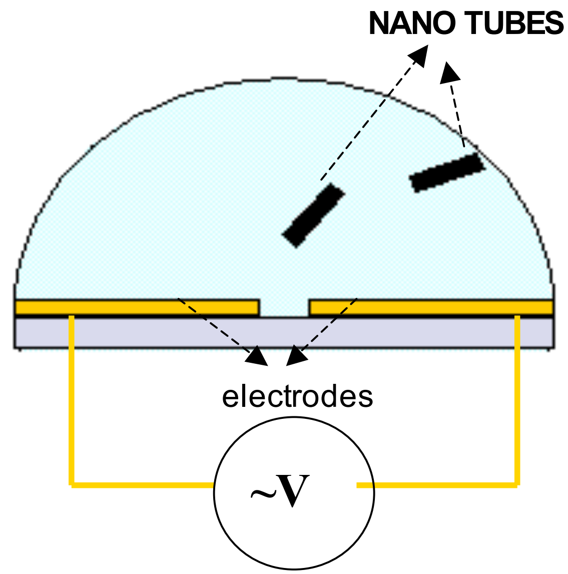
NANO-ASSEMBLY OF NANOTUBES and NANOFIBERS (DIELECTROPHORESIS)

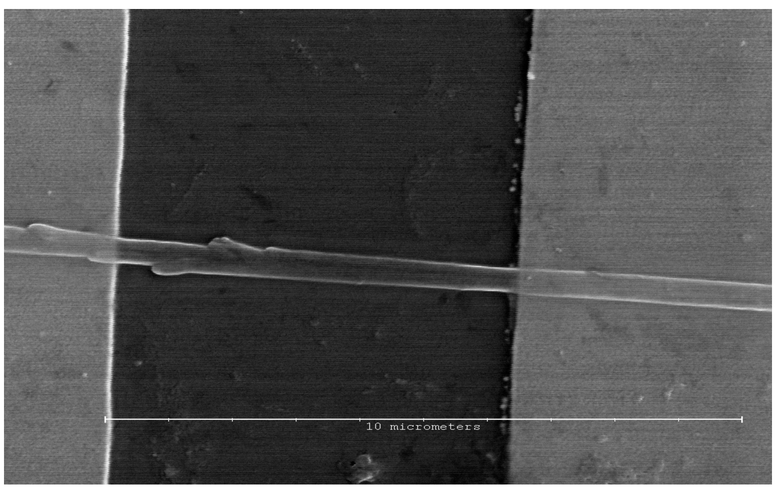


Electrodes patterned on SiO_2

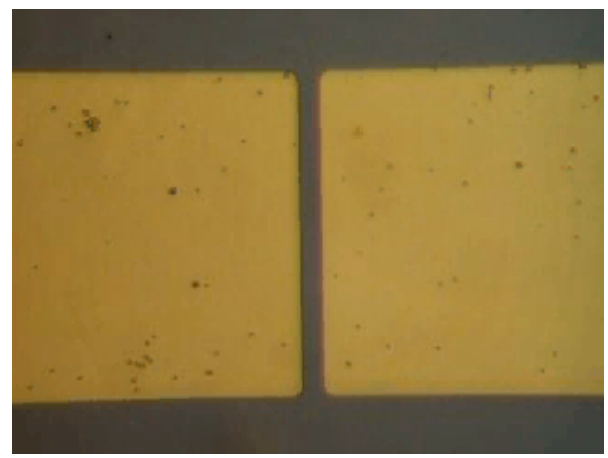


Straight and open-ended CNTs fabricated in alumina template membrane by Jean-Claude Bradley's group at Drexel

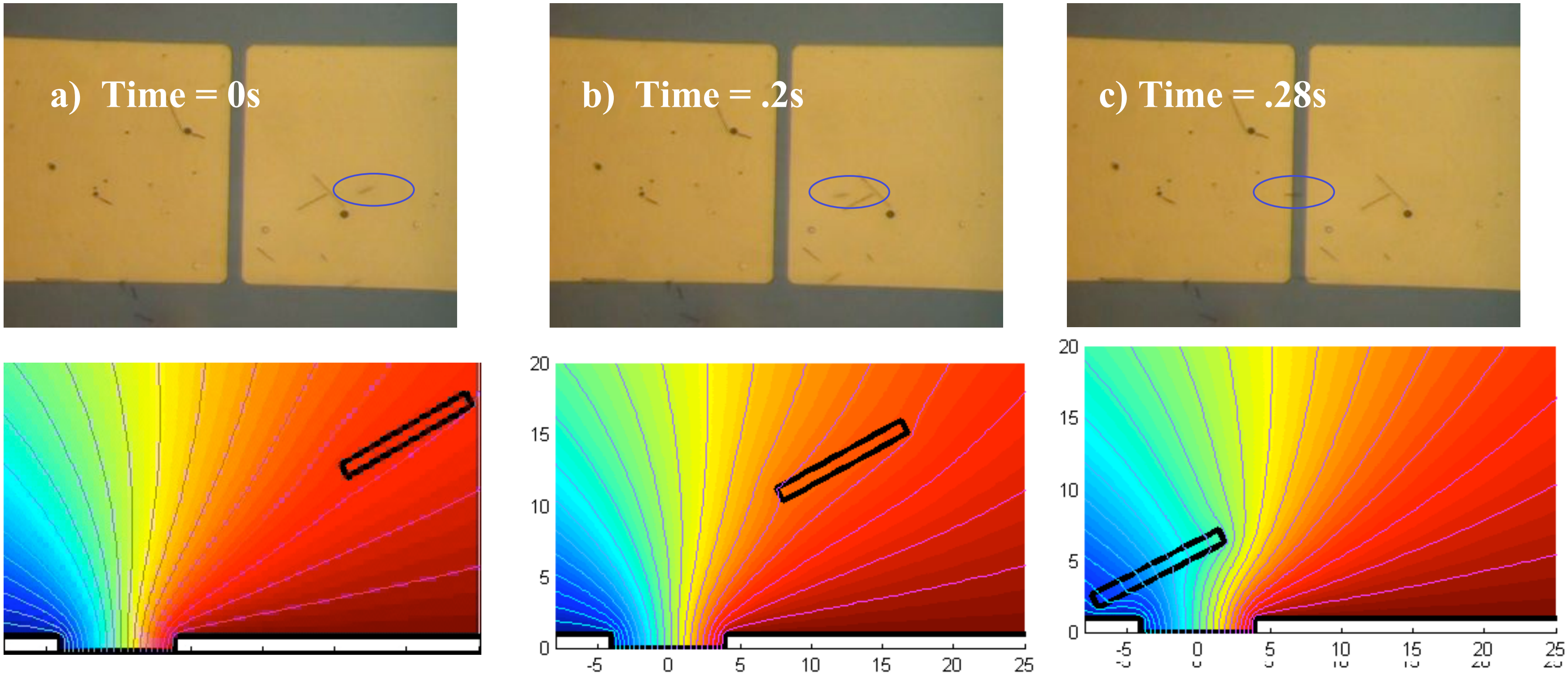




Nanotubes assembled in the gap between two electrodes

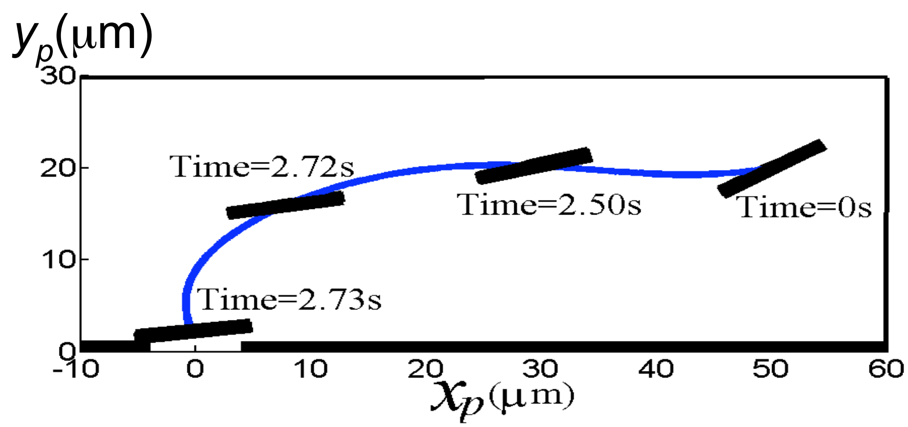


Visualization of the trapping process

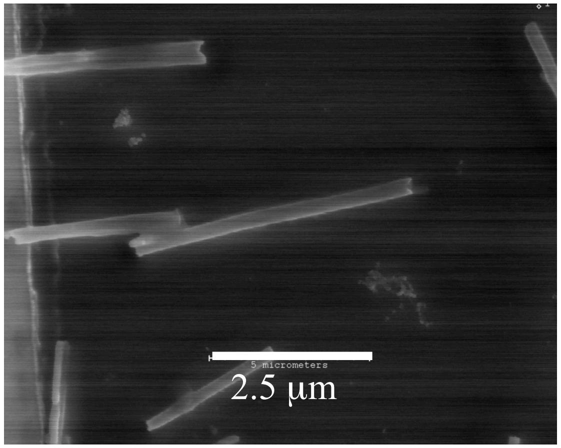


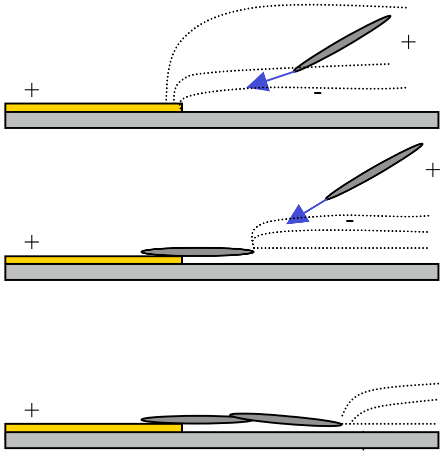
M. Riegelman, H. Liu, S. Evoy, H. H. Bau, Nanofabrication of Carbon Nanotube (CNT) Based Fluidic Device,Proceedings of NATO-ASI: Nanoengineered Nanofiberous Materials, Antalya, Turkey, Sept. 1st-12th, 2003.

