

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

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Dec. 2004

Need of Environmental Sensors

The Washington Post

WEDNESDAY, FEBRUARY 2, 1994

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

Unters

By Justin Washington

Recent public school water samples taken from drinking fountains, officials in Washington state say, show levels of lead that are



WASA official Jodye Levy Russell takes a water sample from a faucet at Lockie 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 the water are most concerned about children younger than 6 and fetuses—those most susceptible to permanent damage from lead poisoning.

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

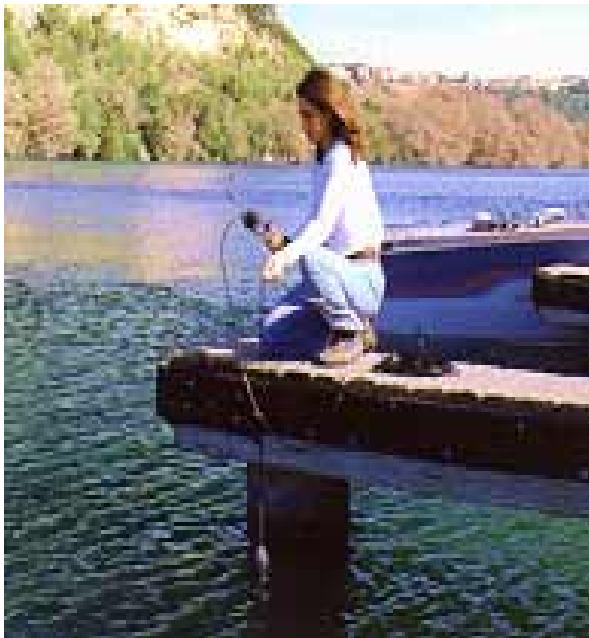
Children who ingest lead usually in the form of dust from deteriorating lead-based paint or

Ammonia release, Feb. 1994



ter of blood. A deciliter is about 100 microliters, and 10 micro-

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

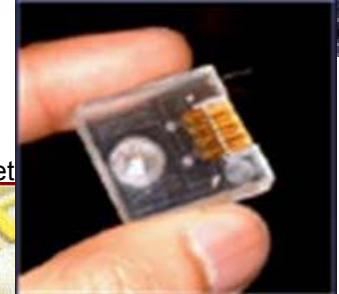
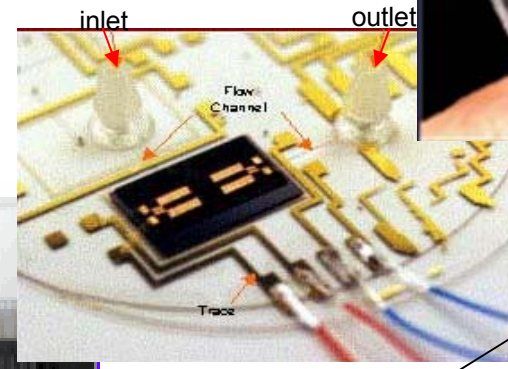
Essential monitoring is integrated into communications equipment

**Need:
Miniaturization
& Integration**

*Signal Processing
& Transmission*

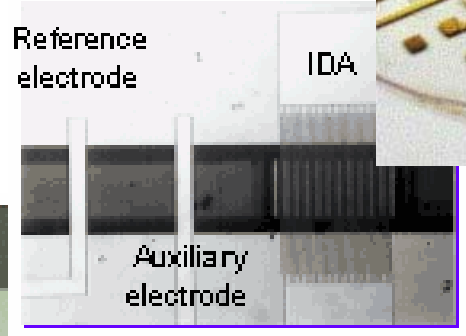


Sample Delivery



~cm

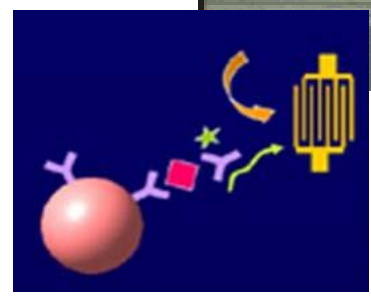
*Sensing
Element
Array*



~mm



~ μ m



~nm

An Integrated Sensor

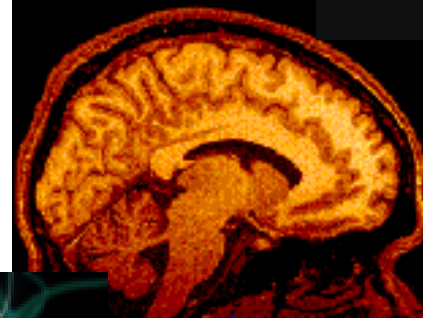
- Sample Delivery
- Sensing Elements
- Signal Processing & Transmission

Emulating Nature...

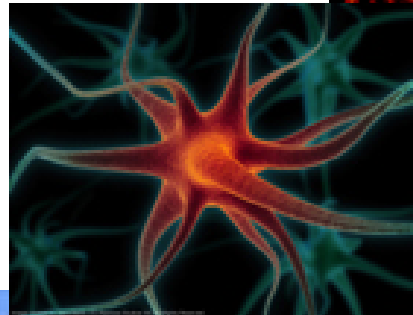
*Data processing, Action,
(cm-m)*



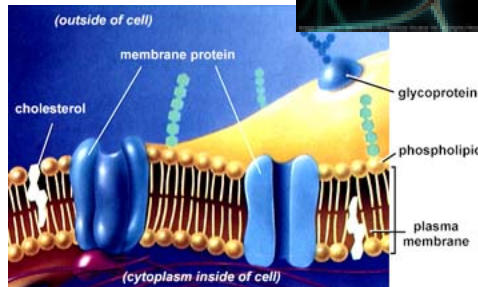
Brain (mm-cm)



Neurons (um)



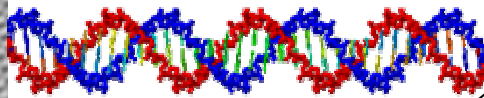
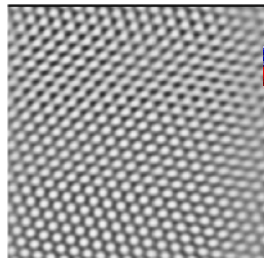
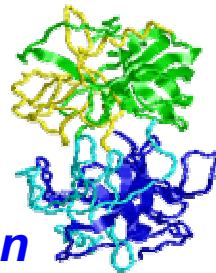
*Proteins (~ 5 nm)
DNA (~ 2nm wide)
Lipids (~ 1 nm)*



macro

micro

*Atoms
of carbon*

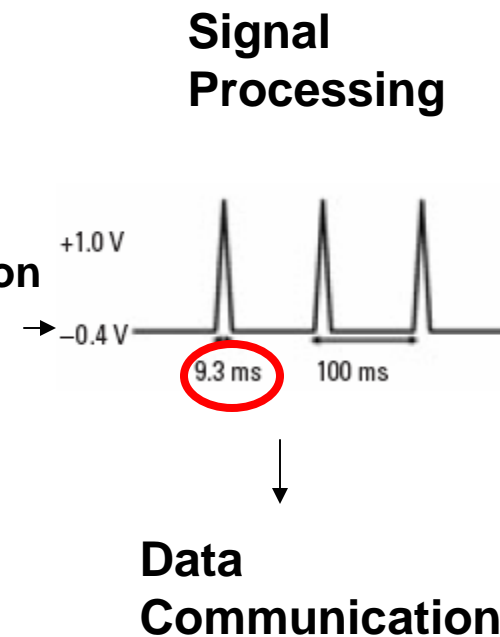
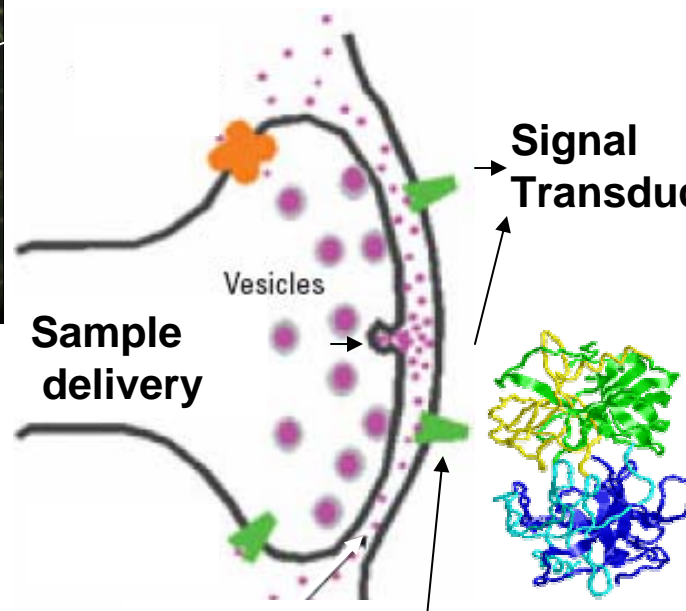
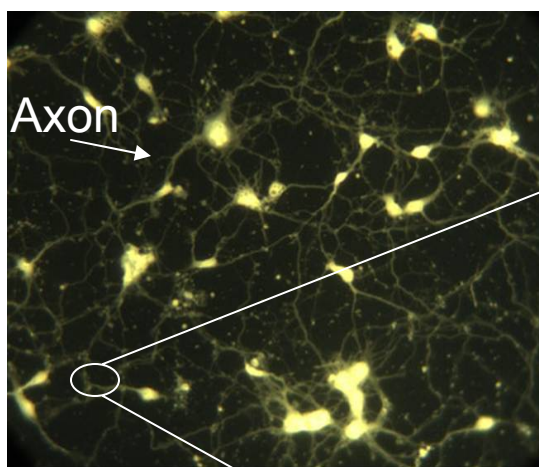


Spacing ~ 1.5 Å

nano

Emulating Nature: Neuronal synapses...

