Nanotechnology Applications for Environmental Sensors: *Integrated Devices for Real-Time Analyses*

NJ Tao

Arizona State University

ASU ARIZONA STATE UNIVERSITY

Need of Environmental Sensors

The Washington Post

WEDNESDAY, FE

High Lead Levels Found in Water At 9 D.C. Schools

Untested Fo

By Justin Blum
Washington Post Staff Wri

Recent testing at 15
lic school buildings fou
ter samples at sever
taken from either a sin
ing fountain—had hig
lead, officials said yeste

In addition, the Arc
Washington reported e
els of lead in water fro
fountains at two of its 2

BY JAMES A. PARCELL—THE WASHINGTON POST

WASA official Jodye Levy Russell takes a water sample from a faucet at Leckie Elementary in Southwest during a testing demonstration earlier this month.

District to Issue Warning on Lead

Health Advisory on Water to Target Pregnant Women, Small Children

Youngsters, Fetuses Are Most Vulnerable

Studies Find IQ, Socialization Problems

By Avram Goldstein
Washington Post Staff Writer

City health officials who plan to issue an alert about lead in tap water are most concerned about children younger than 6 and fetuses—those most susceptible to permanent damage from lead poisoning.

Rapidly growing bodies and unborn children are far more likely to absorb lead that has been swallowed or inhaled, and it poses a grave threat to their long-term health and well-being, experts say.

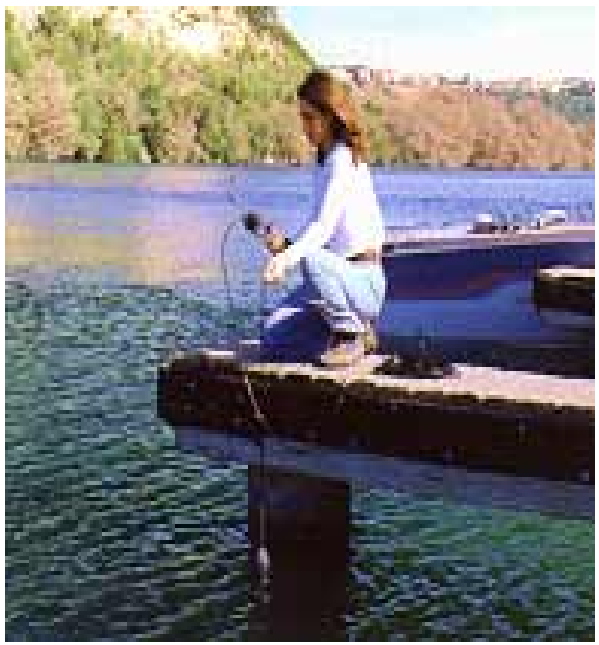
Children who ingest lead—usually in the form of dust from deteriorating lead-based paint or

juvenile delinquency. Lead is a serious social problem as well as a drag on our educational system."

Lead tricks brain cells into absorbing lead when they seek calcium, the most abundant mineral in the human body and one that is necessary to enable thoughts to form. Calcium is critical to cardiac health, the development of bones and teeth and other functions.

The CDC estimates that each year more than 400,000 children in the United States have lead in their blood at levels that exceed the national standard, which is 10 micrograms of lead per deciliter of blood. A deciliter is about

Water Quality Monitoring



Current
Manual test

Near Term
Wireless system
With single probe

Future
Wireless system with
PWB array probes

Air Quality Monitoring

Current

Only select personnel (Hazmat) typically carry portable equipment

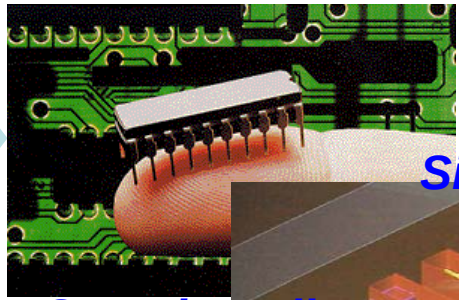
Near Term

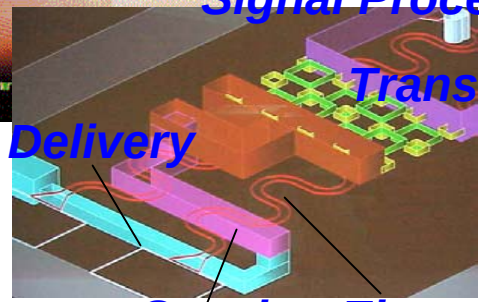
Provide wireless connectivity of portable equipment to communicate to incident commander

Future

Essential monitoring is integrated into communications equipment

Need: Miniaturization & Integration





Signal Processing & Transmission

Sample Delivery

Sensing Element Array

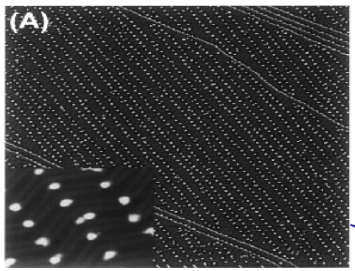
An Integrated Sensor

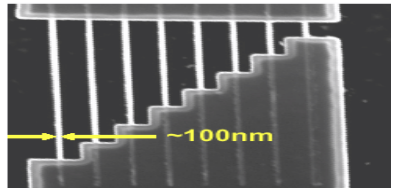
- **Sample Delivery**
- **Sensing Elements**
- **Signal Processing & Transmission**

This will happen no matter what !!!

What role will ‘NANO’ play?

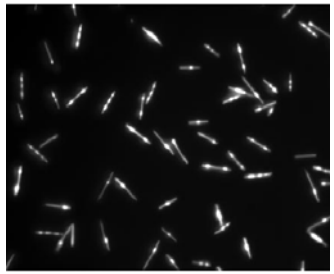
NANO-Solution ?