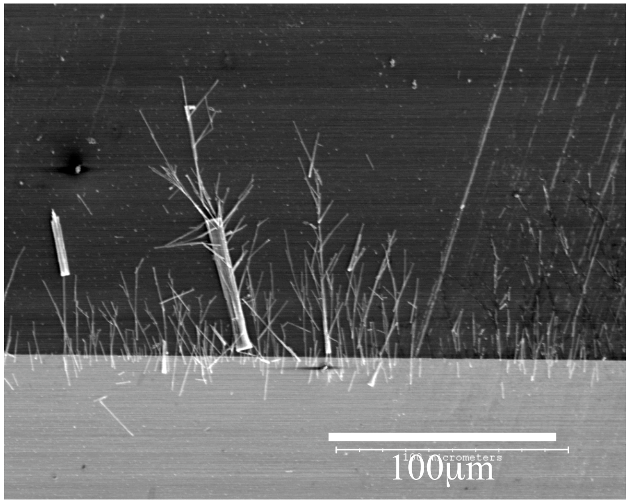
Riegelman, M., Liu, H., and Bau, H. H., 2005, Controlled Nano Assembly and Construction of Nanofluidic Devices, accepted for publication in Trans ASME, J. Fluid Engineering.

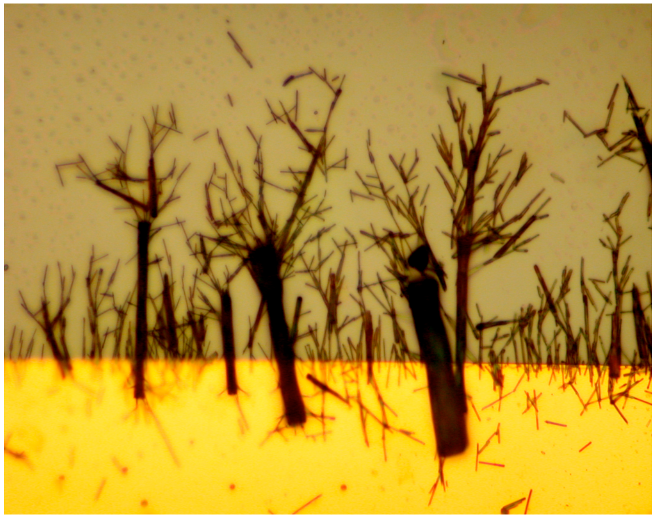


Chain and Tree Formation

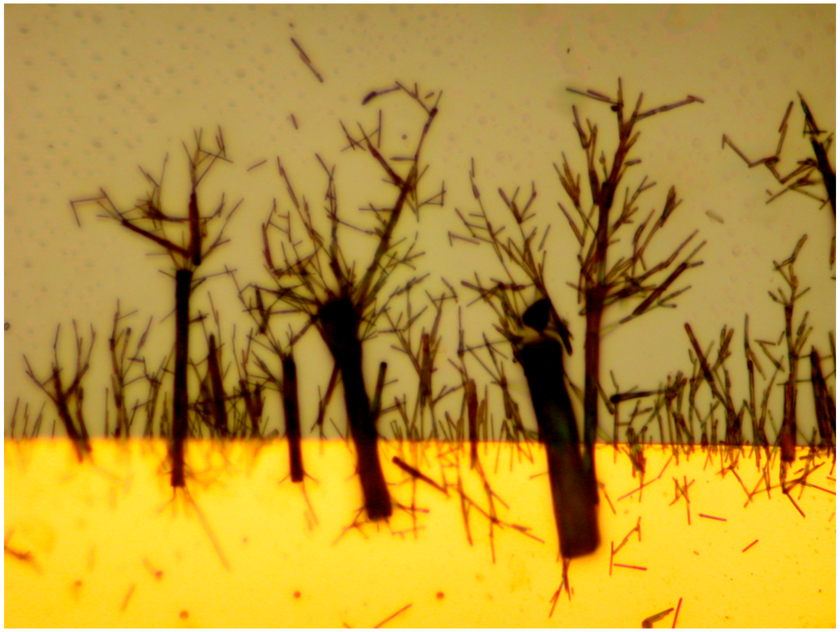




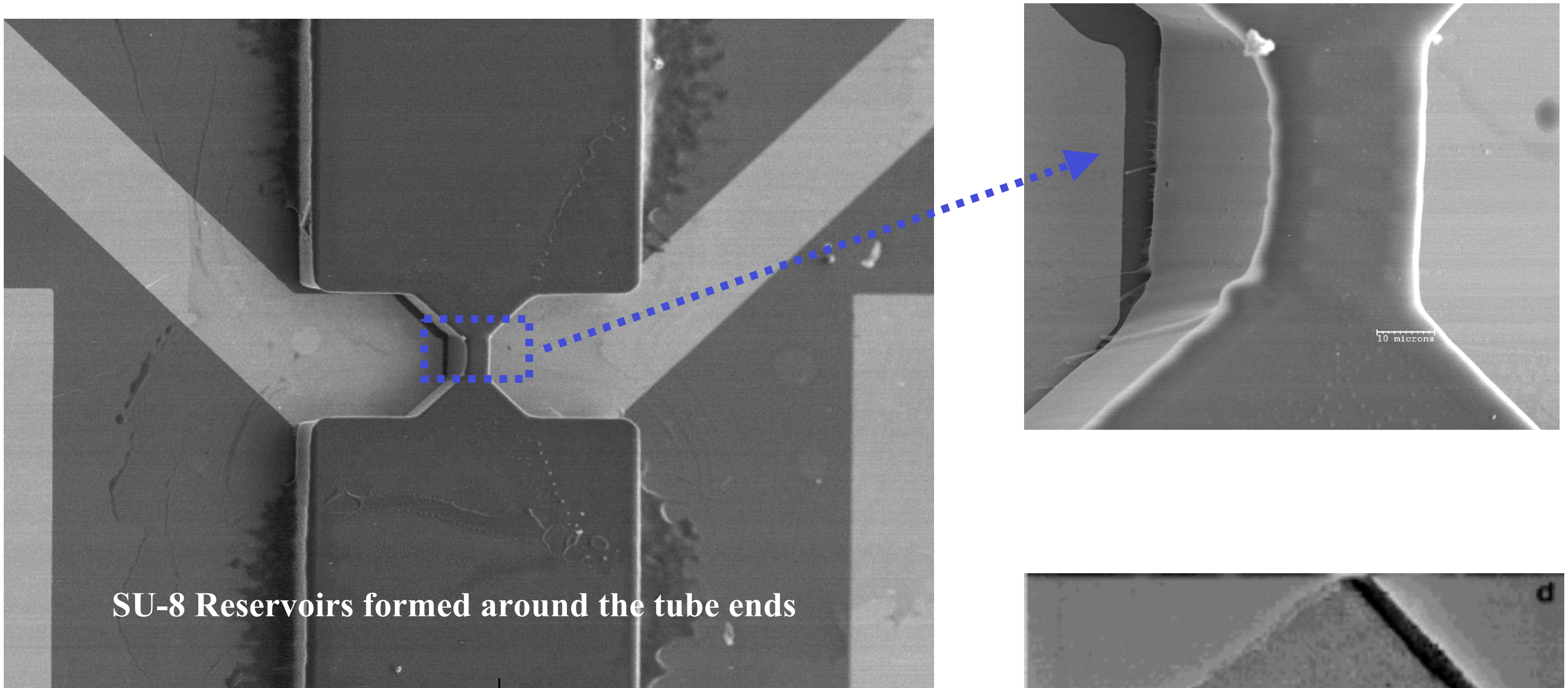


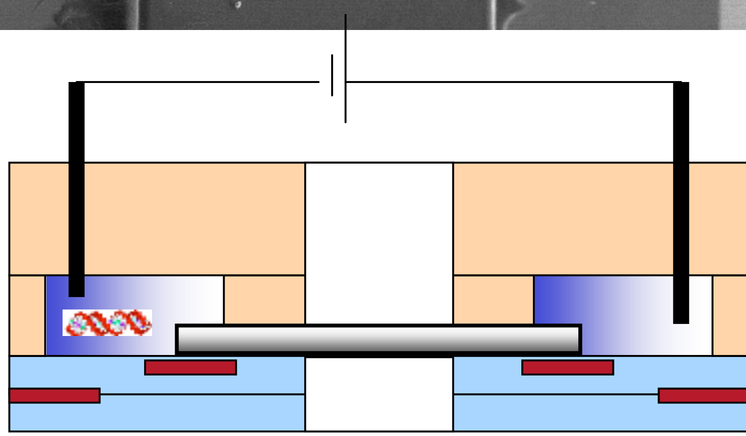


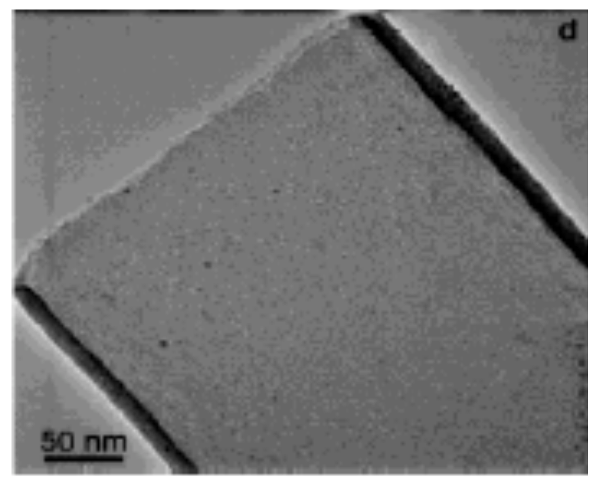
Carbon Nanotube Trees

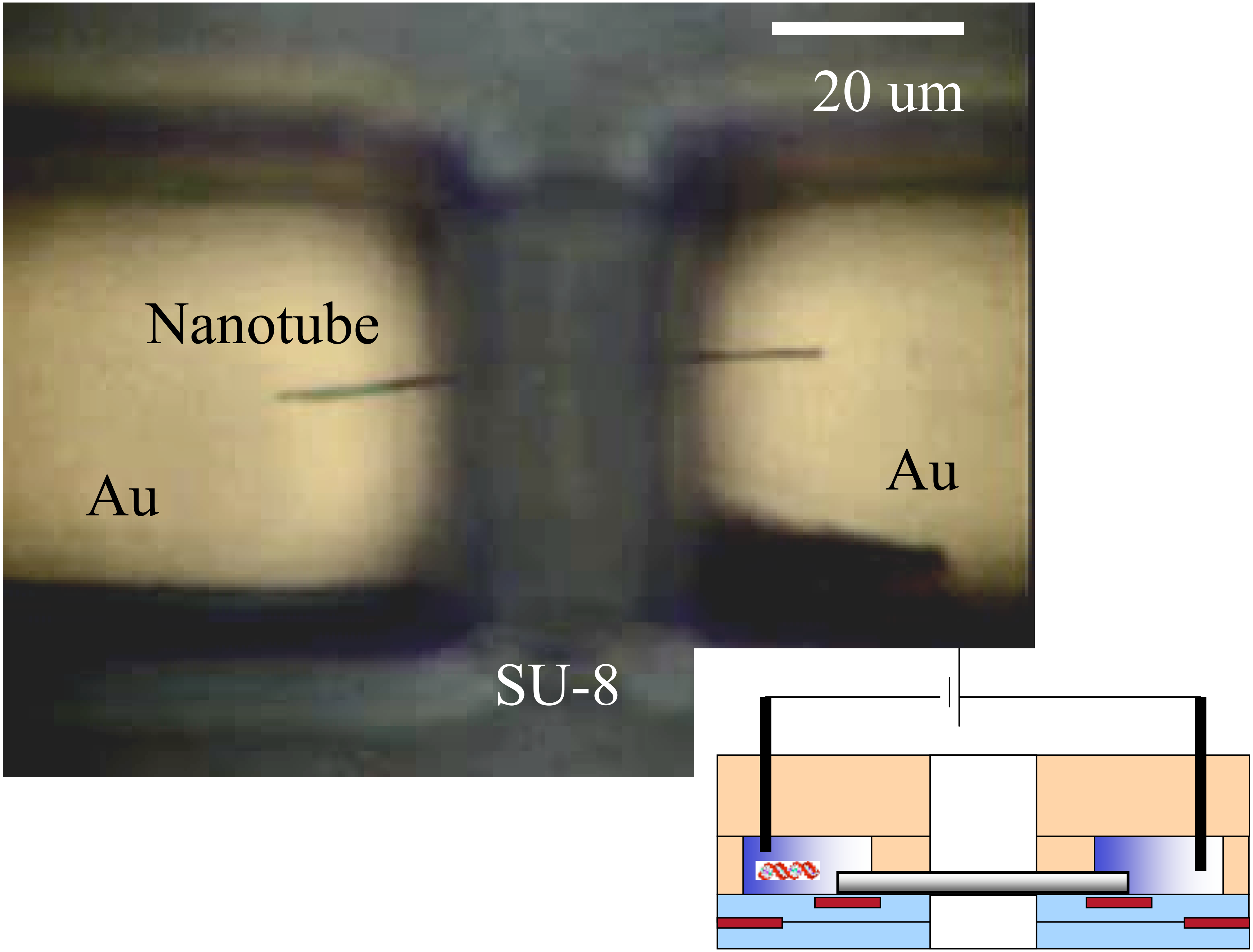


Nanotube-Based Fluidic Devices