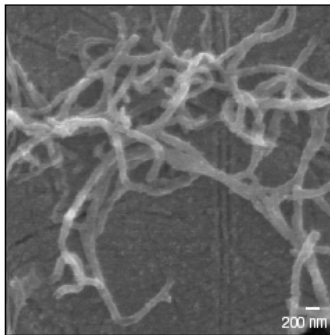
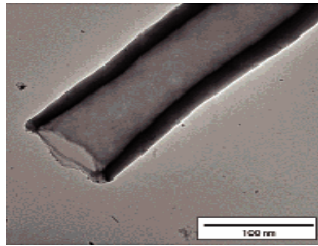
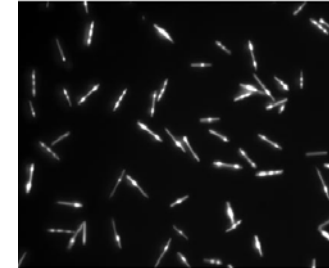
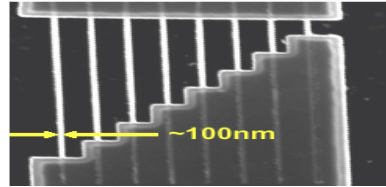
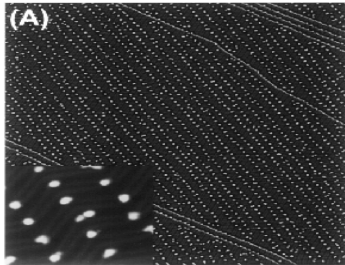
Perfect feed-back system to imitate...



- 100nm gap
- Sub second response
- High specificity
- Response to nM concentrations

What role does 'NANO' play?

NANO-Solution ?



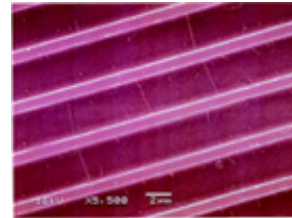
Particle

Resonator

Rod

Peptide
Tube

Carbon
Tube

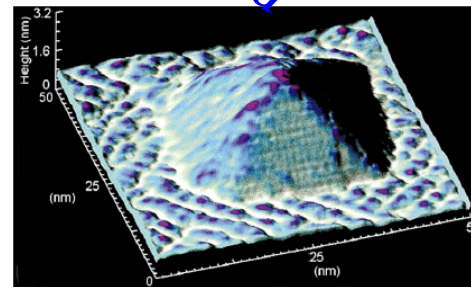
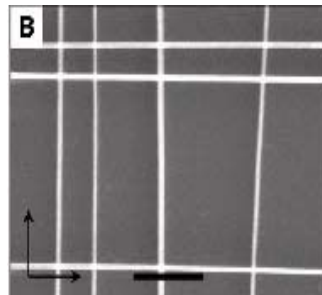
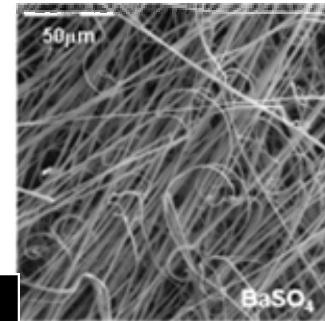


Fibers

Belt

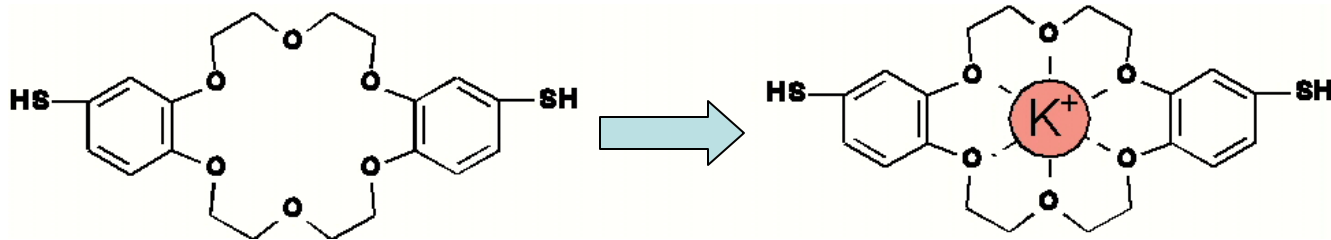
Wire

Pyramid



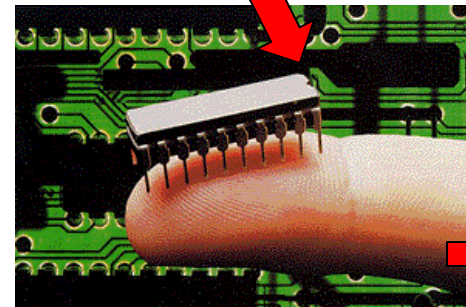
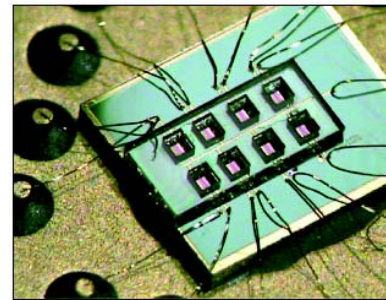
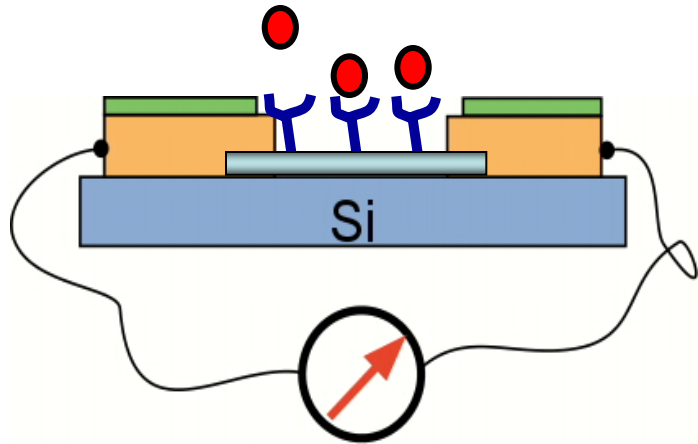
Signal Transduction

- Convert a Chemical Binding Event into a Readable Signal



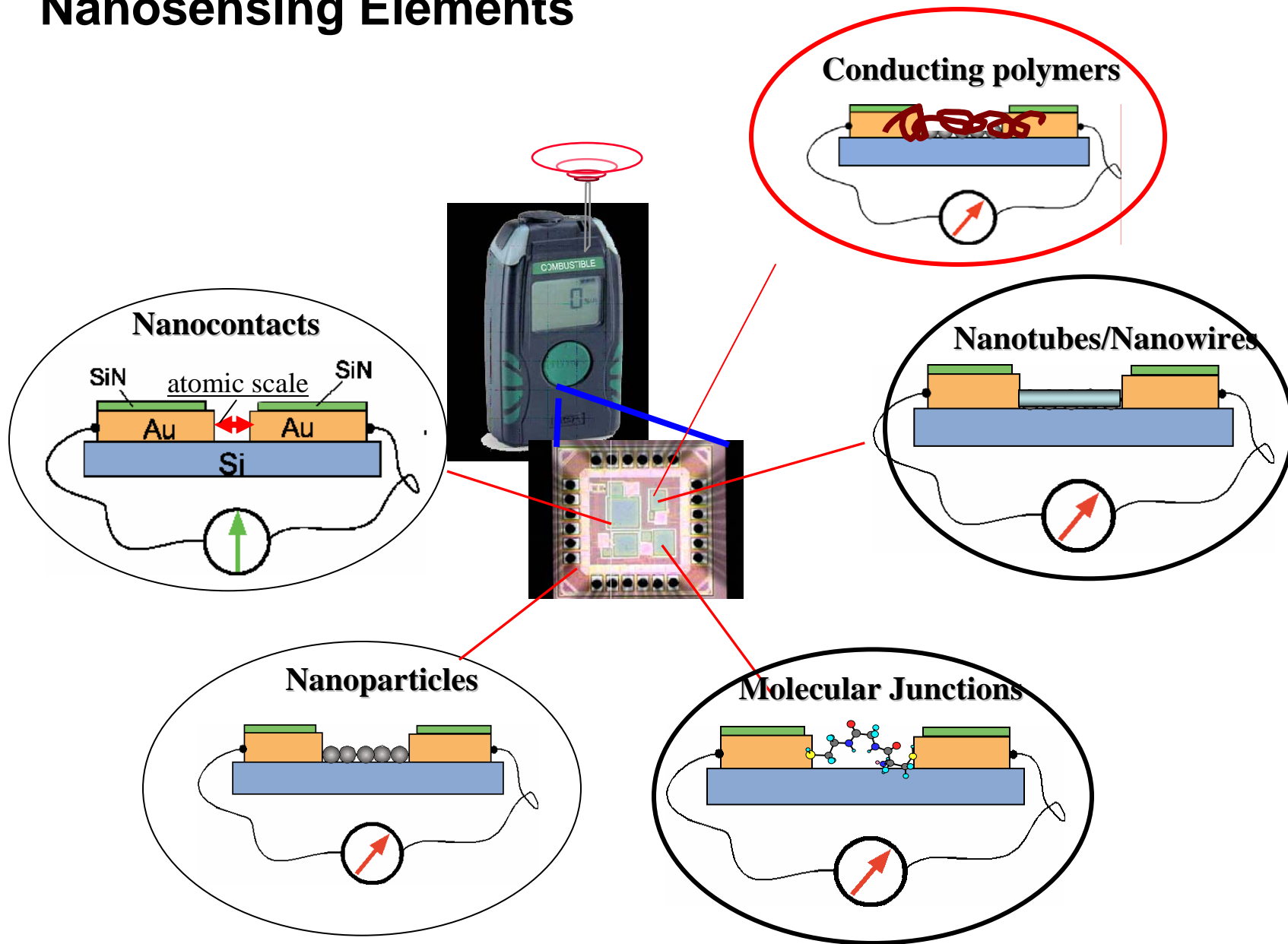
- Optical (Trogler/Gawley/Lavine/Anderson...)
 - Electrochemical (Wang/Sadik/...)
 - Mechanical (Shih/...)
- Electrical (Kan/Mitra/Subramanian/Tao)