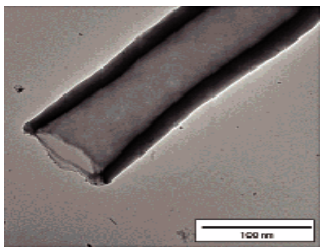


Resonator

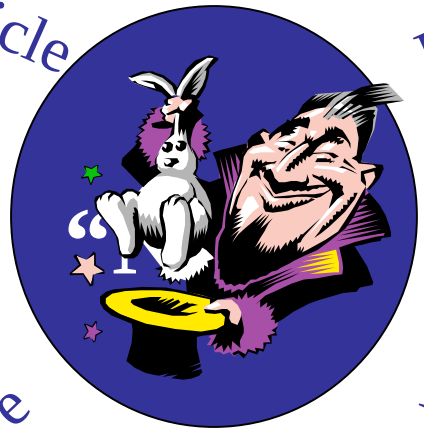
Particle



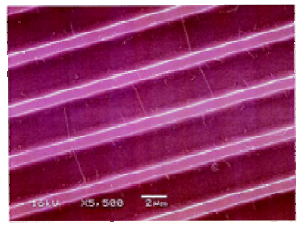
Rod

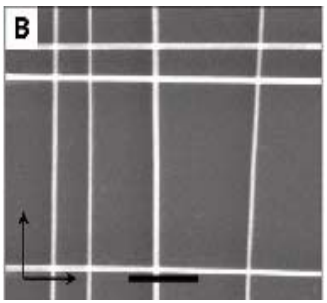


Peptide
Tube



Carbon
Tube

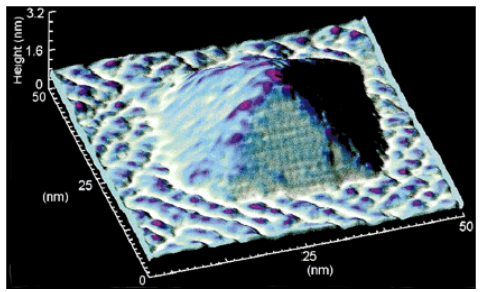


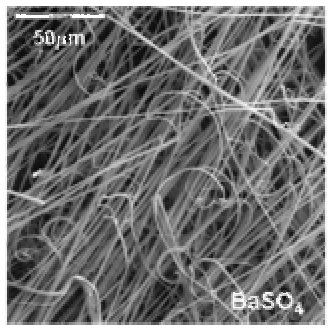


Wire

Belt

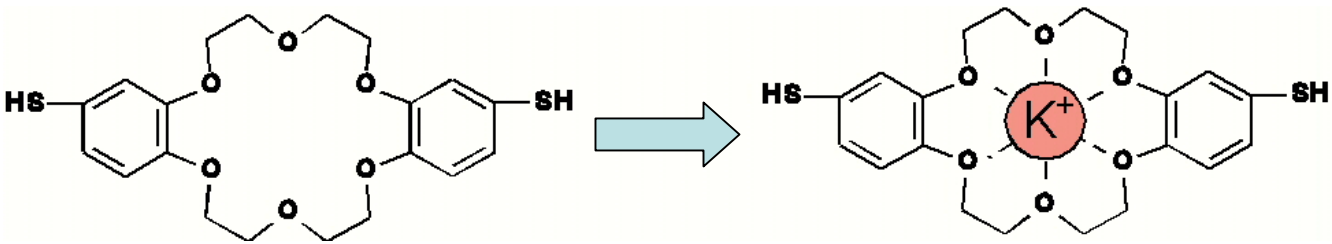
Pyramid





Signal Transduction

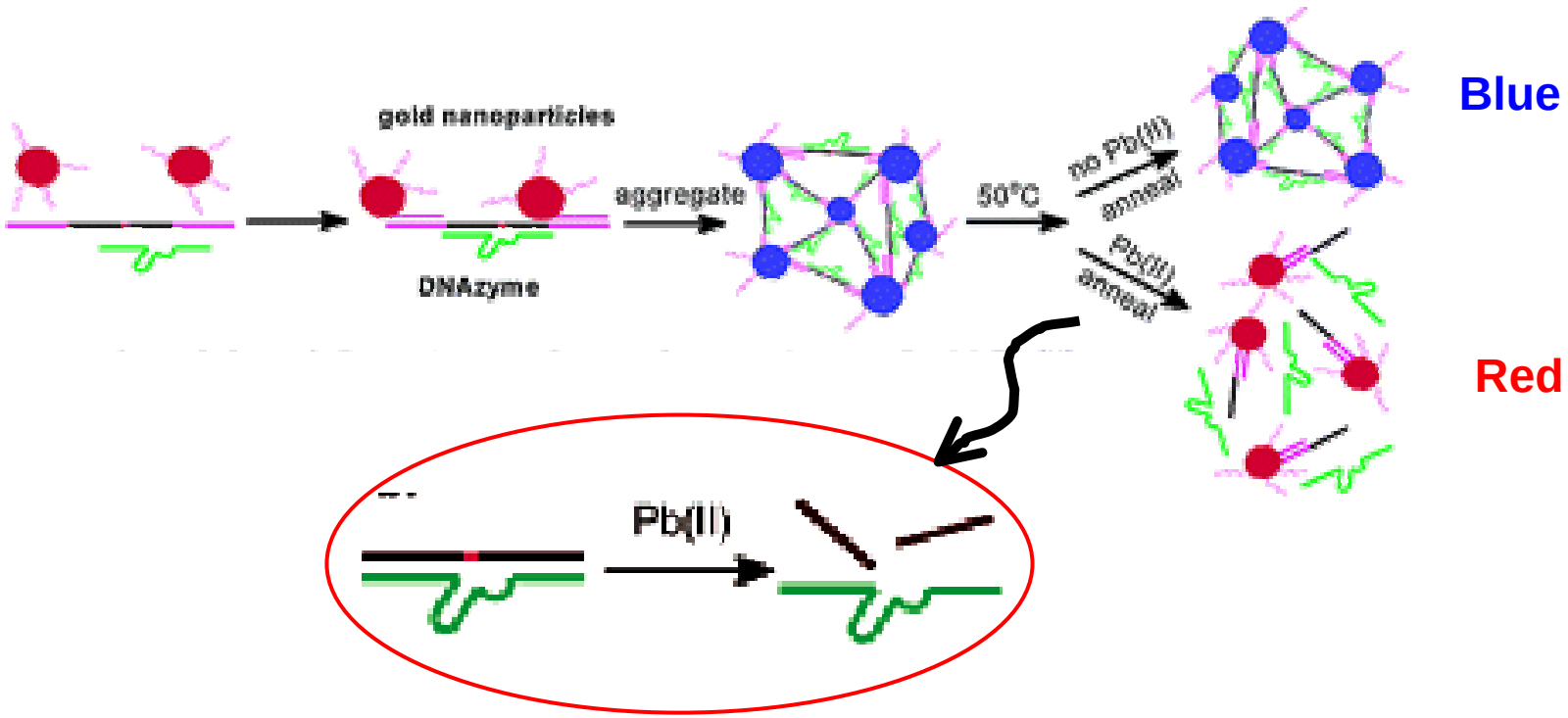
- Convert a Chemical Binding Event into a Readable Signal



- Optical (Trogler/Gawley/Lavine/Anderson)
- Electrochemical (Wang/Sadik/…)
- Mechanical (Shih/…)
- Electrical (Kan/Mitra/Subramanian/Tao)

Optical Detection - Nanoparticles

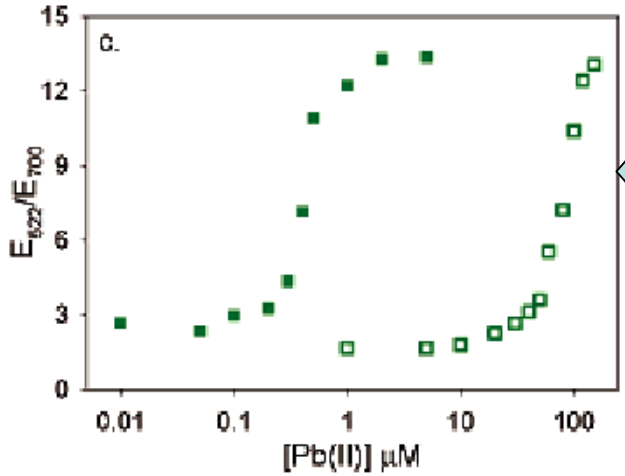
Metal Ion Colorimetric Sensor



Yi Lu, JACS, 2003

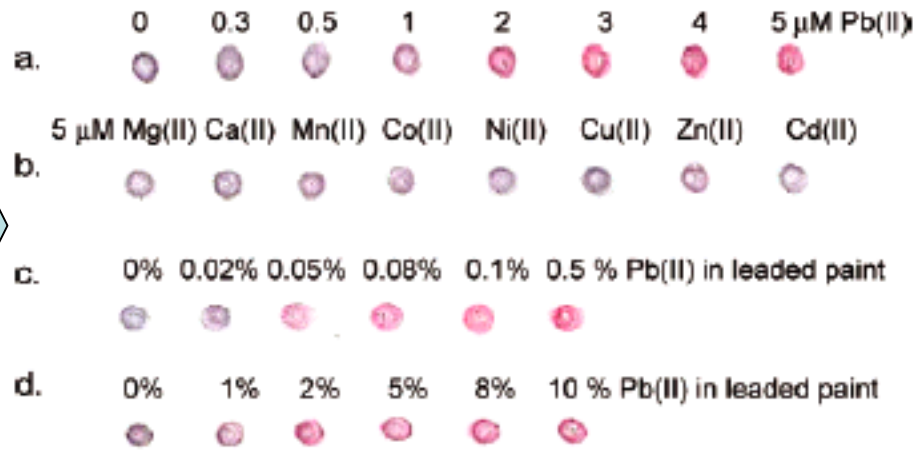
Optical Detection- Nanoparticles

Metal Ion Colorimetric Sensor



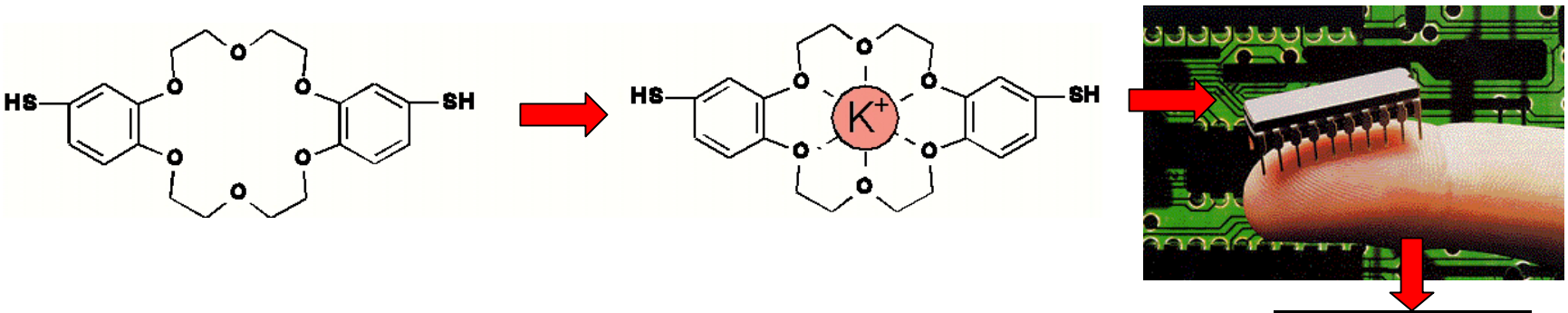
Adjustable Dynamic Range. When the enzyme strand is the active 17E only, the Pb(II) detection range is 0.1-4 μM (solid green squares). When the ratio of 17E and 17Ec is 1:20, the Pb(II) detection range is 10-200 μM (open green squares).

The color of the sensor developed on an alumina TLC plate with different metal ions and Pb(II) concentrations.



You just look at it !