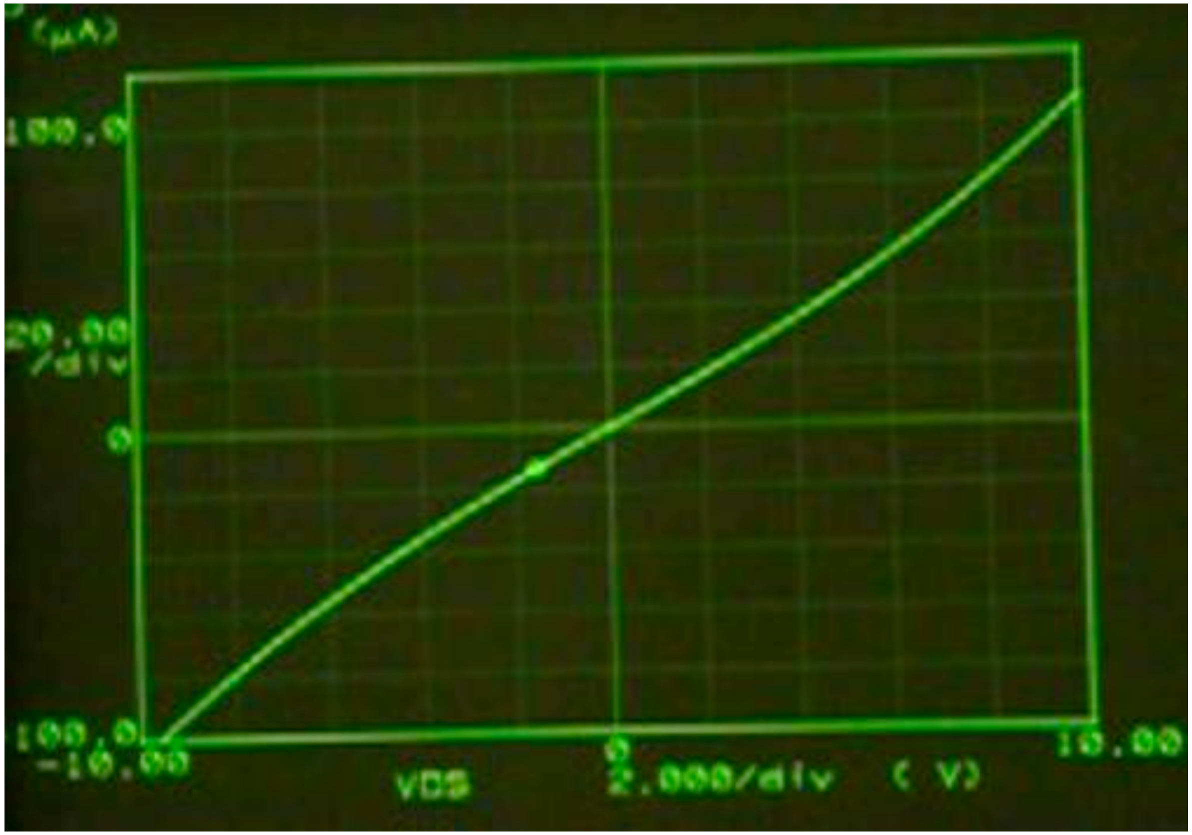





20 um
Nanotube
Au
Au
SU-8

The Electrical Resistance of Individual Nanotubes

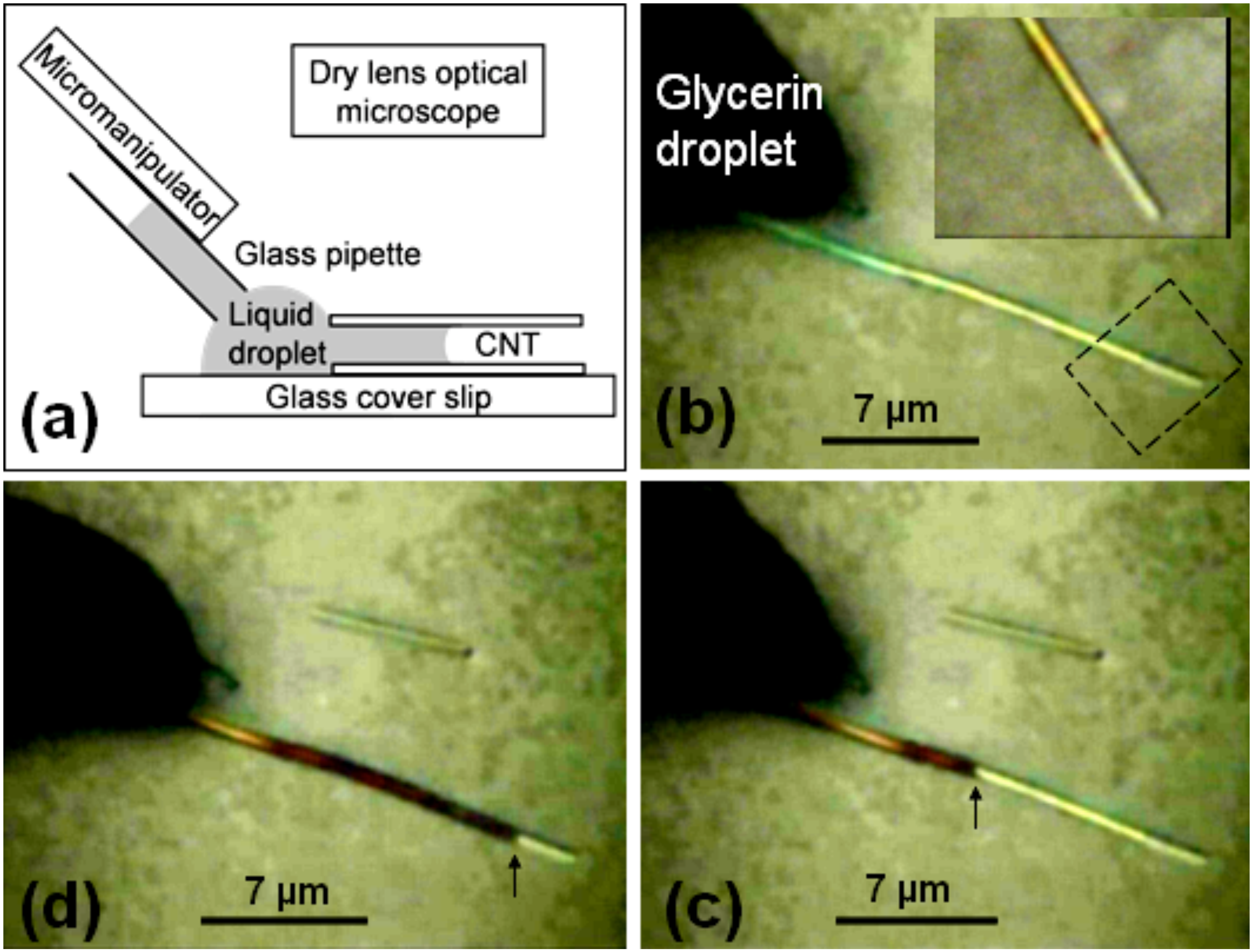
Current



Potential

Nominal Resistance (at zero current): 280 kOhm

NANOTUBE FILLING BY CAPILLARY ACTION



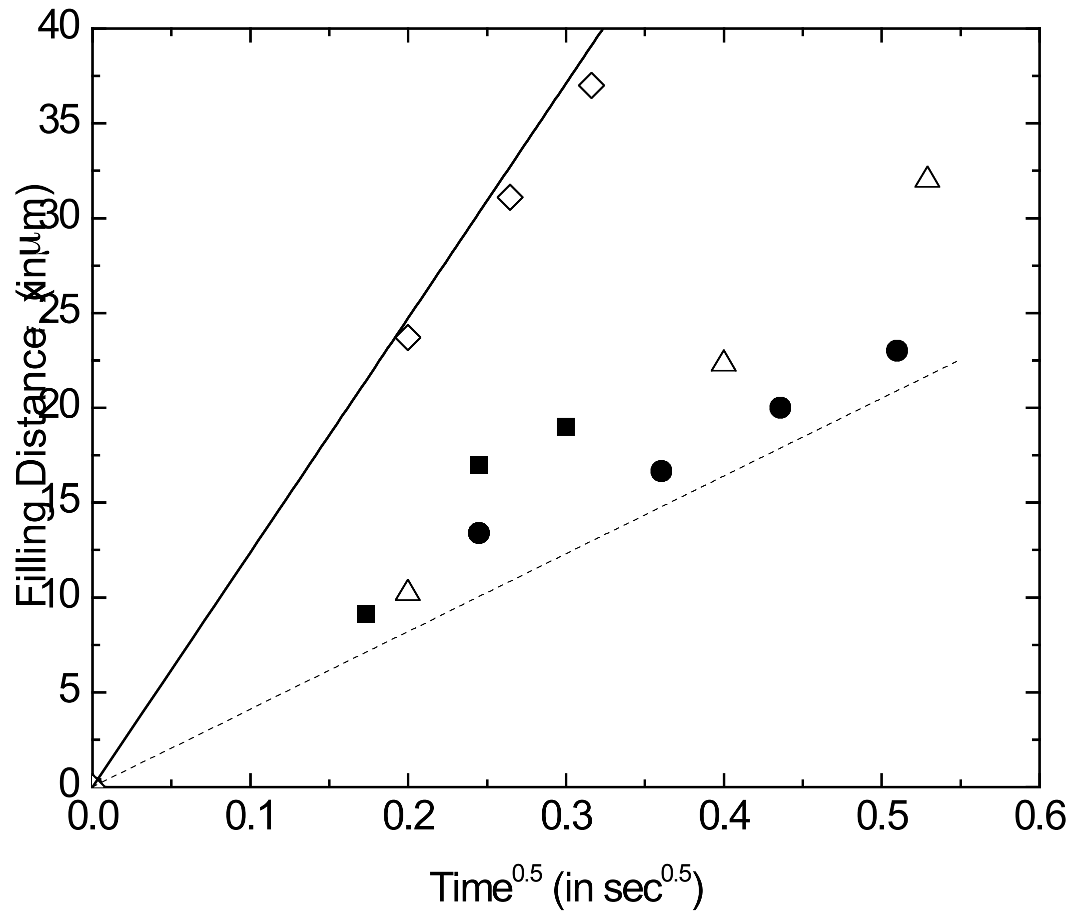
Kim B., M., Sinha, S., and Bau, H., H., 2004, Optical Microscope Study of Liquid Transport in Carbon Nanotubes, <u>Nano Letters</u> *4* (11), 2203 – 2208

Capillary filling of CNT with glycerin

Washburn equation :

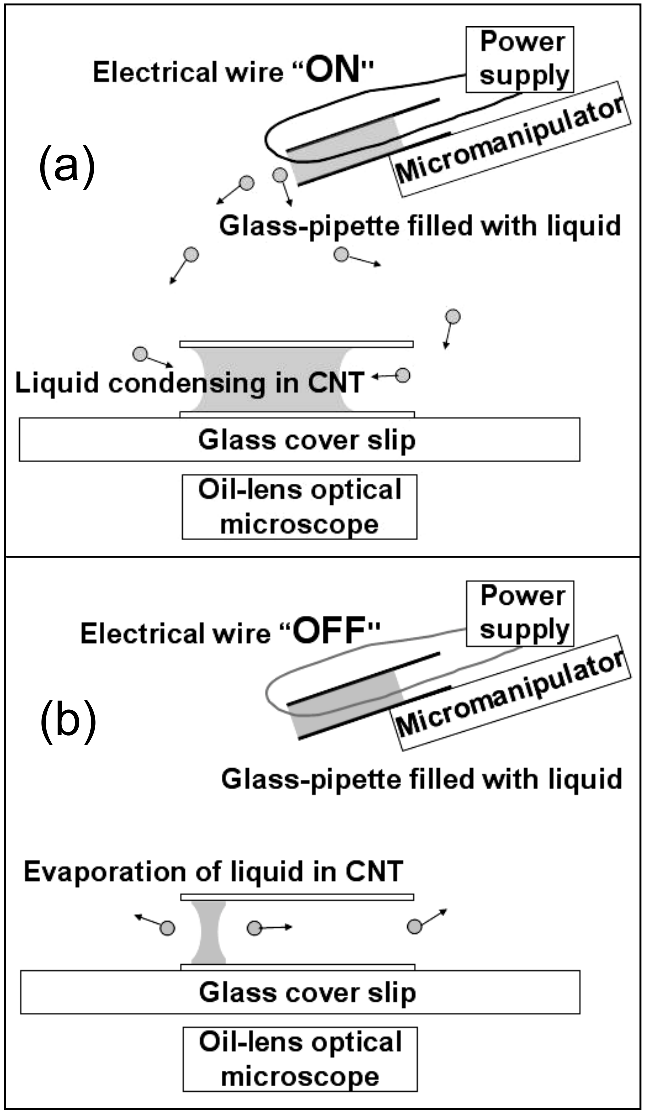