Electrical Detection – Reading chemical information electronically

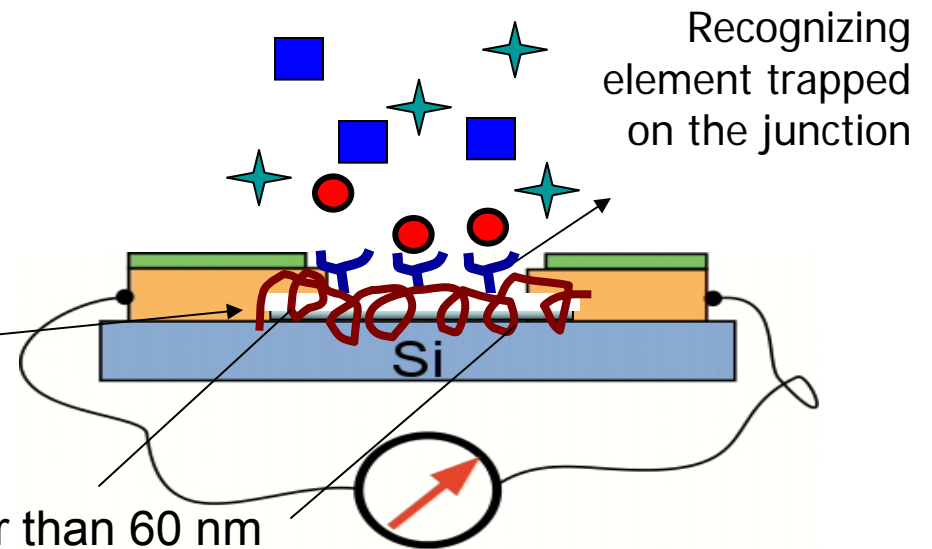
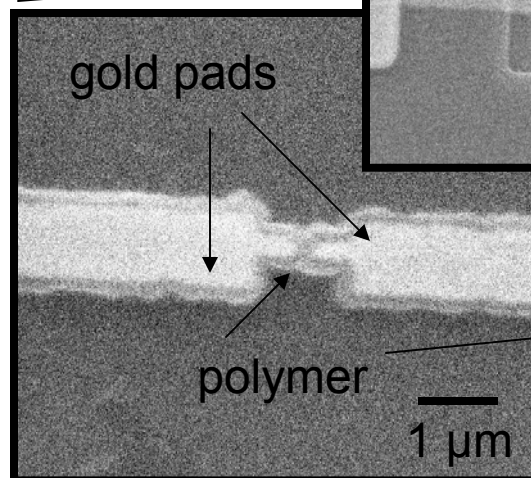
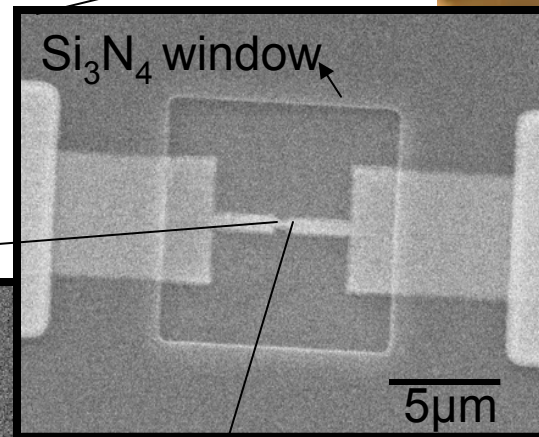
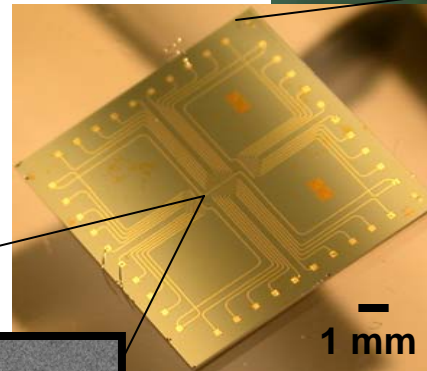
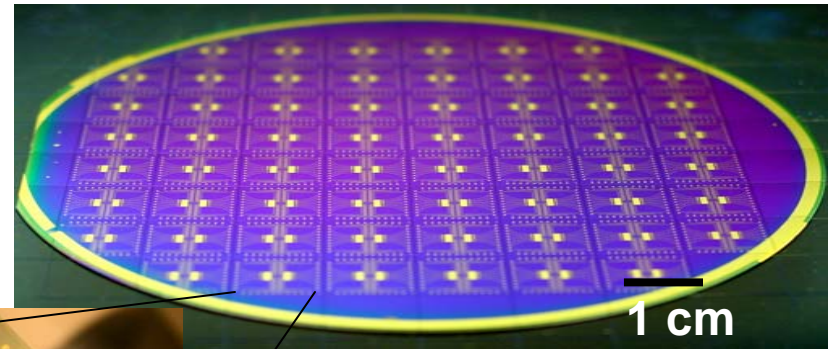


- High degree of integration
 - for a miniaturized device for simultaneous detection of different species
- Easy to process/display/transmit the data
 - needed for a fully automated device
- Compatible with microelectronics
 - taking advantage of existing microtechnology

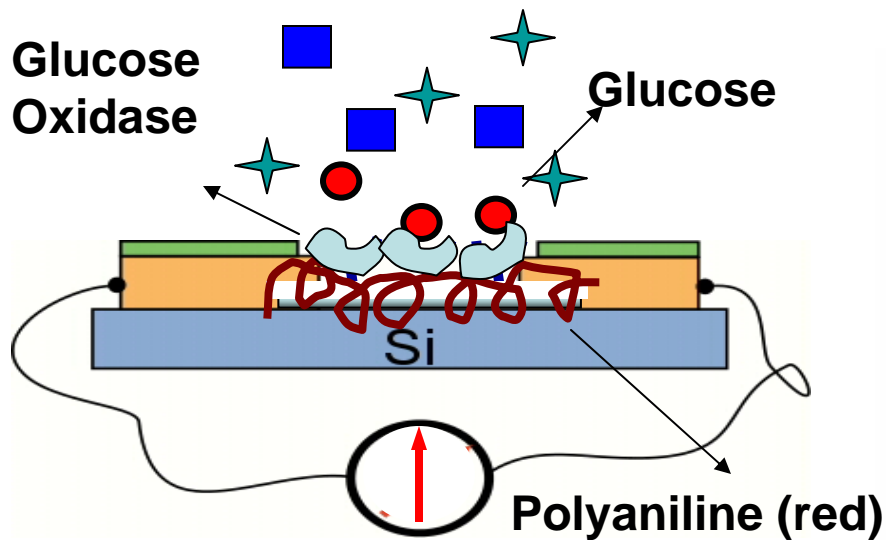
Arrays of Electrically Wired Nanosensing Elements