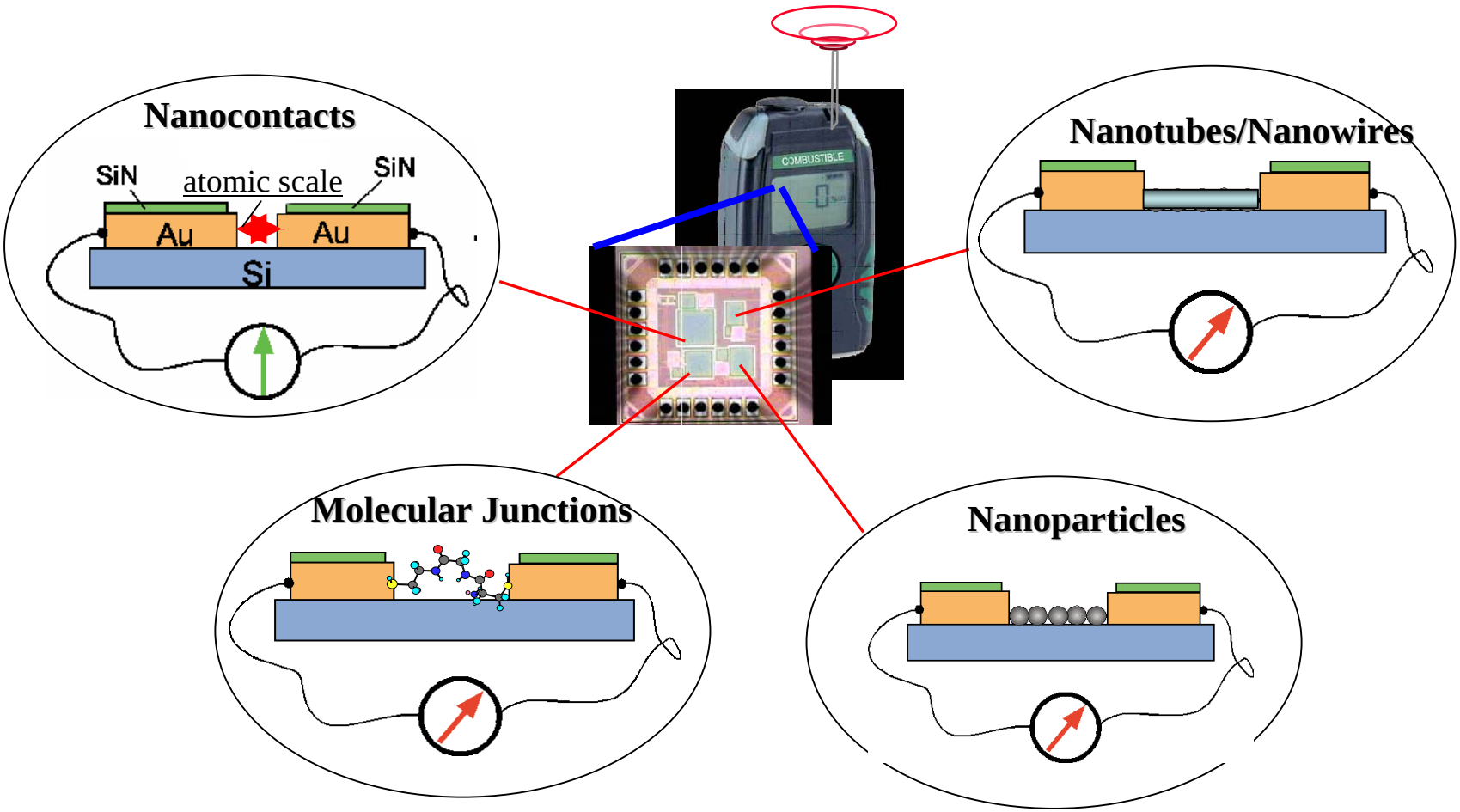
Electrical Detection – Reading chemical information electronically



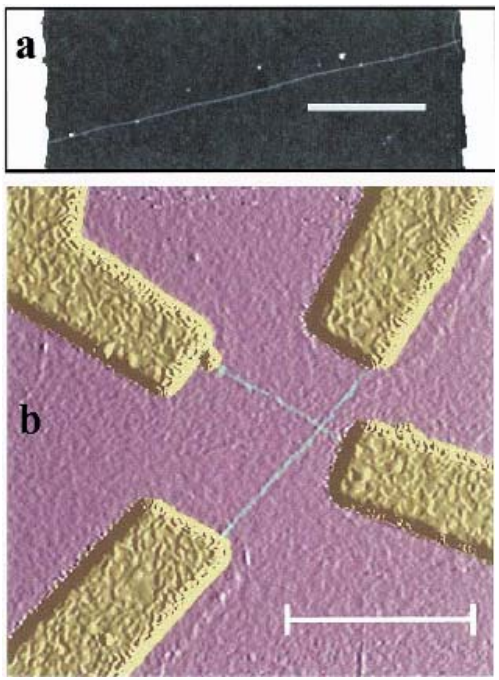
- Easy to process/display/transmit the data
  – needed for a fully automated device
- High degree of integration - for a miniaturized device for simultaneous detection of different species
- Compatible with microelectronics
  – taking advantage of existing microtechnology

Arrays of Electrically Wired Nanosensing Elements

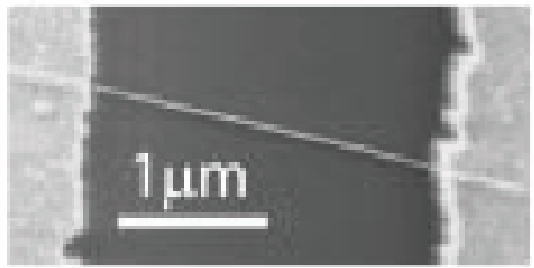
- An integrated sensor that can detect different species