$$x(t) = At^{0.5}$$

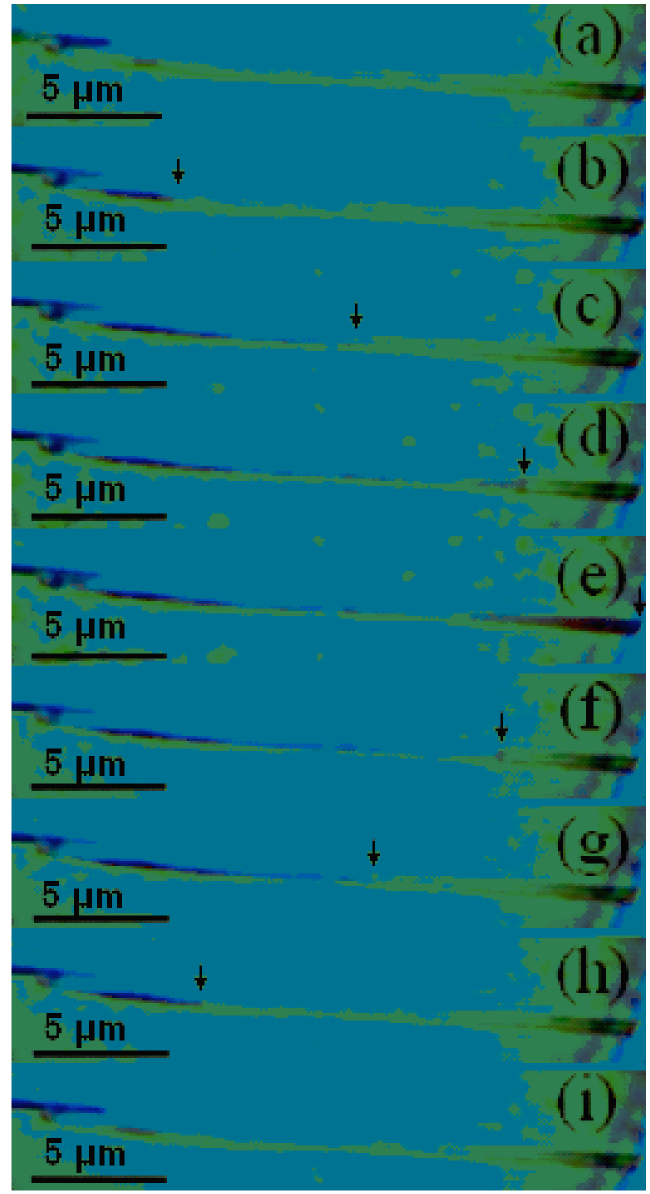
$$A = \sqrt{\left(\frac{\sigma R \cos\theta}{2\mu}\right)}$$



The distance of a 96% glycerin- air interface (μm) from the tube's inlet as a function of the square root of time (s) when the tube's length is 19 (solid squares), 23 (solid circles) 32 (upright triangles), and 37 (diamonds) μm. The solid line corresponds to theoretical predictions for a tube diameter of 500nm and a contact angle of 70^{o}. The dashed line corresponds to a tube diameter of 700nm and a contact angle of 30^{o}.