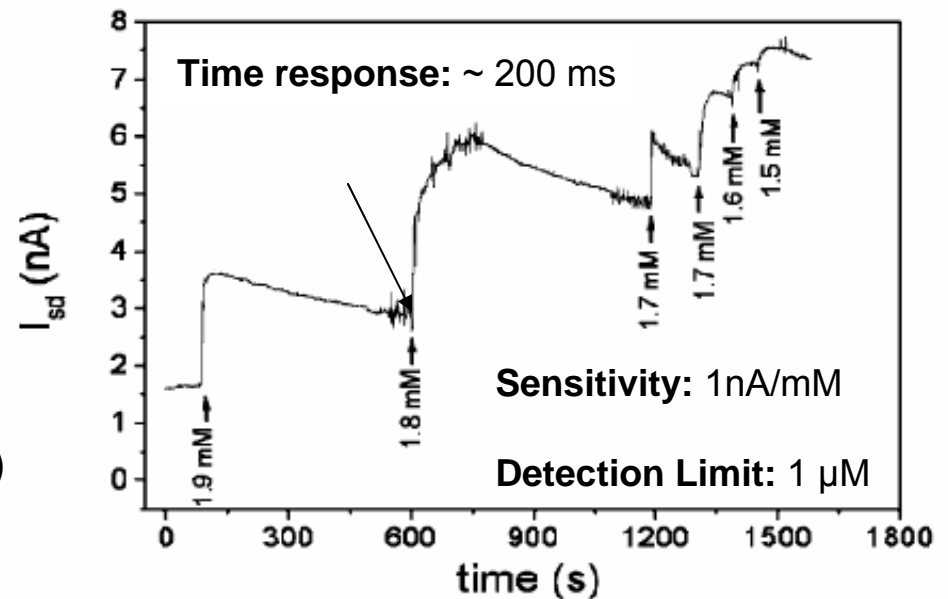
Conducting Polymer FET Sensors



Glucose Sensor



E. Forzani, H. Zhang, L. Nagahara, I. Amlani, R. Tsui, and N.J. Tao *Nano Letters* 4, 9 2004



- ✓ 300 times faster
- ✓ 100 times more sensitive than similar sensors on 20 μ m gap.

Why nanosensors are better than microsensors ?



Gap smaller than 60 nm



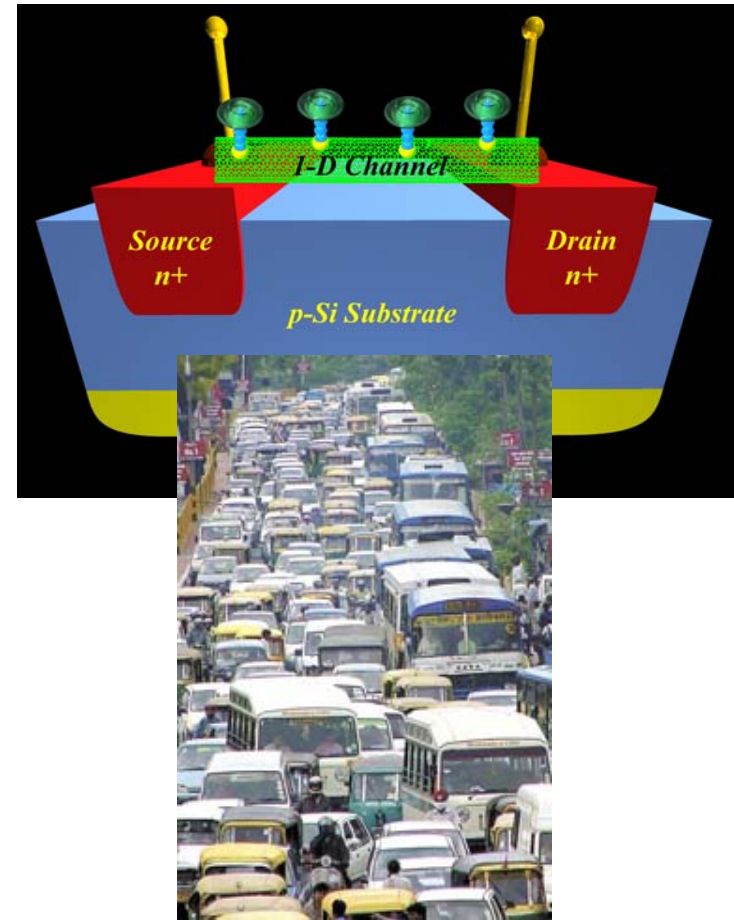
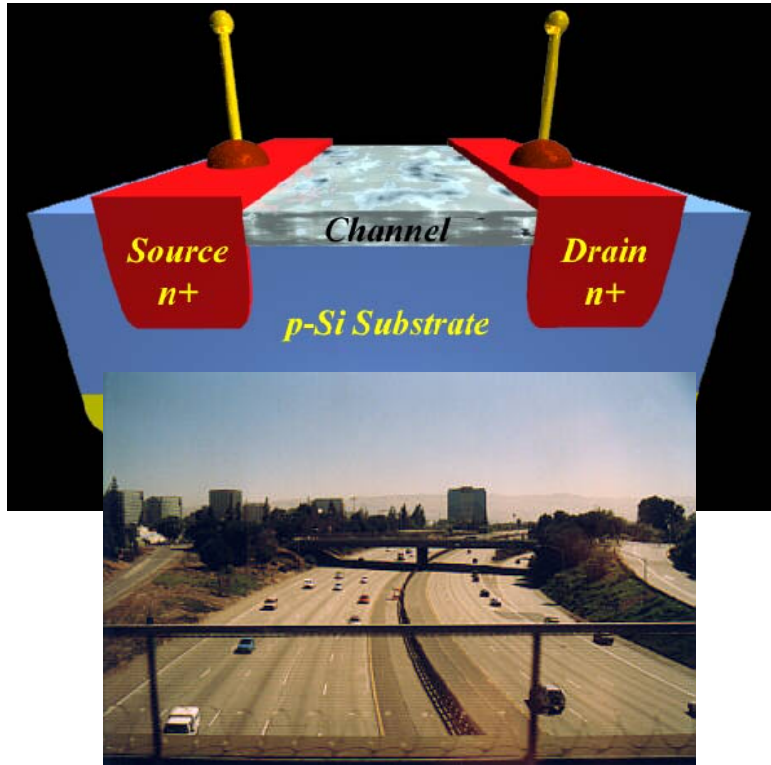
Gap ~ (20 x 900) μm

The clue:

2D sensors

vs

1D sensors



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

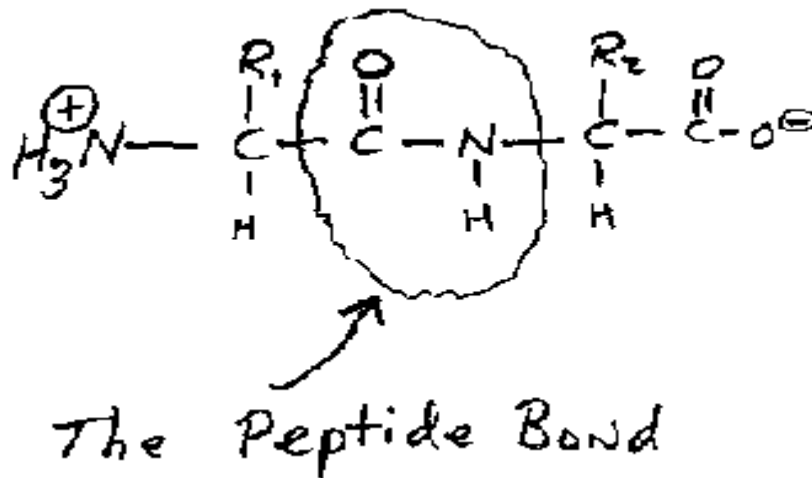
Narrowing the channel to one dimension, detection sensitivity is enhanced.

ChemFET (Kan/Mitra/Subramanian)