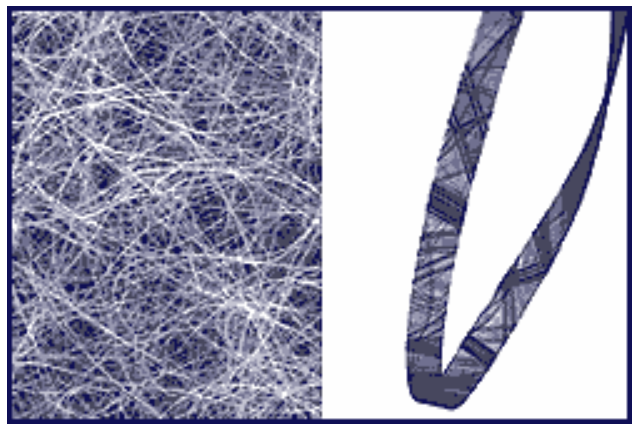
Nanotubes/wires/belts Sensors



Nanotubes

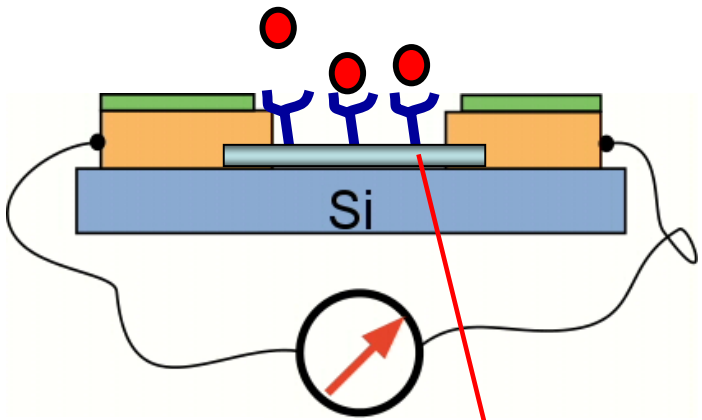


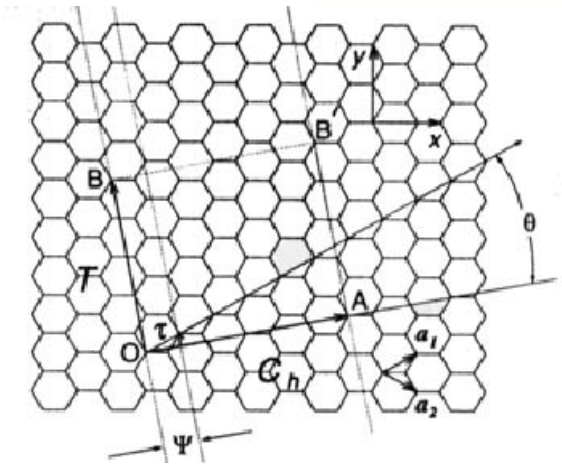
Nanowires

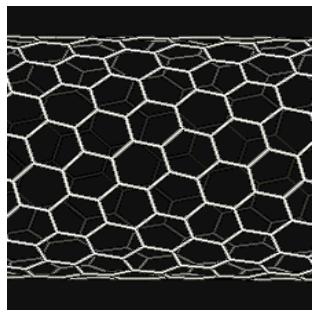


Nanobelts

Carbon Nanotube FET Sensors





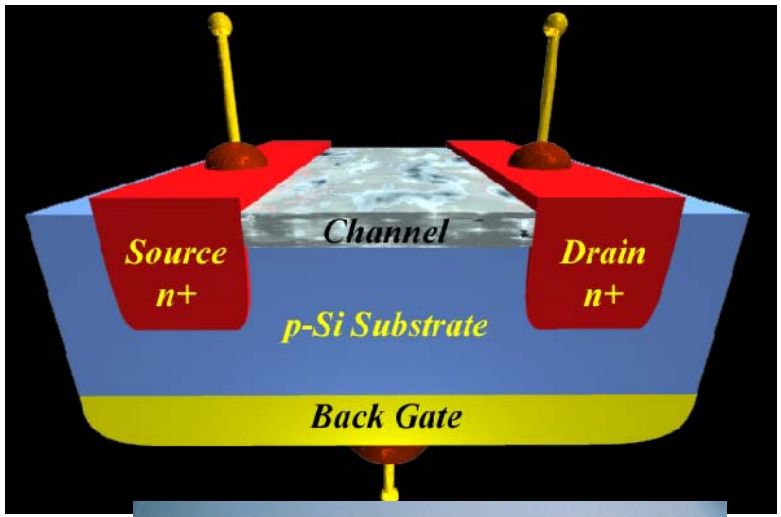


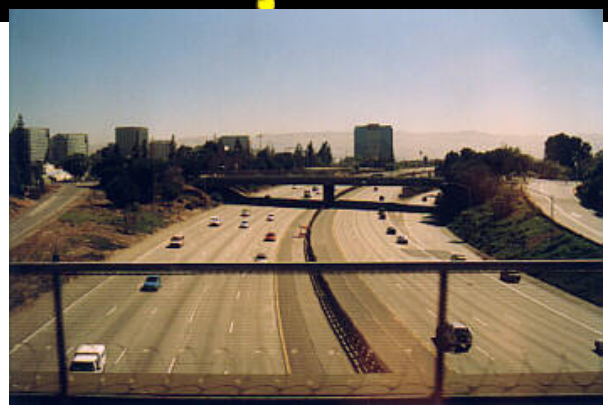
•Kong, J.; et al. *Science* **2000,** *287*, 622.

•Zhou, C.; Kong, J.; Dai, H. *Appl. Phys. Lett.* **2000,** *76*, 1597.

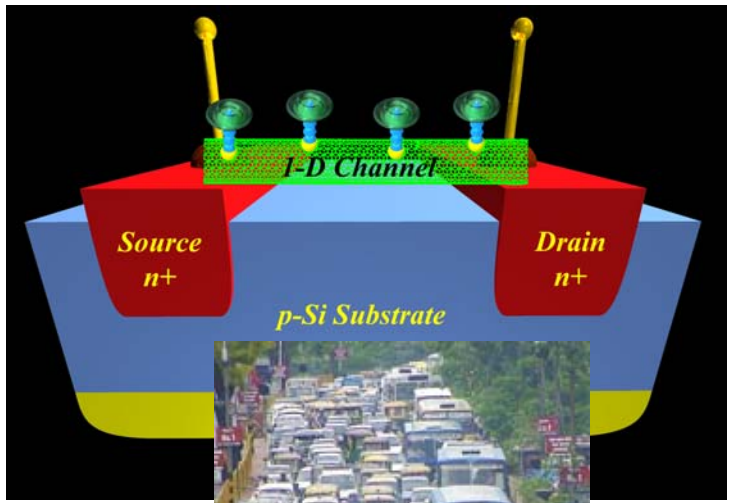
•Collins, P. G.; Bradley, K.; Ishigami, M.; Zettl, A. *Science* **2000,** *287*, 1801.

The Principle





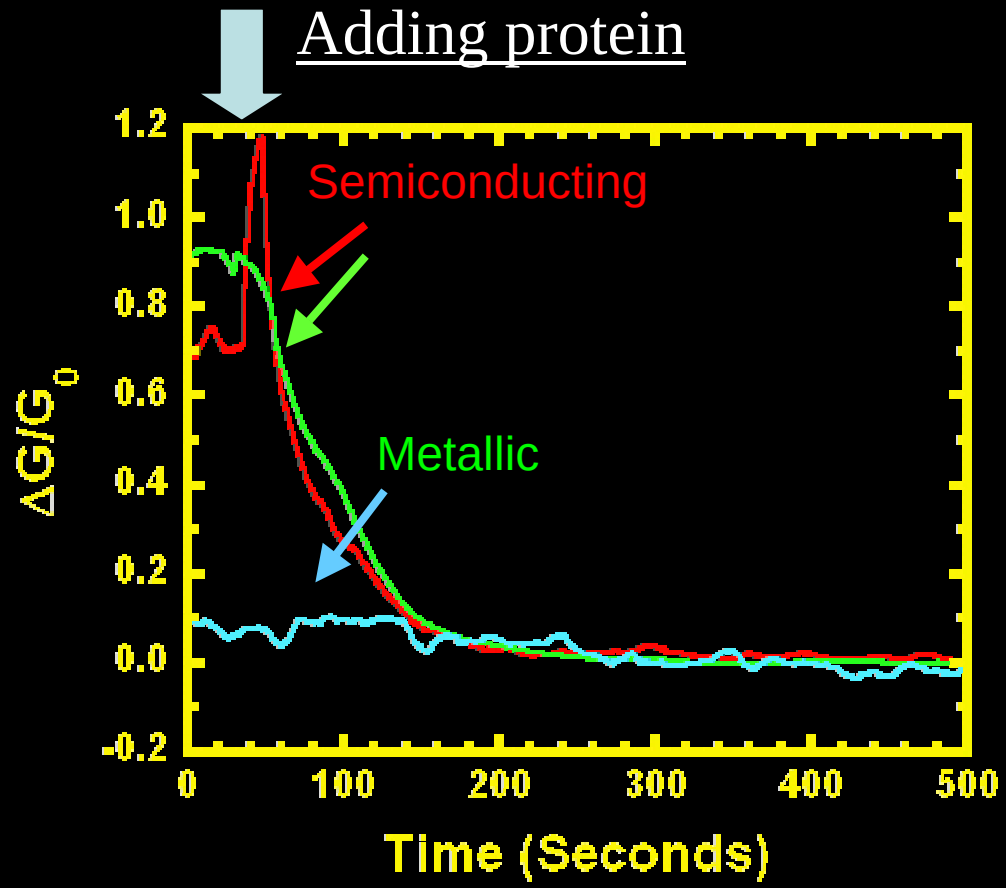
In a conventional FET, conduction through the channel region is two dimensional (i.e., many pathways).



Narrowing the channel to one dimension, detection sensitivity is enhanced.

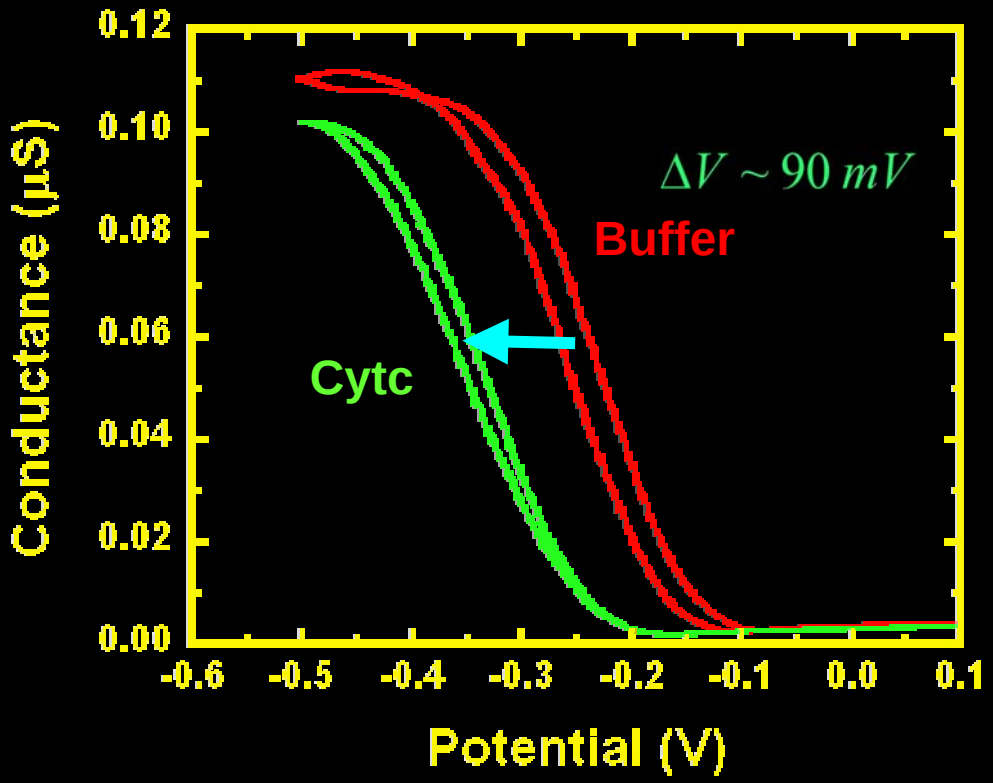
ChemFET (Kan/Mitra/Subramanian)