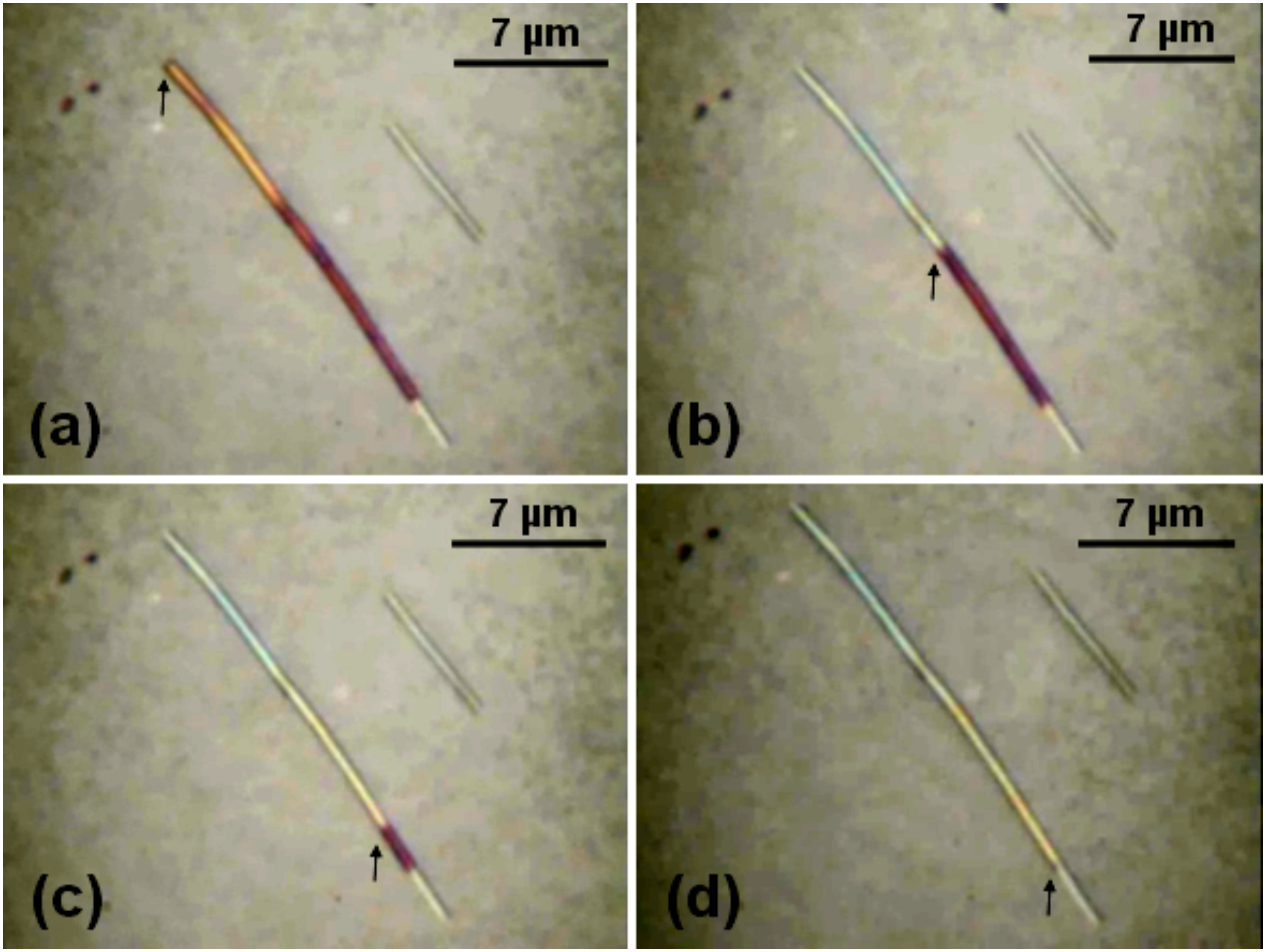
NANOTUBE FILLING/EMPTYING BY CONDENSATION/EVAPORATION





Condensation of ethylene glycol in a CNT

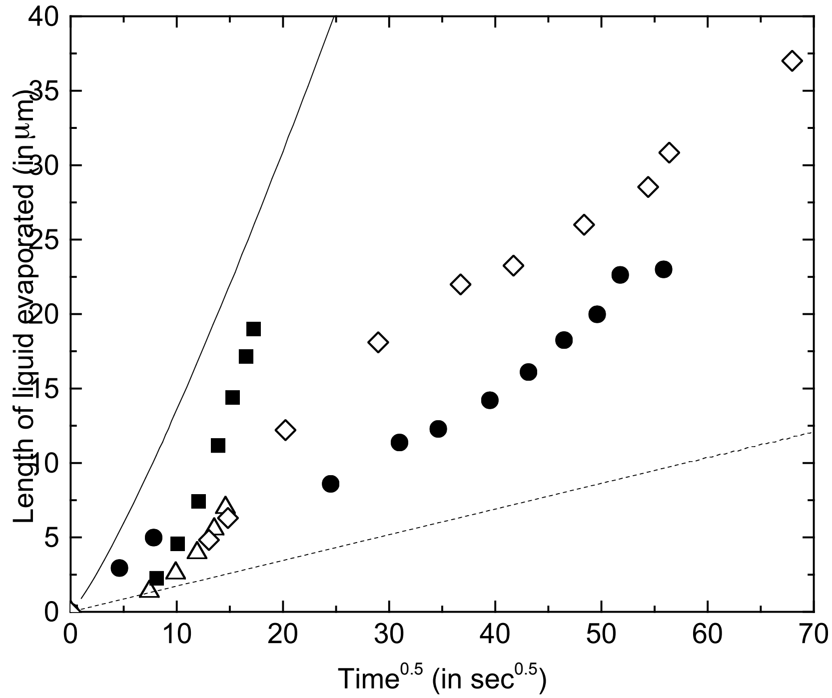
EVAPORATION FROM A NANOTUBE



THE RATE OF EVAPORATION OF A LIQUID IN A NANOTUBE

$$\Delta L_{total} = \frac{4\rho_{sat}}{\rho_{liq}}\sqrt{\frac{Dt}{\pi}}$$

$$\Delta L_{total} = \frac{\rho_{sat}}{\rho_{liq}}\left(\frac{5}{3}R^{\frac{2}{5}}\left(\frac{D\ t}{R}\right)^{\frac{3}{5}} + 2\sqrt{\frac{D\ t}{\pi}}\right)$$



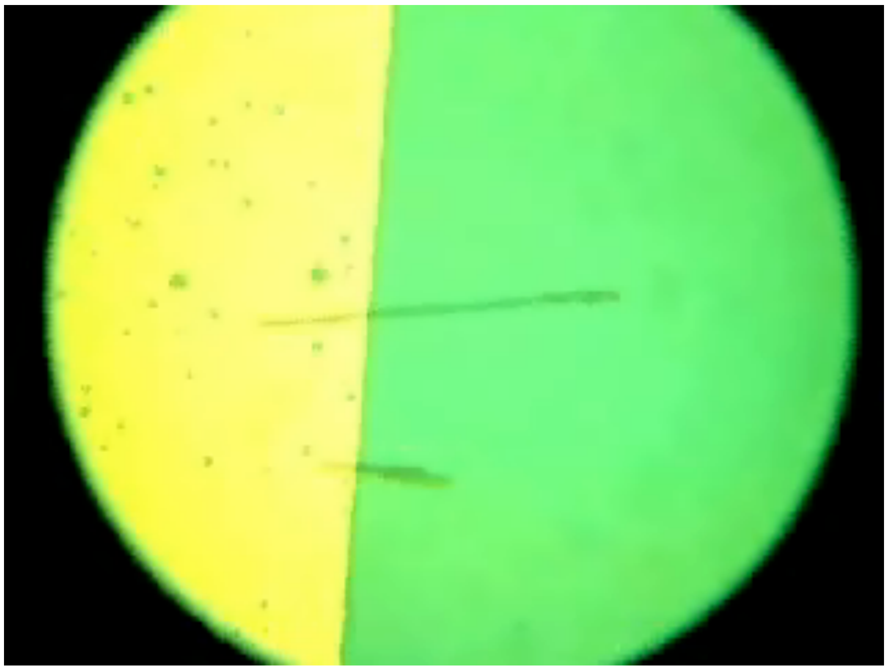
The difference between the original length of the glycerin slug at time t=0 and the slug's length at time t as a function of the square root of time ($t^{0.5}$) when the tube's length is 7 (upright triangles), 19 (solid squares), 23 (solid circles), and 37 µm (diamonds). The symbols and lines represent, respectively, experiments and theoretical predictions (tube diameter: 600nm). The dashed and solid lines correspond, respectively, to a slug located away from the tube's ends and a slug pinned to one of the tube's ends.