**Is it necessary using real biological recognizing elements
for environmental applications?**

Peptides

Molecular Probe:  = peptides

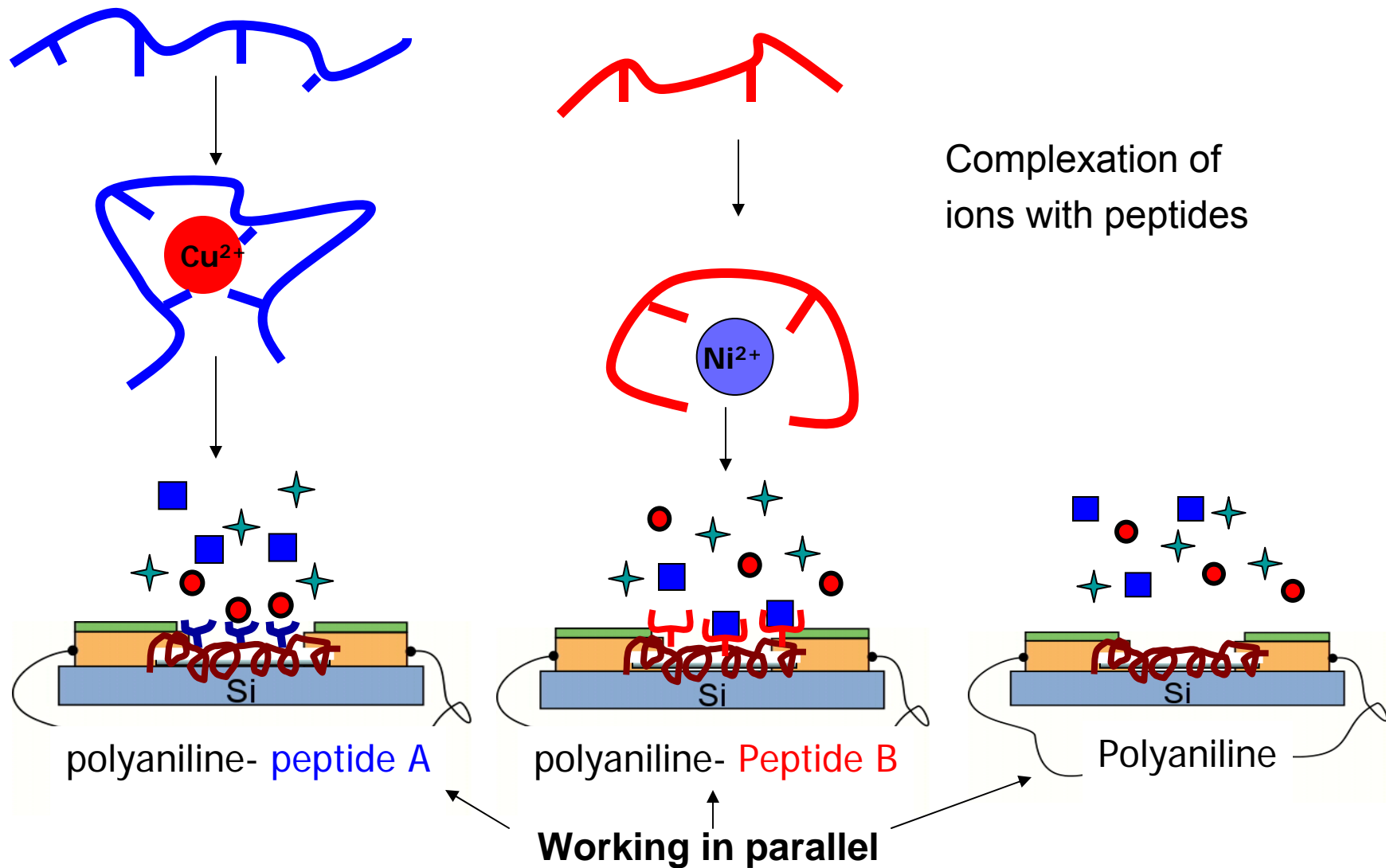


20 amino acids:

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

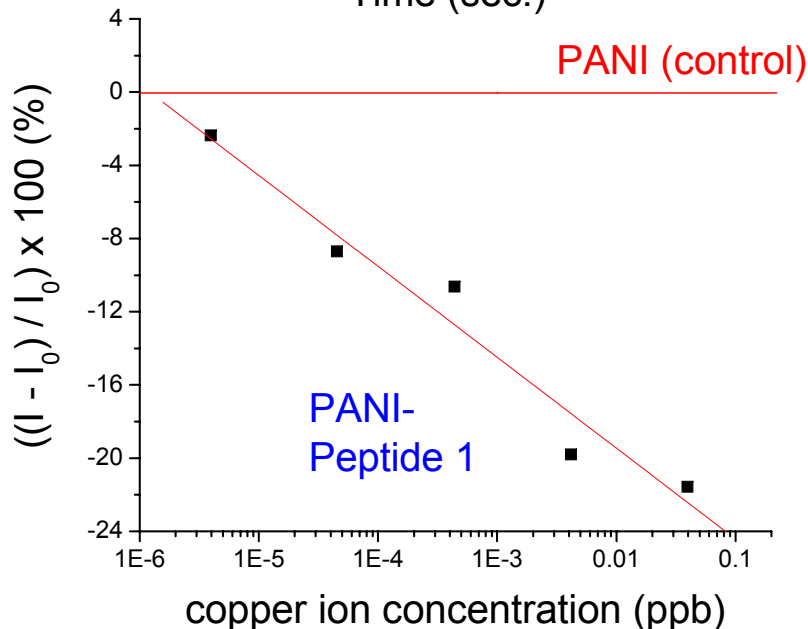
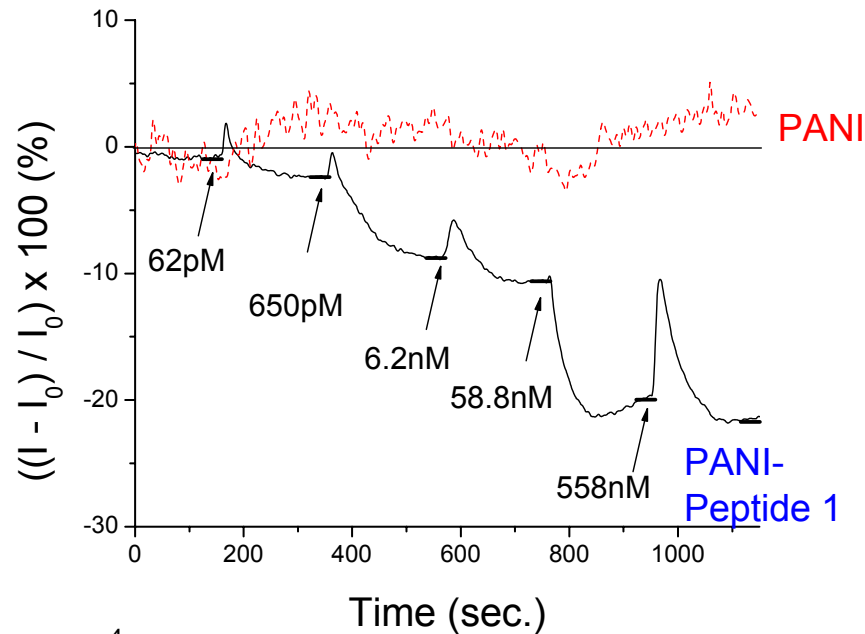
- ✓ Building blocks of protein – Proteins in Nature as guidance
- ✓ Unlimited Choices (4 amino acids $\rightarrow 20 \times 20 \times 20 \times 20 = 160,000!$)
- ✓ Powerful Combinatorial Chemistry

Copper and nickel ion sensors



Copper and nickel ion sensors

Cu²⁺ detection on polymer nanojunctions



- Changes physical-chemical structure and electrical properties → Real time detection
- D.L.(Cu²⁺): 4 ppt, D.L.(Ni²⁺): 22.5 ppt
- Reusable device (6 times) for metal ion detection
- Drinking water analysis (Tempe): (0.34 ± 0.03) ppm. Result in agreement with AAS.

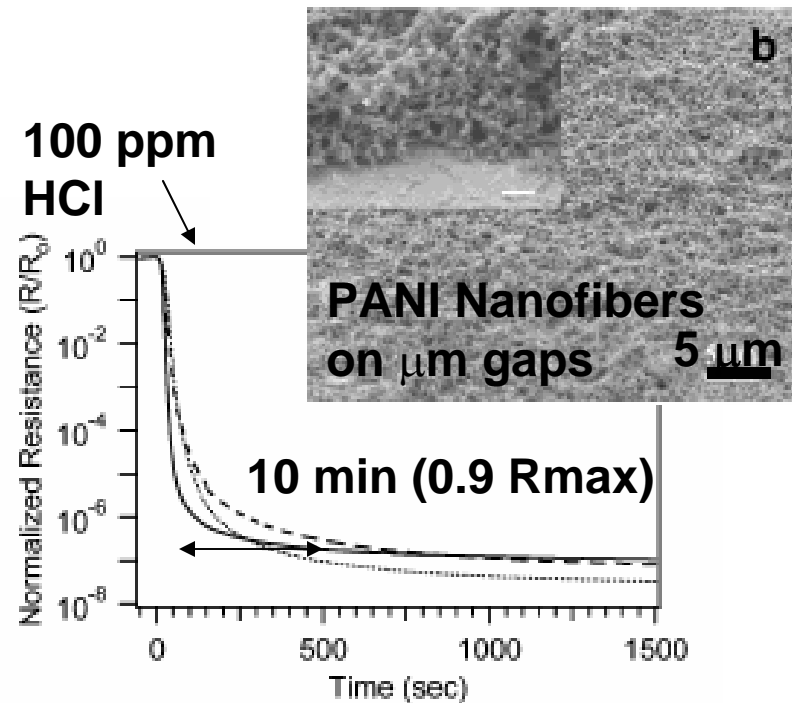
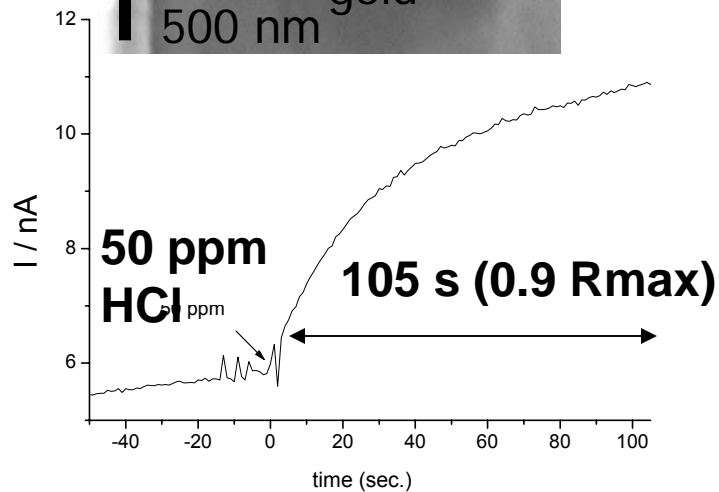
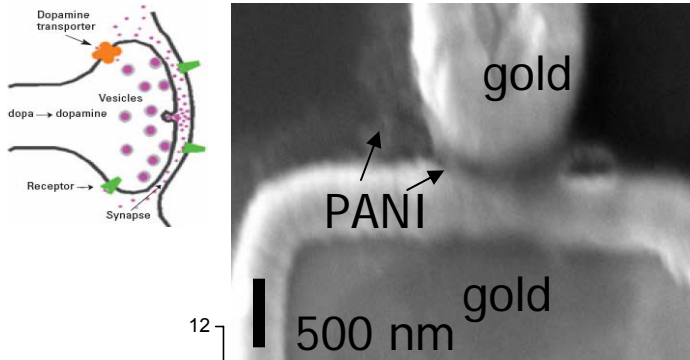
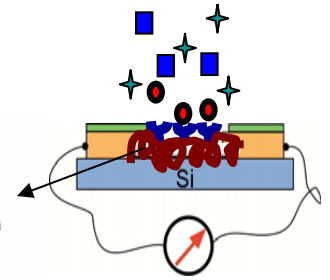
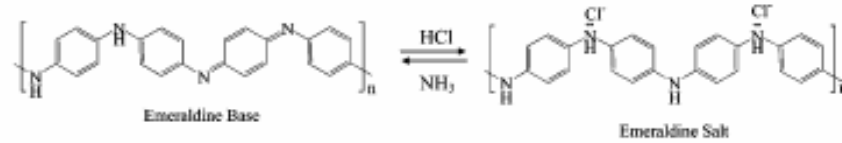
Comparison with 100 μm gap FET (polycarbazole):