Protein Adsorption on p-SWNTs



Boussaad et al. Chem. Comm. 2003

Conductance vs. Electrochemical Gate Potential



$$\Delta Q = C\Delta V$$

$$C_{\mathrm{SWNT}} = 4x10^{-10}\ F/m$$

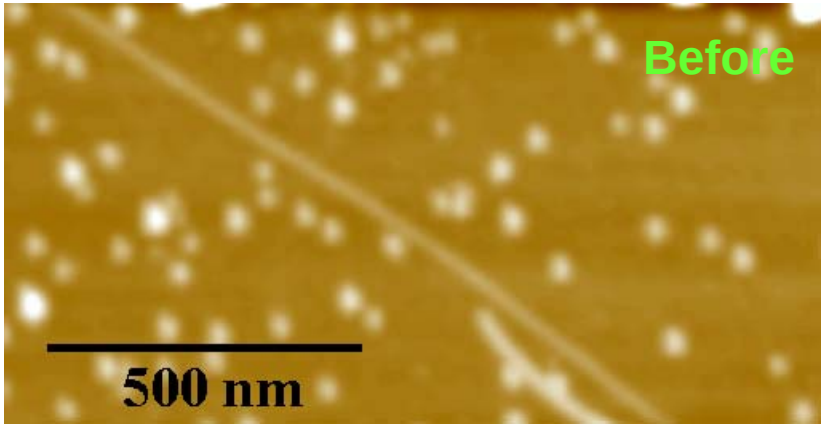
$$L_{\mathrm{SWNT}} = 1\ \mu m$$

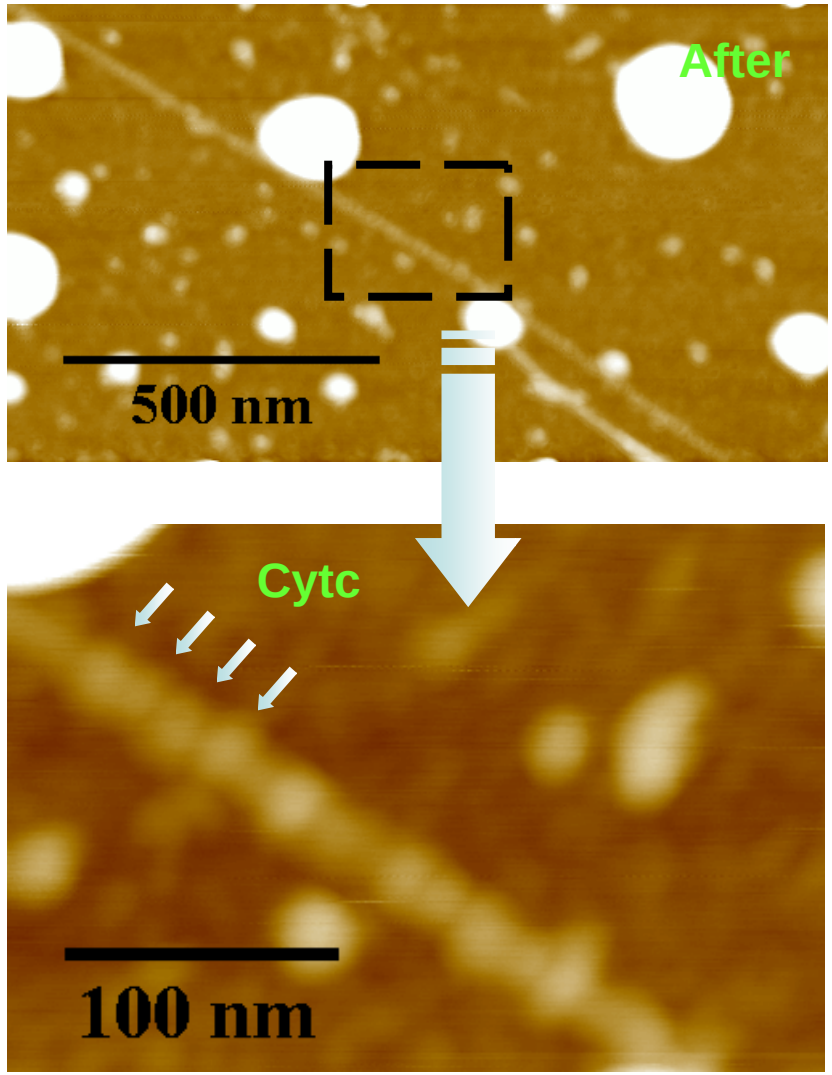
$$Cytc = +10\ e/\ protein @\ pH7$$

$$\#\,\mathrm{Cytc} = \frac{4x10^{-10}\,\mathrm{F/m\ x\ 10^{-6}\,m\ x\ 0.09\ V}}{10\ x\ 1.6x10^{-19}\,\mathrm{C}}$$

$$= \sim 20\ \mathrm{Cytc\ molecules}$$

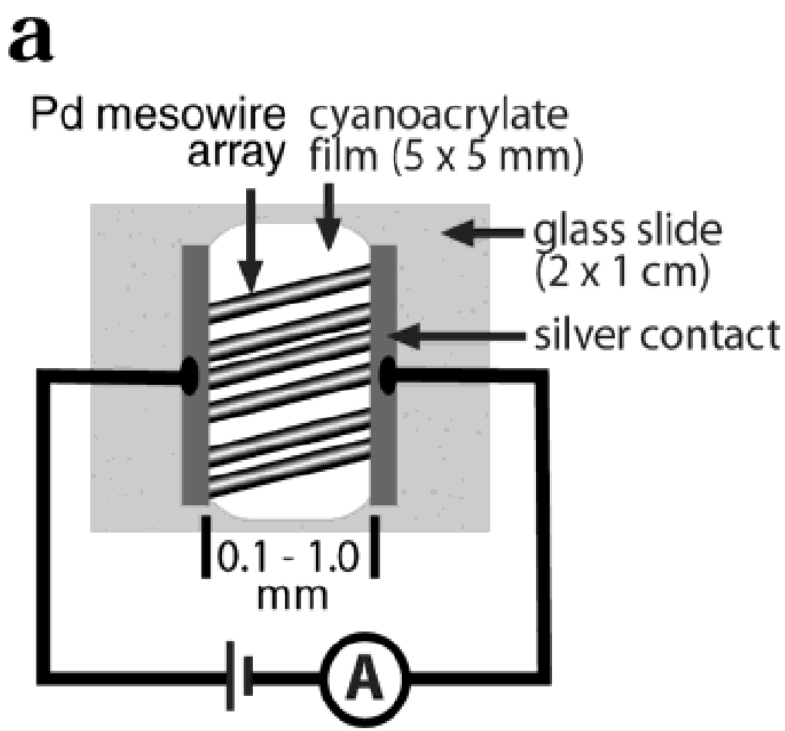
AFM Measurements

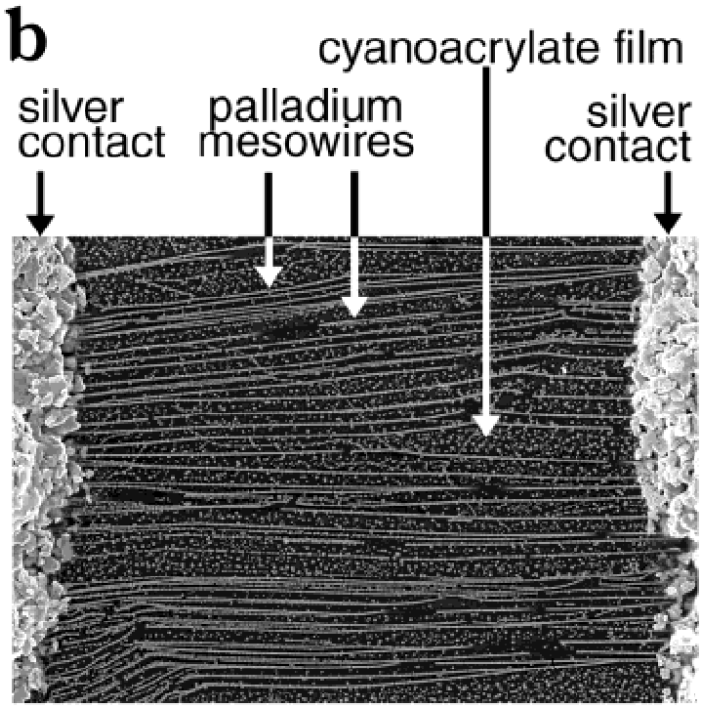




Based on the AFM images, the number of cytc molecule adsorbed onto the SWNT is ~30-40.

Pd Nanowire Hydrogen Sensor

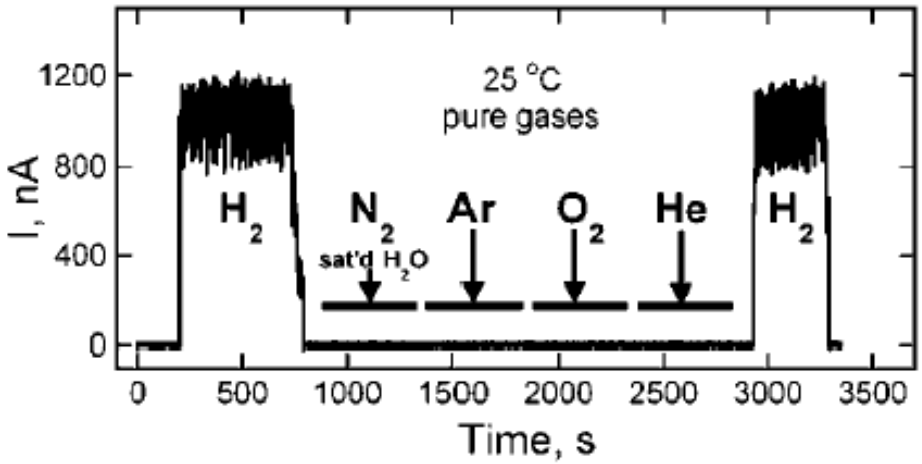




•Walter, E. C.; Favier, F.; Penner, R. M. *Anal. Chem.* **2002,** *74,* 1546.