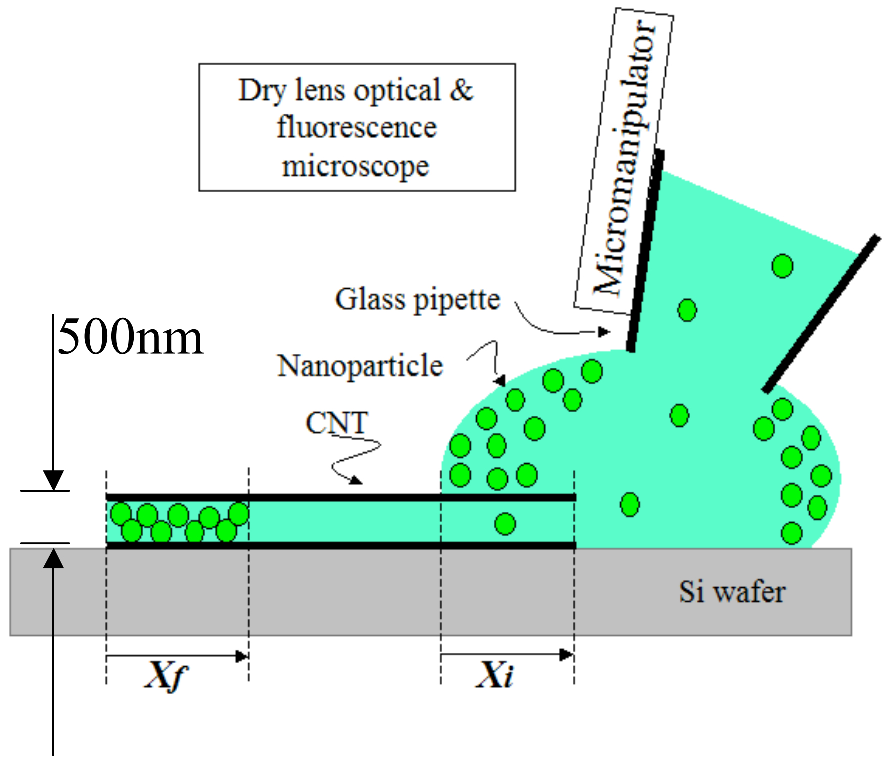
Evaporation of ethylene glycol slug contained in a CNT

Filling a Nanotube with Particles

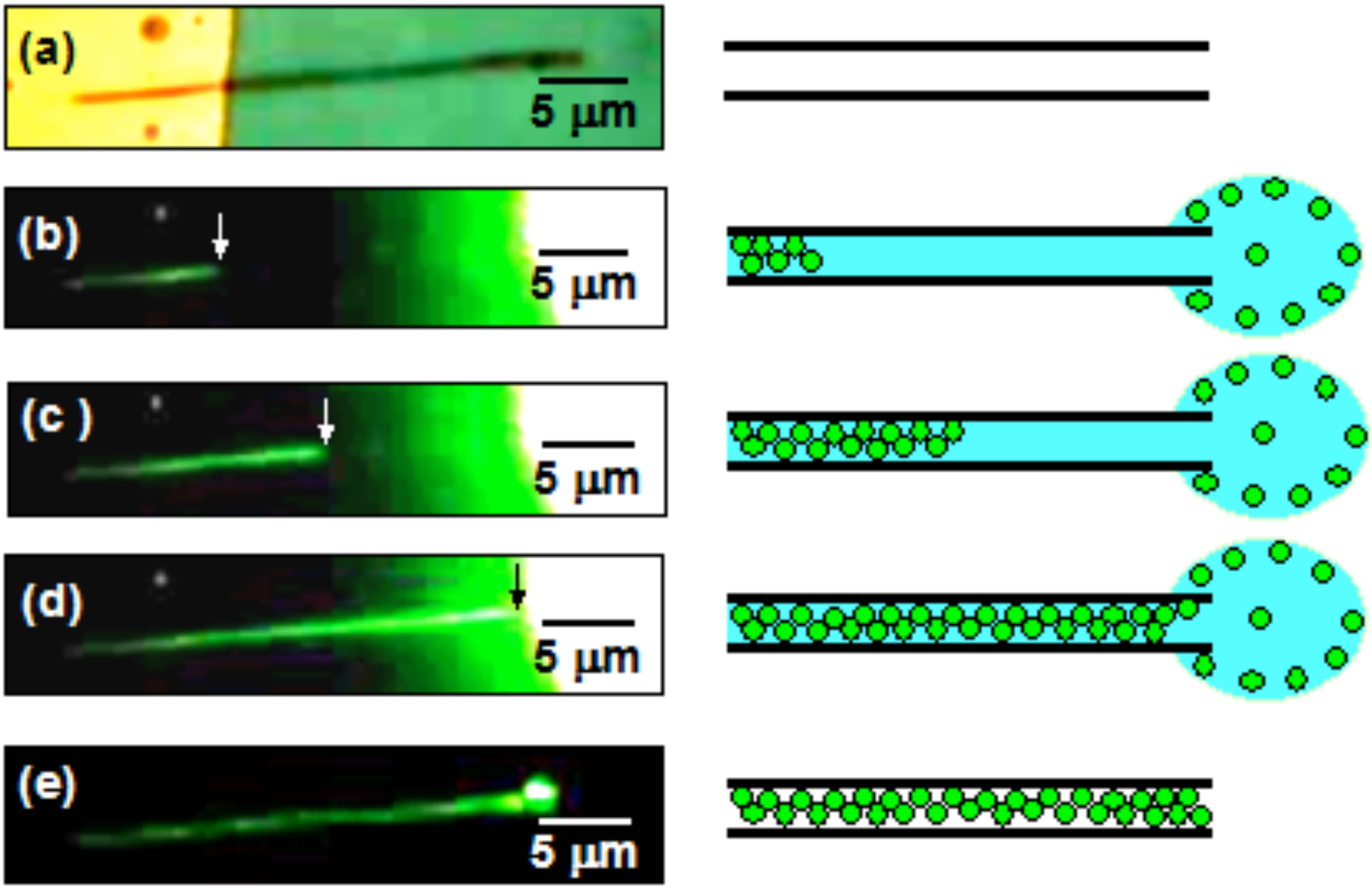
Carbon Nanotube Diameter: 500nm

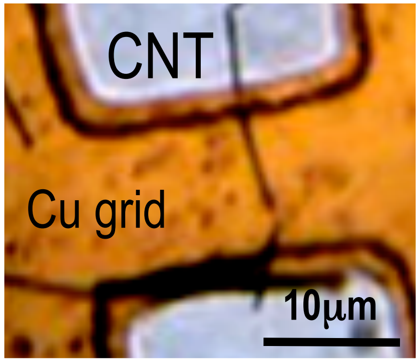
Particles ~40nm, Fluorescent Polystyrene