✓ 4 x 10⁴ times more sensitive

✓ 500 times faster

Other example of conducting polymer nanojunctions:

- Ammonia/HCl vapor detection:

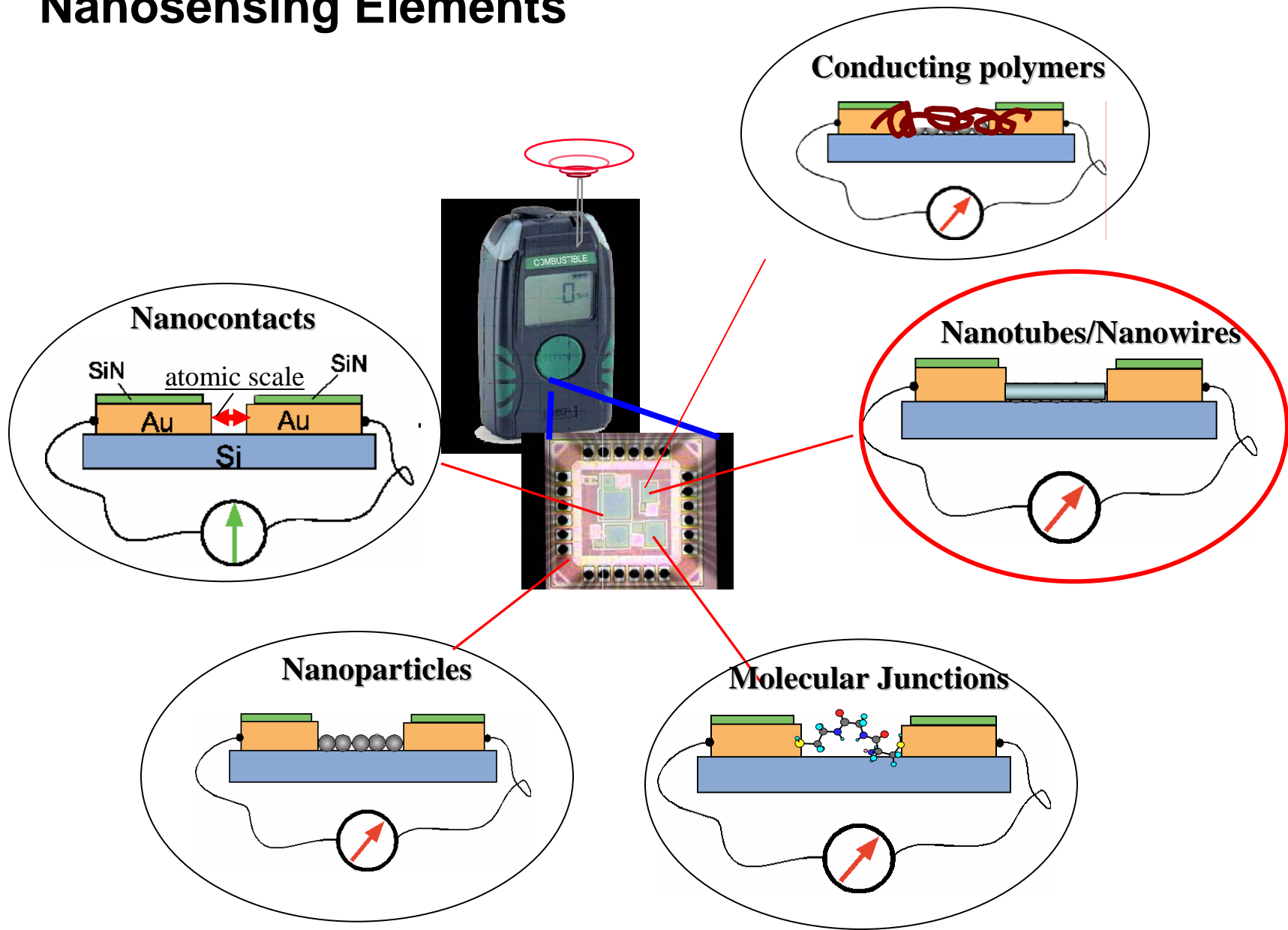


Díaz Aguilar, E. Forzani, X. Li, L.A. Nagahara, I. Amlani, R. Tsui and N.J. Tao (in preparation),2004.

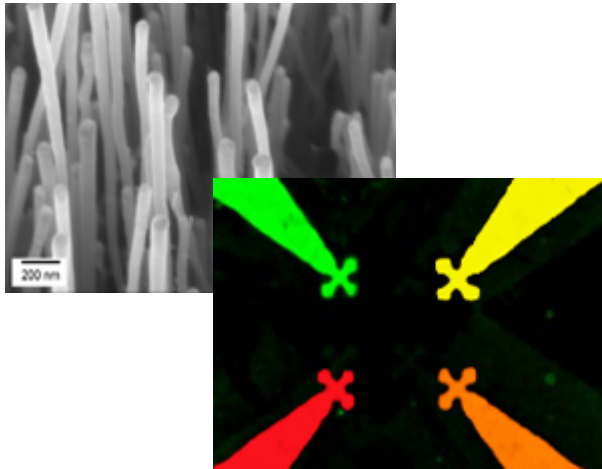
J. AM. CHEM. SOC. 2003, 125, 314-315, NANO LETTERS 2004, Vol. 4, No. 3, 491-496

No only dimensions of the sensing elements but also distribution and size gap in FET is important to get good analytical performance.

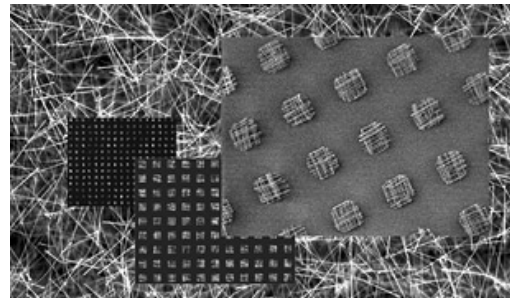
Arrays of Electrically Wired Nanosensing Elements



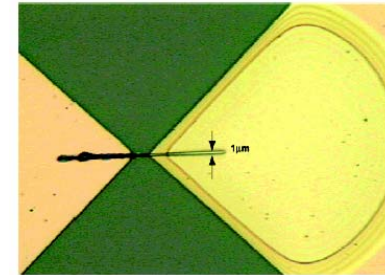
Nanotubes/wires/belts Sensors



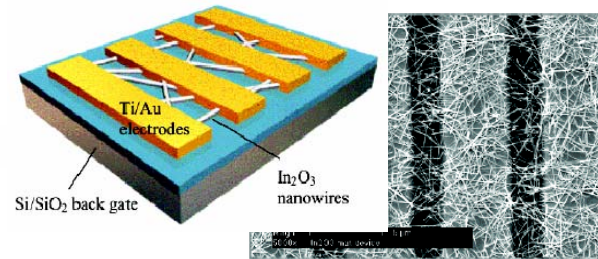
R.J. Hamers & co-workers
(<http://hamers.chem.wisc.edu/>)