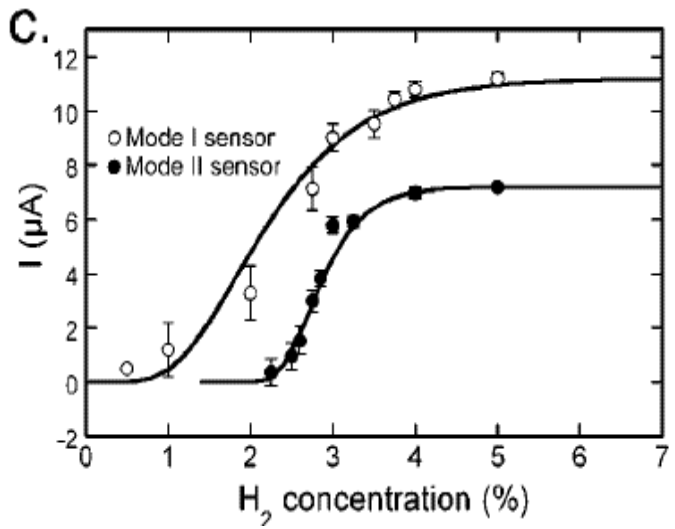
•Favier, F.; Walter, E. C.; Zach, M. P.; Benter, T.; Penner, R. M. *Science* **2001,** *293,* 2227

Pd Nanowire Hydrogen Sensor



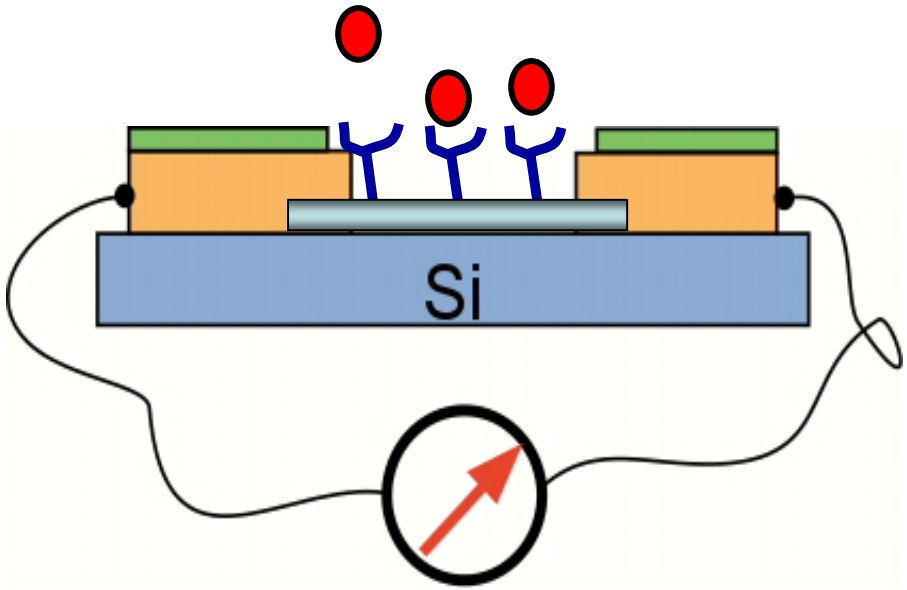
Response of the sensor to four gases

- ❑ Response to hydrogen only!
- ❑ The conductance increases from zero in the presence of hydrogen

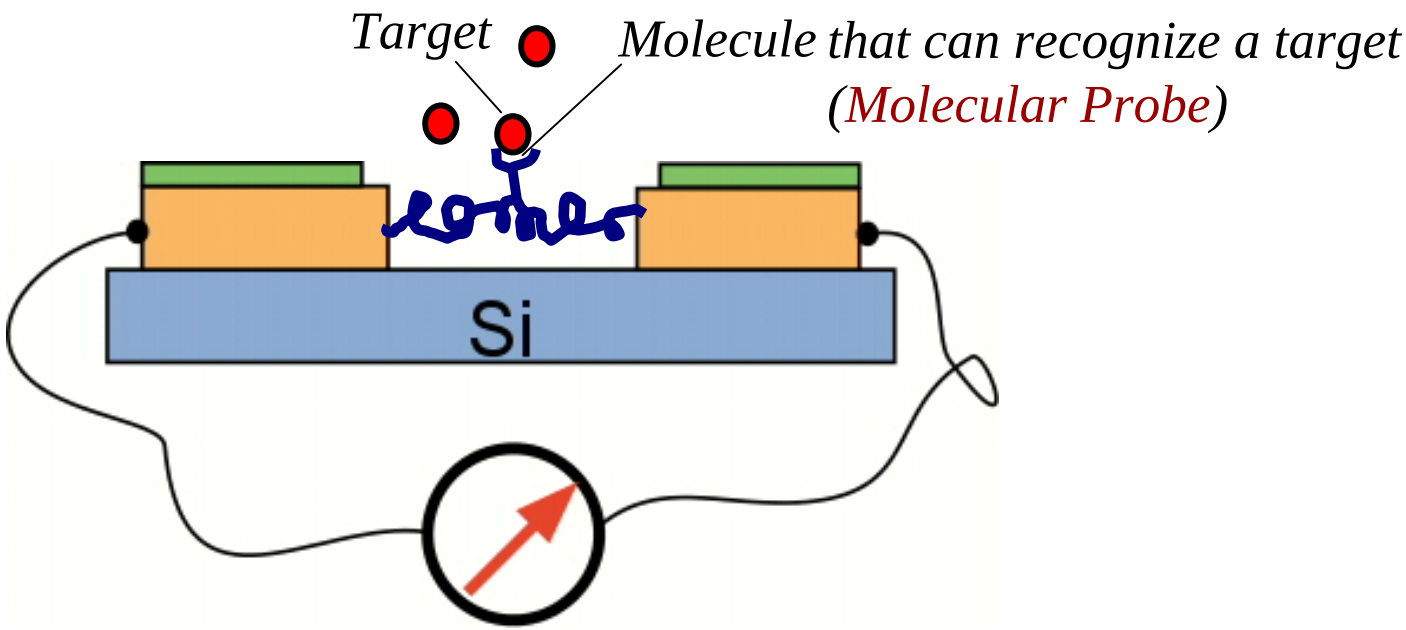


- ✓ The detection limit of the sensor is ~ 0.5% H_2.
- ✓ Response time ~ ms.
- ✓ Different wires for different gas molecules

Nanotube/wire/belt FET Sensors



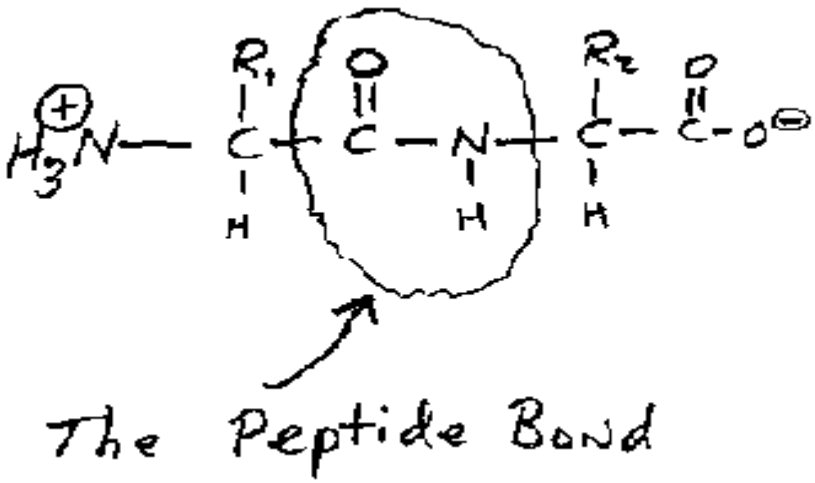
Molecular Junction Sensor



- ✓ Direct approach
- ✓ Single molecule detection

Peptides

Molecular Probe: = peptides

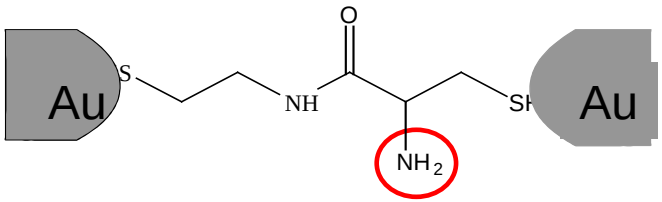


20 amino acids:

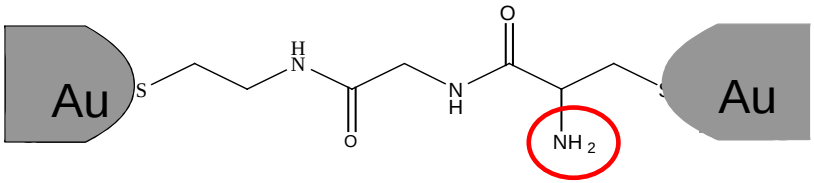
Gly	Ala
Val	Leu
Ile	Pro
Pen	tyros
Tyr	Ser
Thr	Met
Cys	His
Lys	Arg
Asp	Glu
Apn	Gln