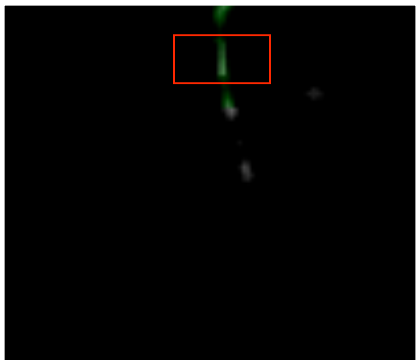


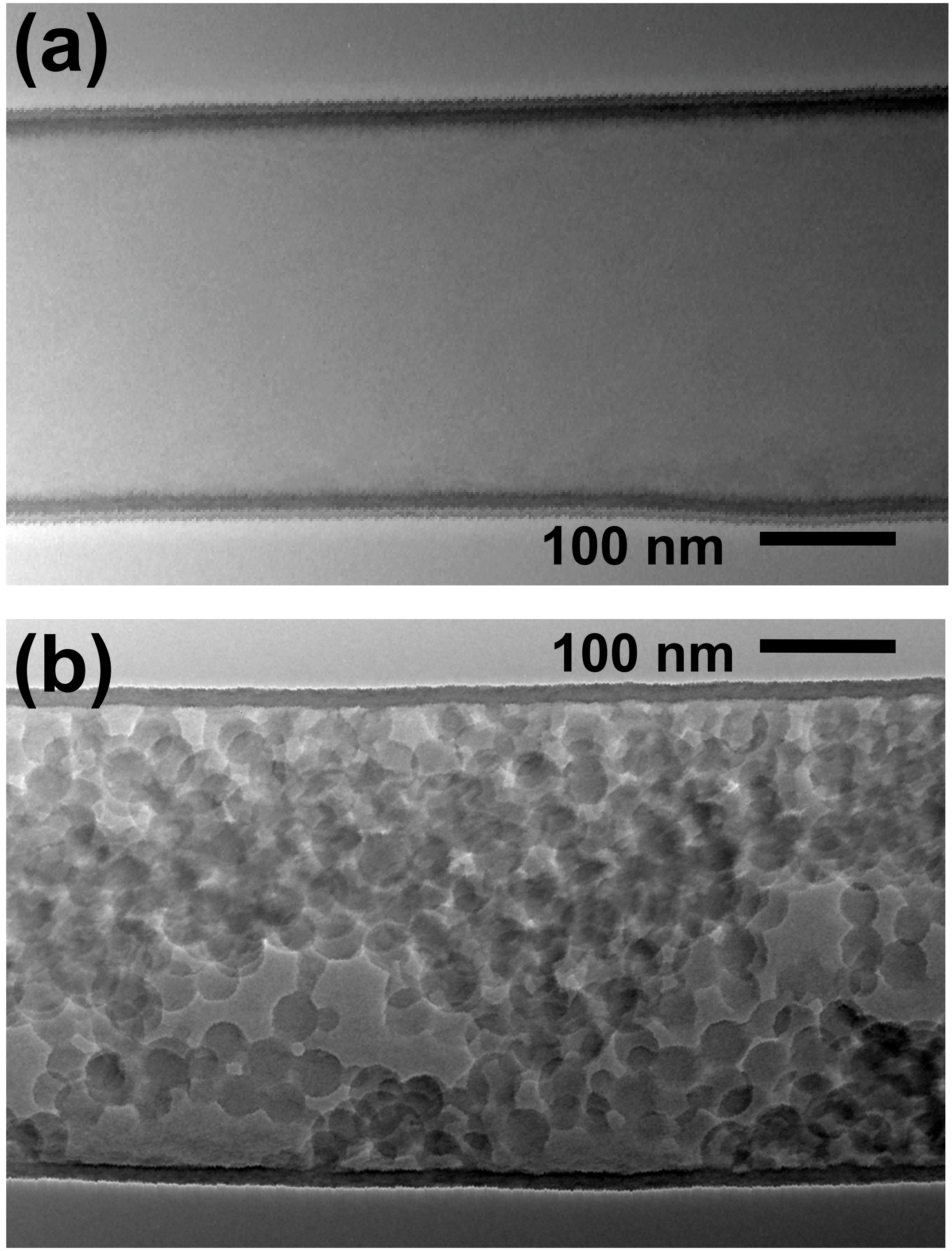


Kim, B. M., Qian, S., and Bau, H., H., 2005, Filling Carbon Nanotubes with Particles accepted for publication in Nano Letters. DOI: 10.1021/nl050278v


(a)
5 µm
(b)
5 µm
(c)
5 µm
(d)
5 µm
(e)
5 µm



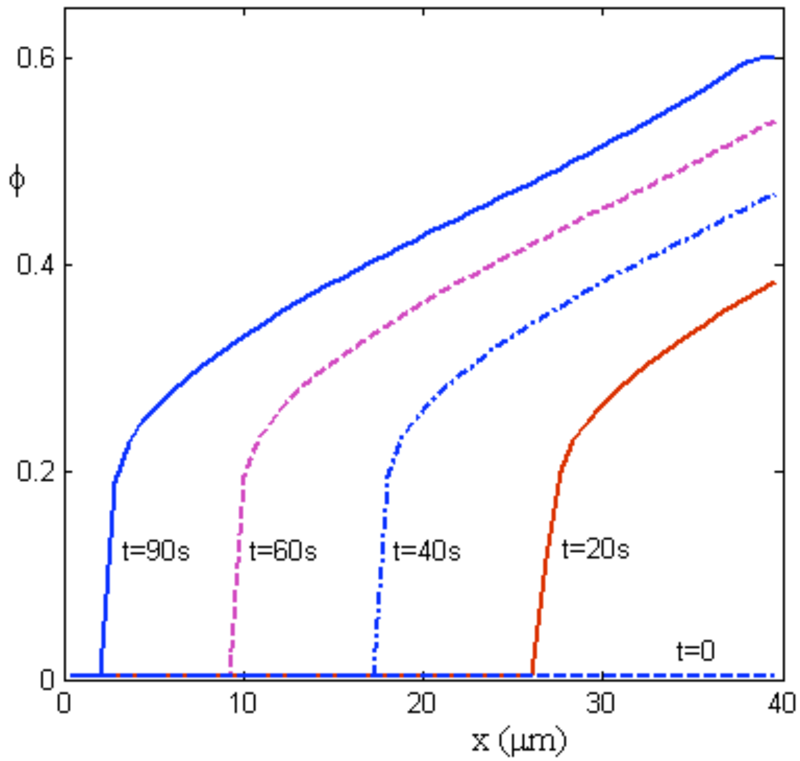




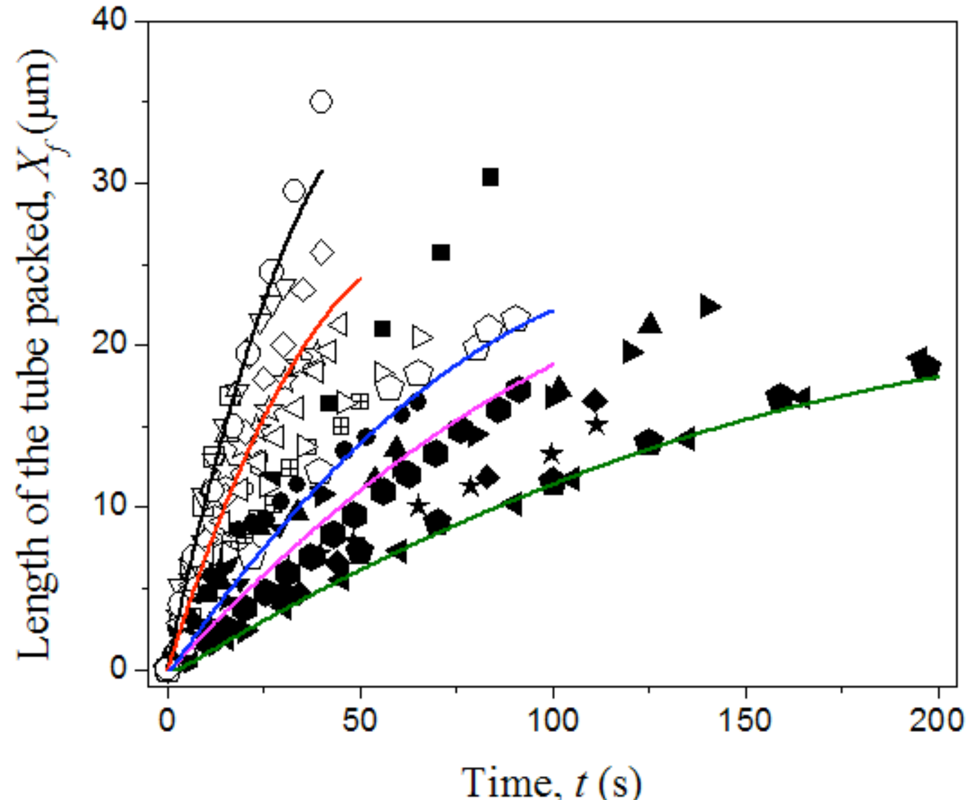
TEM Observations

(a) Empty tube

(b) A tube filled with particles



Particle volume fraction as a function of distance from the tube's inlet at various times



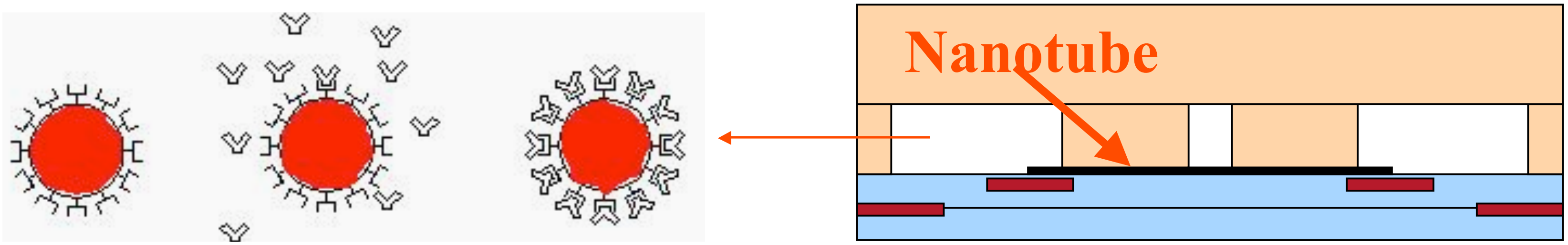
Fluorescing length as a function of time for various inlet particle volume fractions

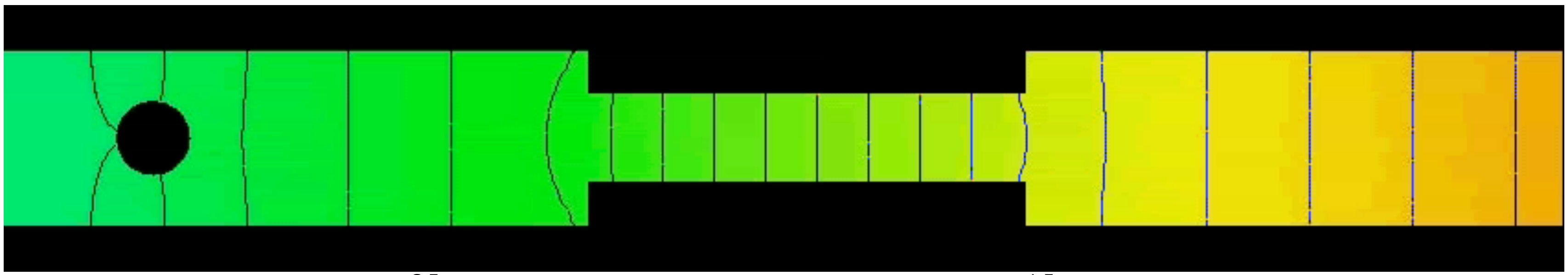
Theoretical predictions based on multi-phase modeling are compared with experimental observations