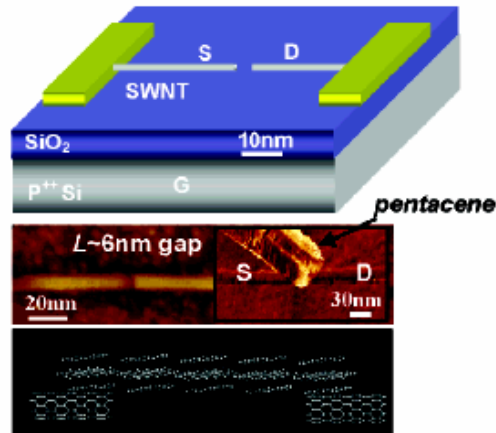
C.M. Lieber and co-workers
(<http://cmliris.harvard.edu/>)



N.V. Myung & co-worker + collaborators
<http://www.engr.ucr.edu/~myung/Research.htm>



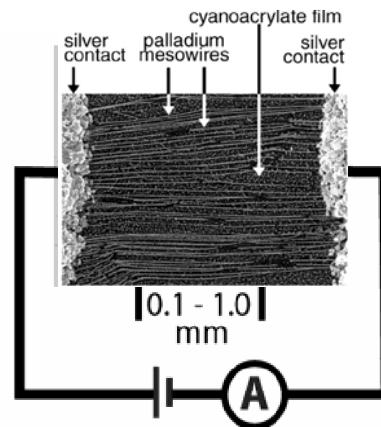
Chongwu Zhou & co-workers,
http://ee.usc.edu/faculty_staff/bios/zhou.html



H.J. Dai and co-workers

(<http://www.stanford.edu/dept/chemistry/faculty/dai/group/hongjie.html>)

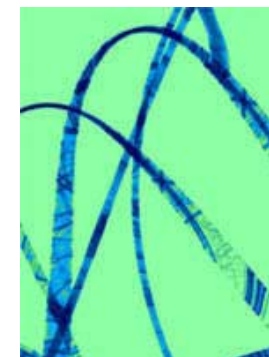
Nanotubes



R.M. Penner and co-workers

(<http://www.chem.uci.edu/people/faculty/rmpenner/>)

Nanowires

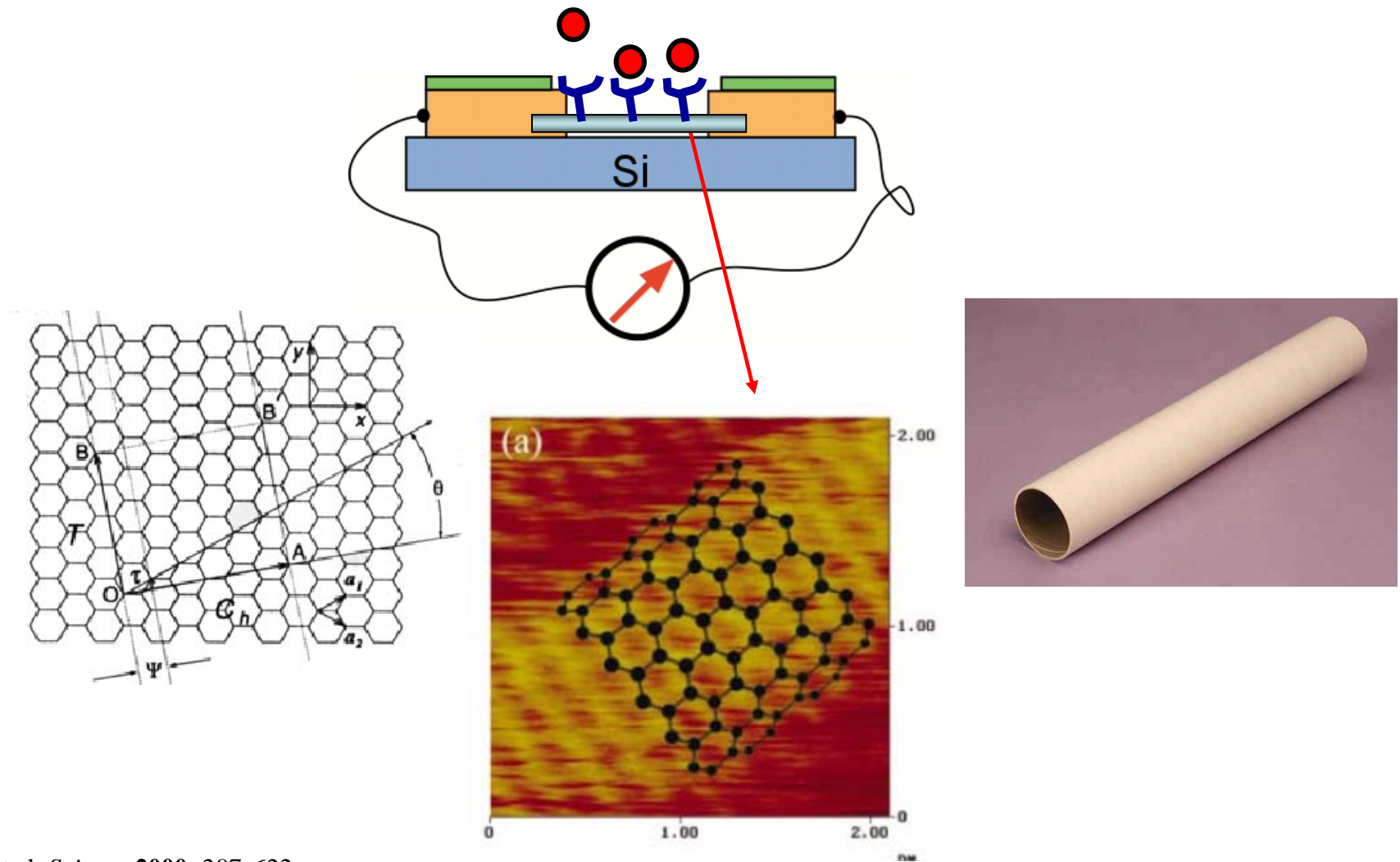


Z.L. Wang and co-workers

(<http://www.nanoscience.gatech.edu/zlwang/Research.htm>)

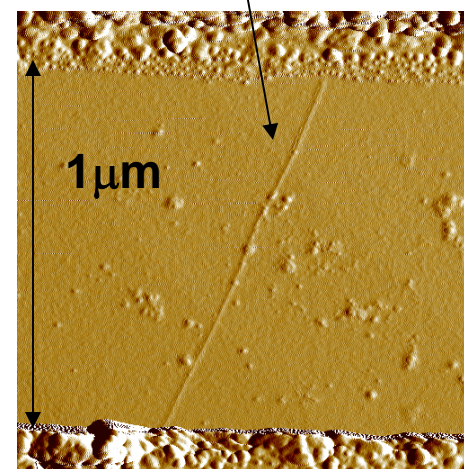
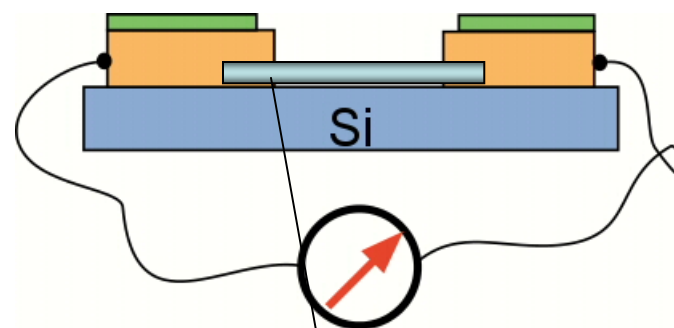
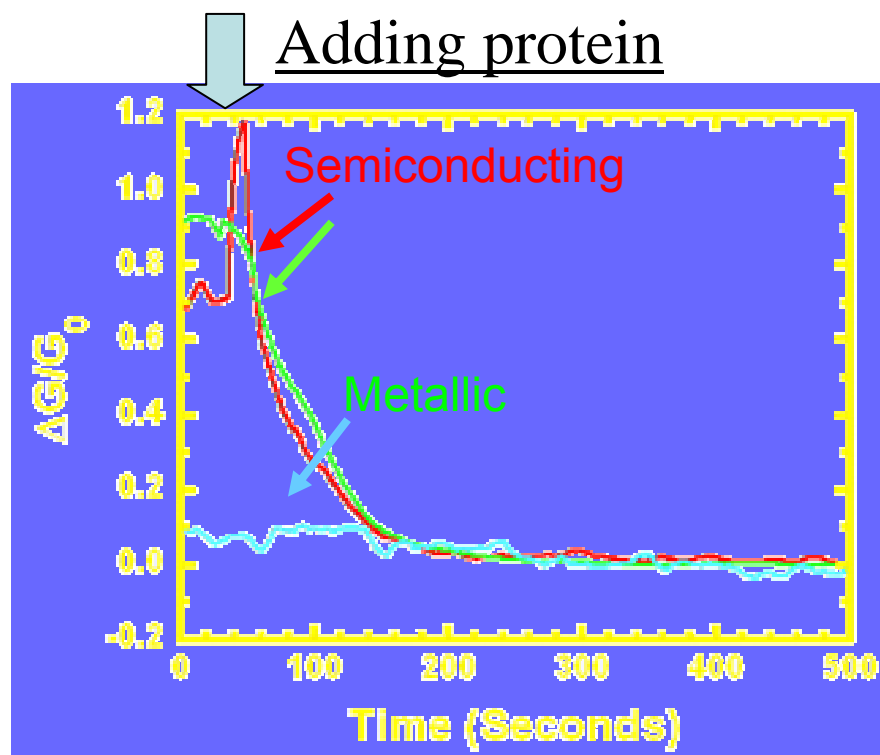
Nanobelts