- ✓ Building blocks of protein – Proteins in Nature as guidance
- ✓ Unlimited Choices (4 amino acids ->20x20x20x20=160,000!)
- ✓ - Powerful Combinatorial Chemistry

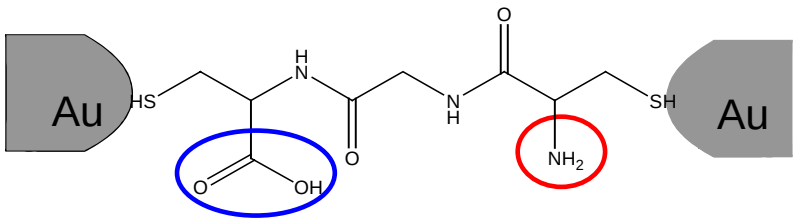
pH Sensor



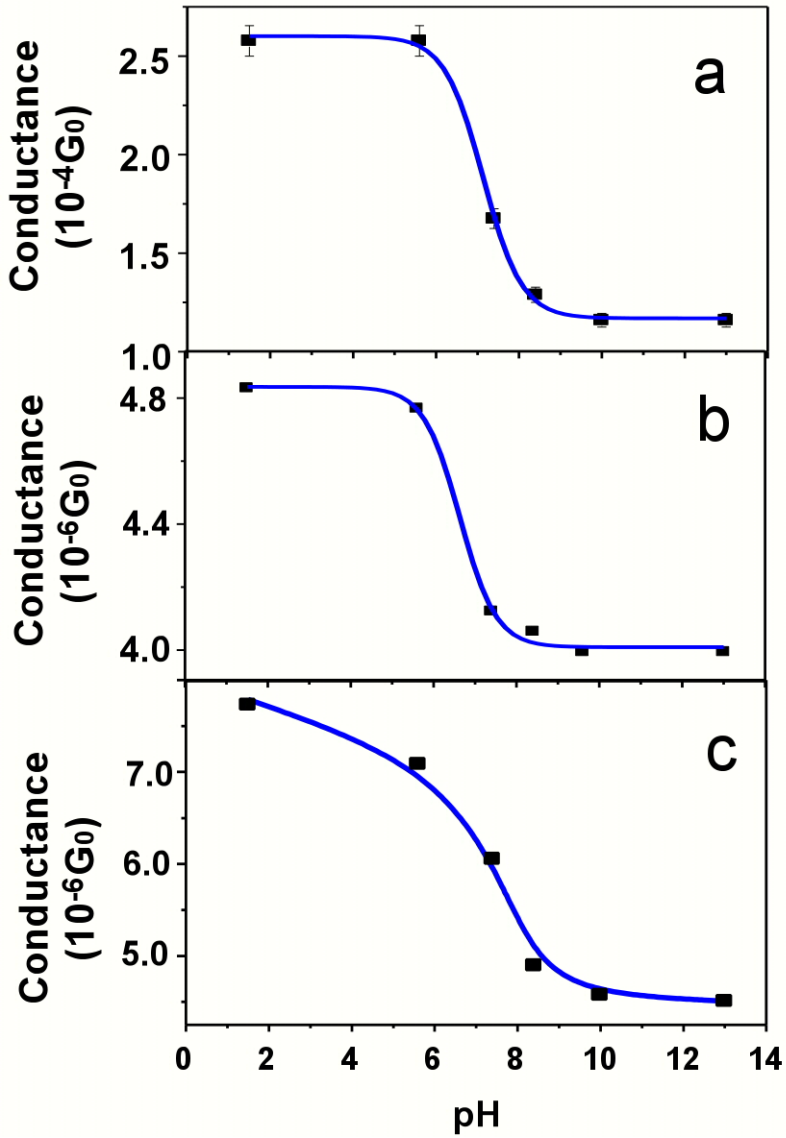
Cystamine-Cysteine



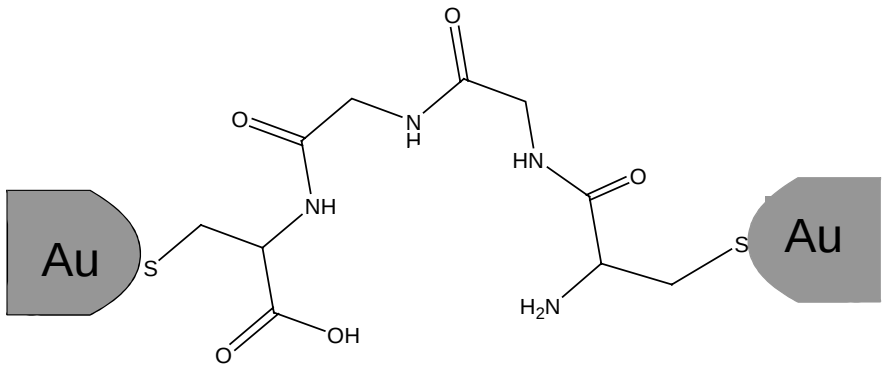
Cystamine-Gly-Cys



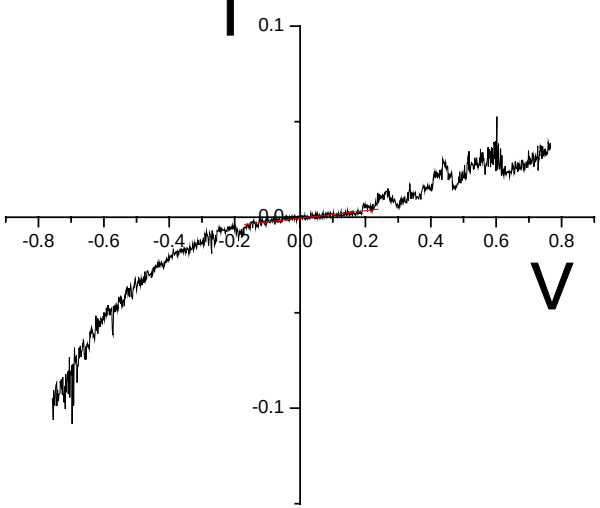
Cys-Gly-Cys



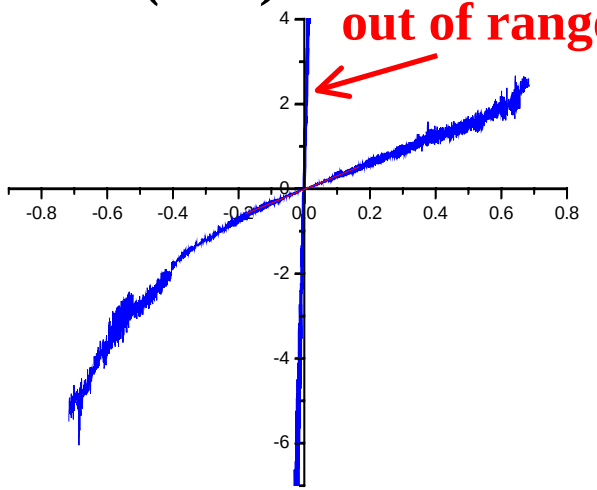
Metal Ion Detection



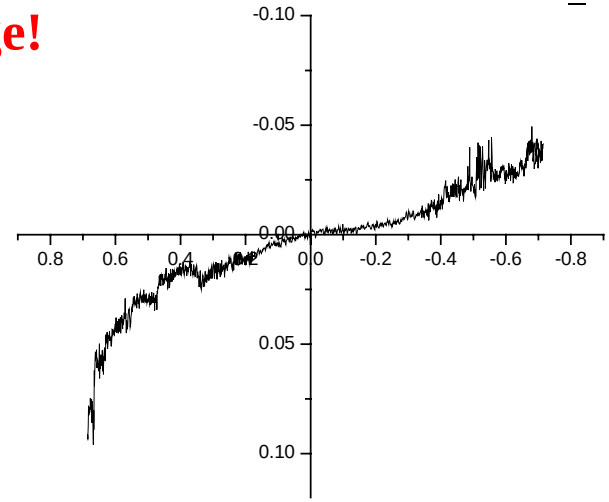
R=52 GΩ



R (Cu^{2+})=0.3 GΩ



Release Cu^{2+} w $HClO_4$



Metal Ion Detection

- Sequence Dependence

Peptides	Number of Ligands	Conductance of peptide	Conductance of Cu complex	Conductance ratio
Cysteamine-Cys	2	1.8 x10^{-4} G_0	1.9 x10^{-4} G_0	~1.1
Cysteamine-Gly-Cys	3	4.2 x10^{-6} G_0	9.1 x10^{-6} G_0	~2
Cys-Gly-Cys	4	5.3 x10^{-6} G_0	2.3 x10^{-5} G_0	~4
Cysteamine-Gly-Gly-Cys	4	5.0 x10^{-7} G_0	Cu^{2+}: 1.6 x10^{-4} G_0 Ni^{2+}: 5.5 x 10^{-5} G_0	~300 ~ 100 (for Ni^{+})