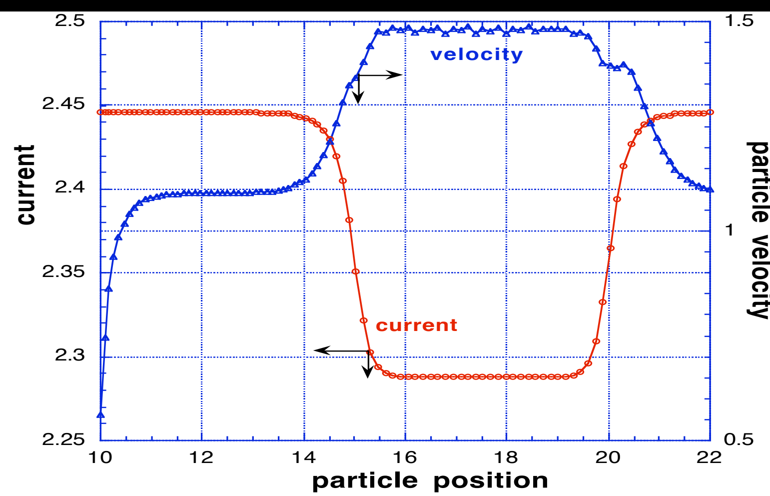
$$\frac{\partial \phi}{\partial t} + \nabla \cdot (\phi\, \mathbf{q}) = \frac{\partial}{\partial x}\left(A(\phi) \frac{\partial \phi}{\partial x} \right)$$

$$A(\phi) = \frac{\phi(1-\phi)^2}{\alpha(\phi)} \frac{d\sigma_e(\phi)}{d\phi}$$

IONIC CURRENT MEASUREMENTS

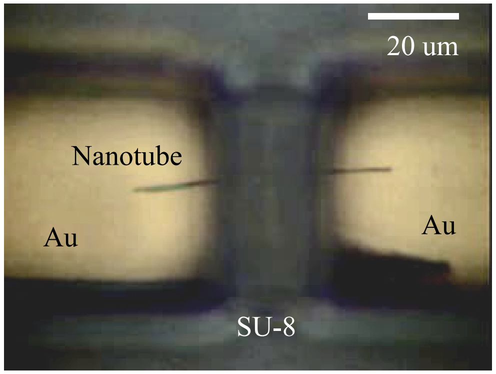


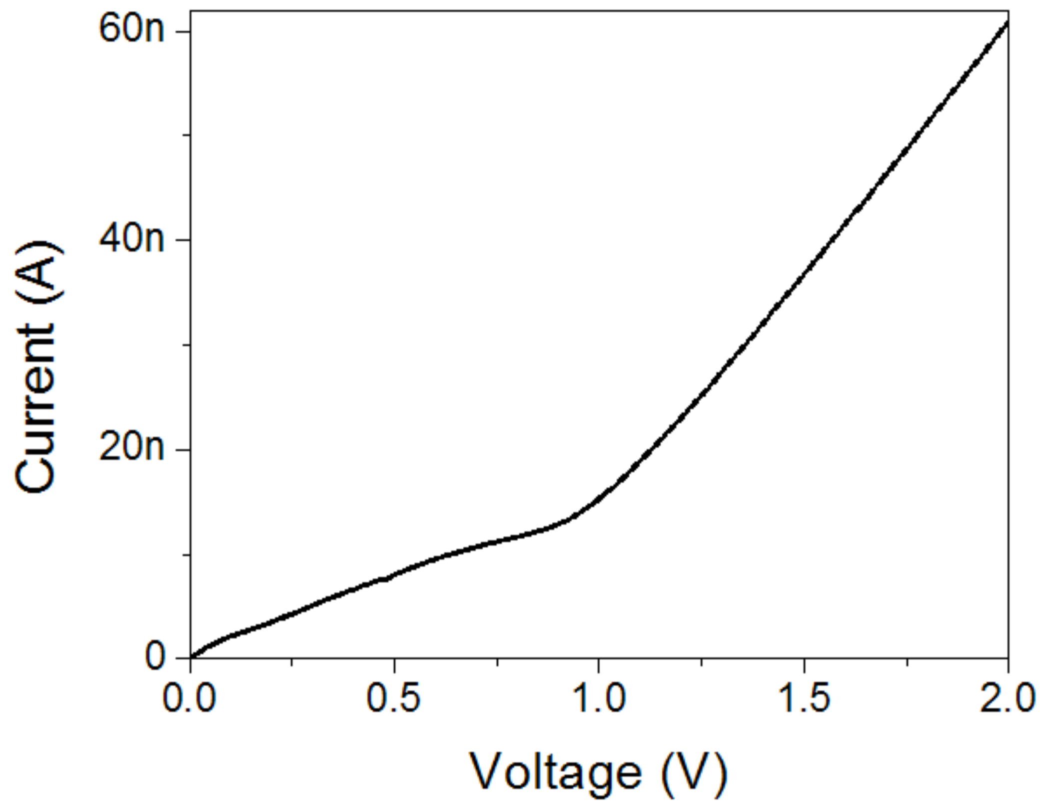




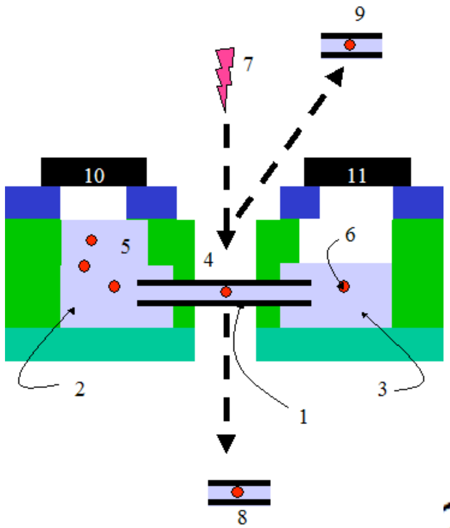
Numerical simulation courtesy of Professor Howard Hu

IONIC CURRENT MEASUREMENT

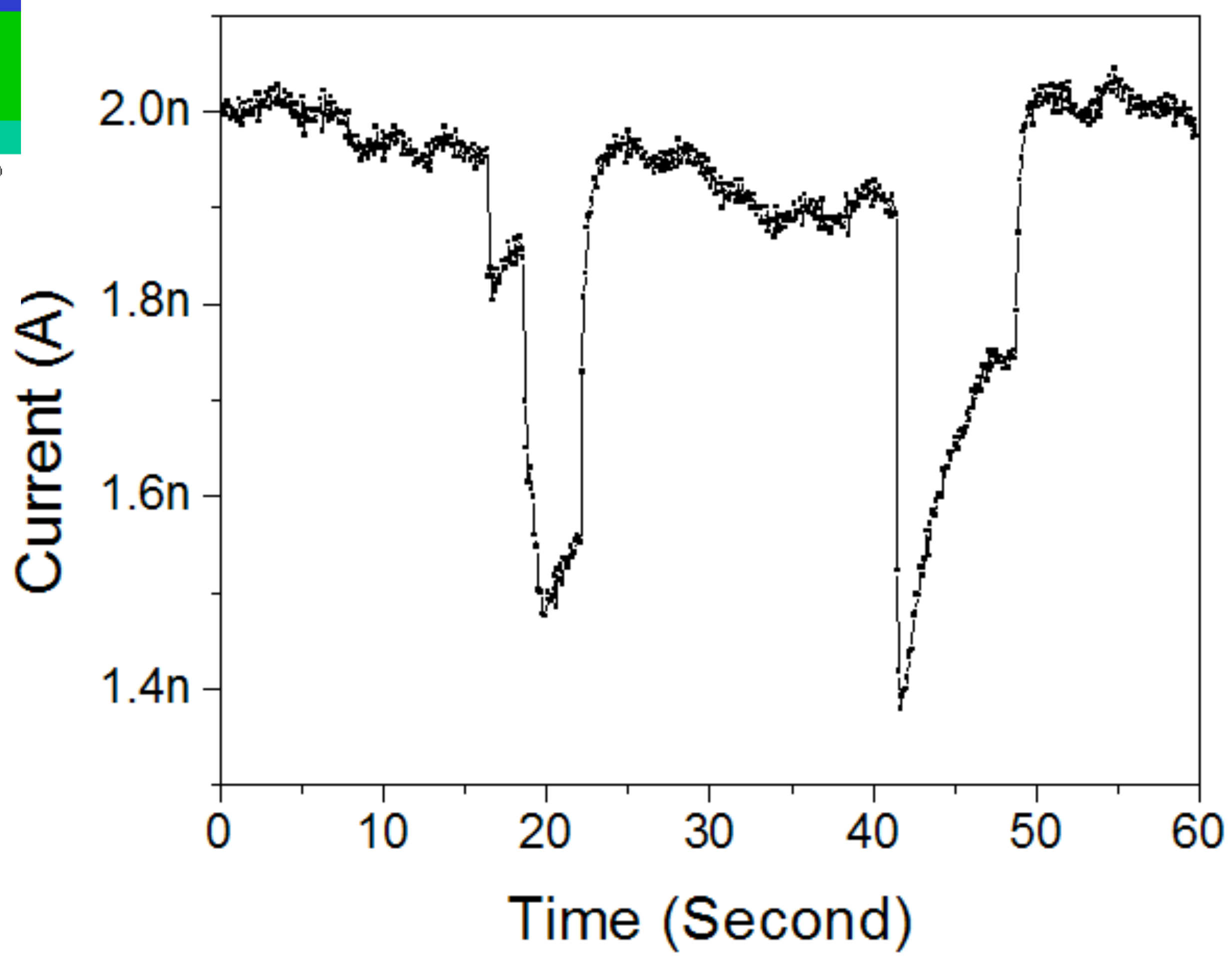




Current as a Function of Potential. 0.1M KCl solution



PARTICLE TRANSLOCATION



Electric Current as a Function of Time. Tube ~500nm diameter, Particles ~100-200nm. 0.1M KCl solution

CONCLUSIONS

Liquids and particles can be readily transmitted through carbon nanotubes

The liquid and particle transport can be monitored with optical and fluorescent microscopy (when the tube is sufficiently large) and with electron microscopy

Electron microscope observations are in qualitative agreement with optical microscope observations

Electron microscopy – a new paradigm in fluid physics measurements