- ✓ Conductance increases upon Cu^{2+} binding
- ✓ Longer peptides give larger conductance changes
- ✓ Metal ion dependence (Cu^{2+} vs. Ni^{+} ions)

An Integrated Nanosensor

for Simultaneous Detection of A Range of Species

Sample Delivery - **Signal Transduction** – Signal Processing – Data Communication

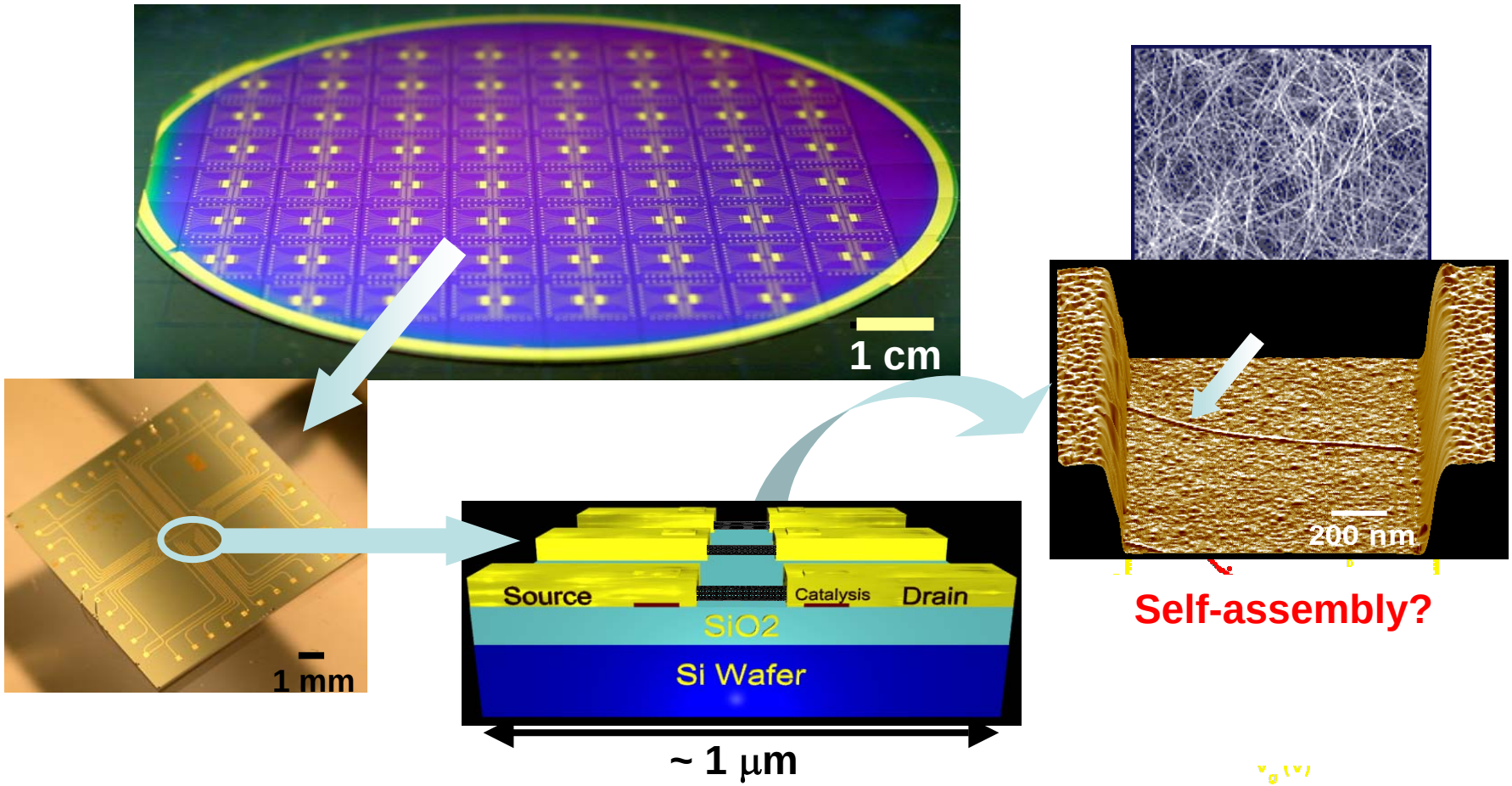
Progress Achieved to Date:

- ❑ Highly sensitive and selective individual nanosensors demonstrated.
- ❑ Common platforms for simultaneous detection of different species demonstrated.

Challenges Ahead

Microtechnology Meets Nanotechnology

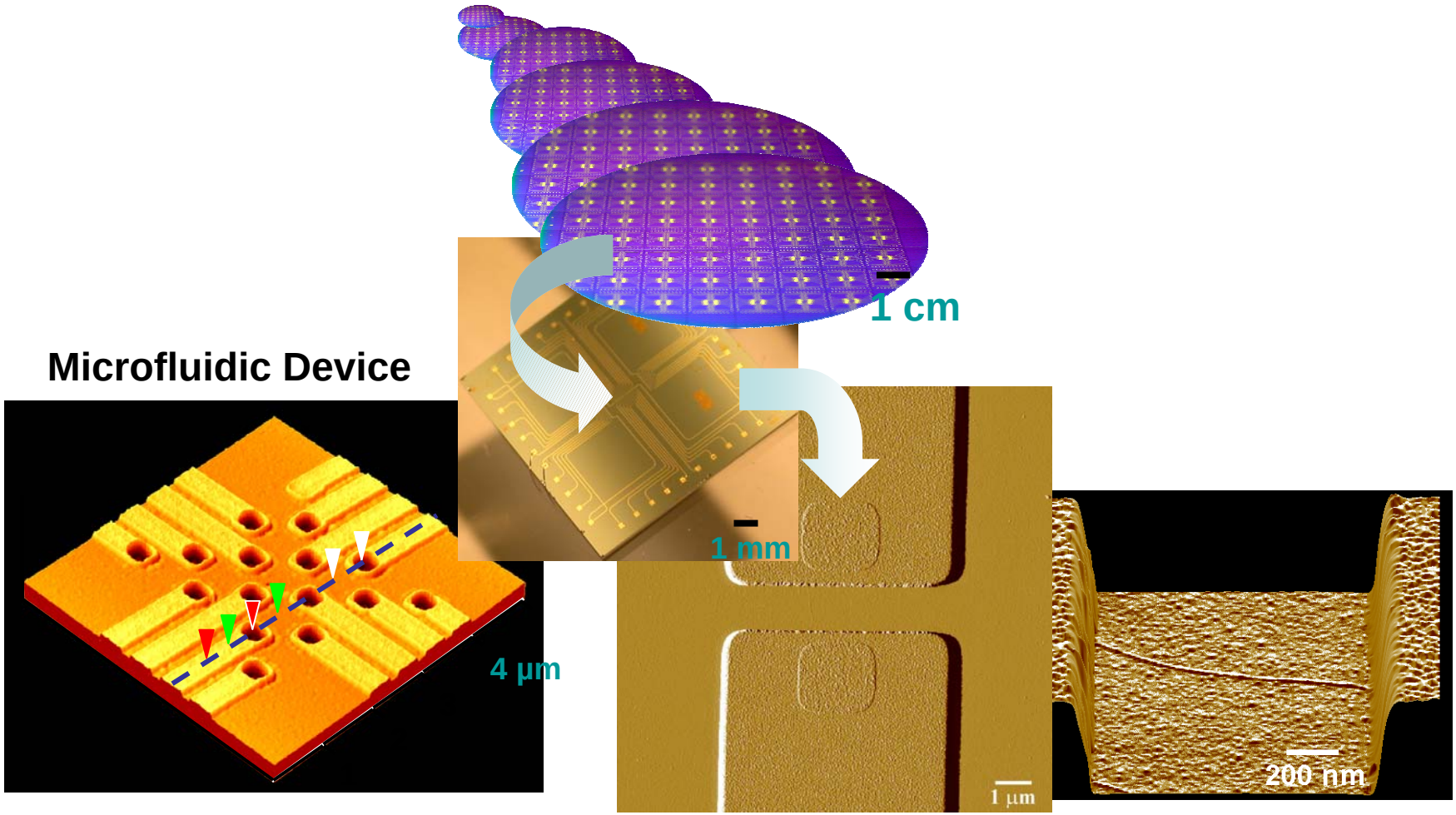
- Interconnection Issues



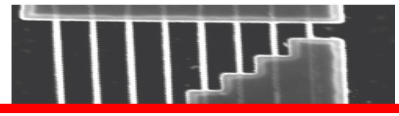
Challenges Ahead

Microtechnology Meets Nanotechnology

- Sample Delivery



Nano-Solution to Big Sensor Problems?



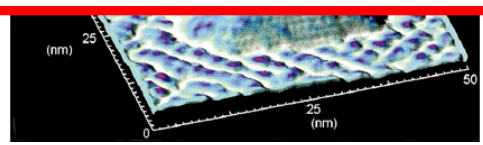
Unique Features:

- Reduced sample solutions
- Small size promises high degree of integration
- High sensitivity for single molecule/ion analysis
- Fast response time

Remaining Challenges:

*An **integrated** device needs to solve the interface between Nano- and Micro-technology:*

- Interconnection issues
- Sample delivery



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