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.
- Hassanien et al., *Appl. Phys. Lett.*, Vol. 79, No. 25, 17 December 2001

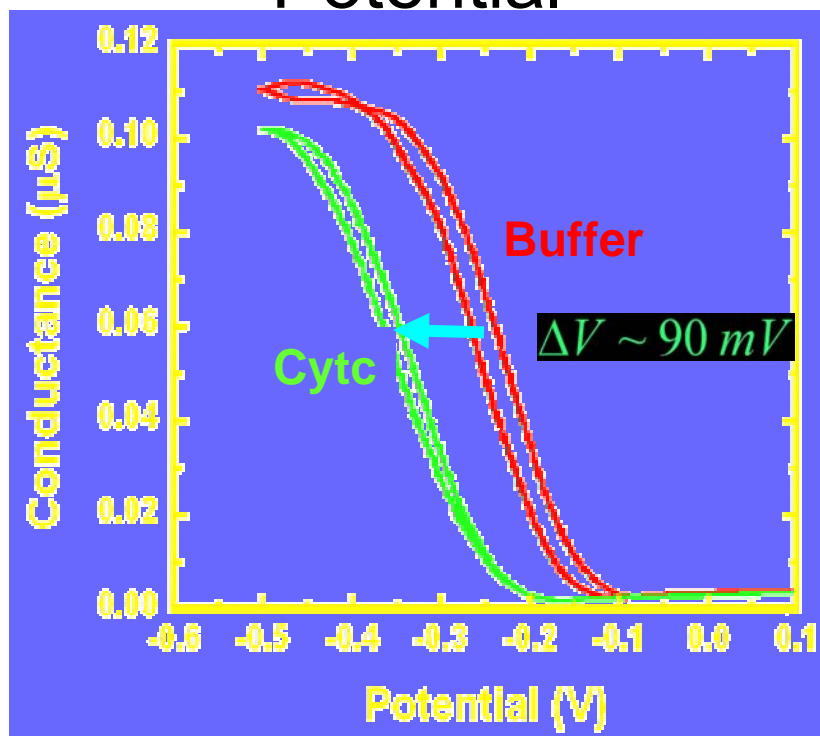
Protein Adsorption on bare carbon nanotubes



AFM image of single wall carbon nanotube (SWNT)

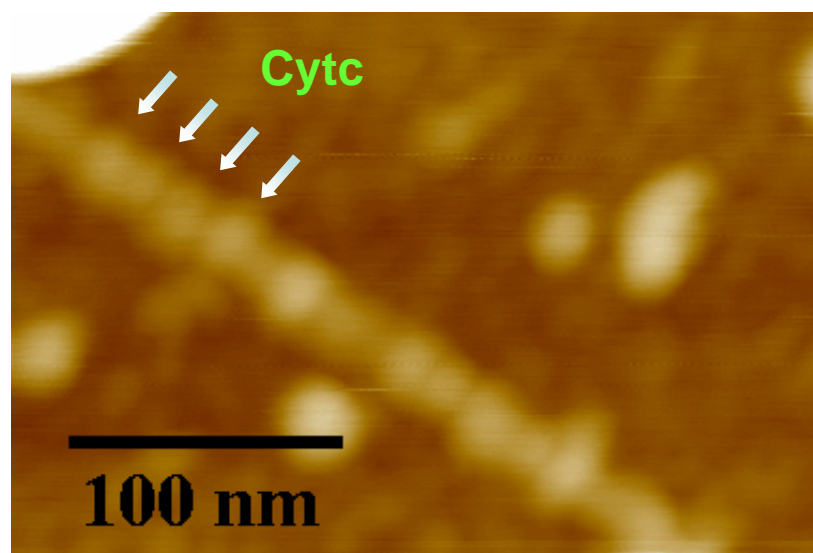
The protein decreases the conductance of p-type SWNT \rightarrow it decreases p-type carriers number

Conductance vs. Electrochemical Gate Potential



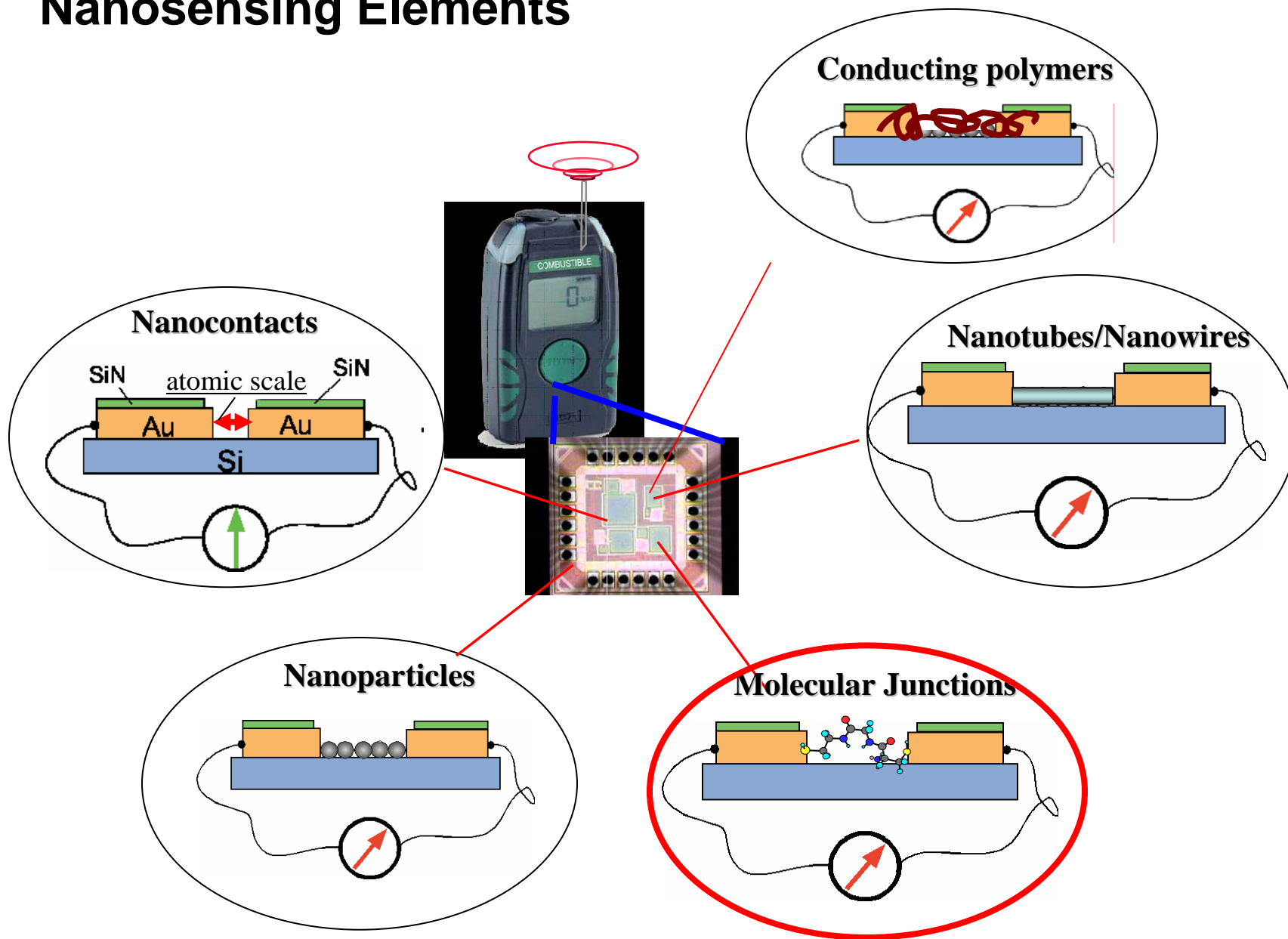
Partial charge transference

$$\begin{aligned} \# \text{Cyt c} &= \frac{4 \times 10^{-10} \text{ F/m} \times 10^{-6} \text{ m} \times 0.09 \text{ V}}{10 \times 1.6 \times 10^{-19} \text{ C}} \\ &= \sim 20 \text{ Cyt c molecules} \end{aligned}$$

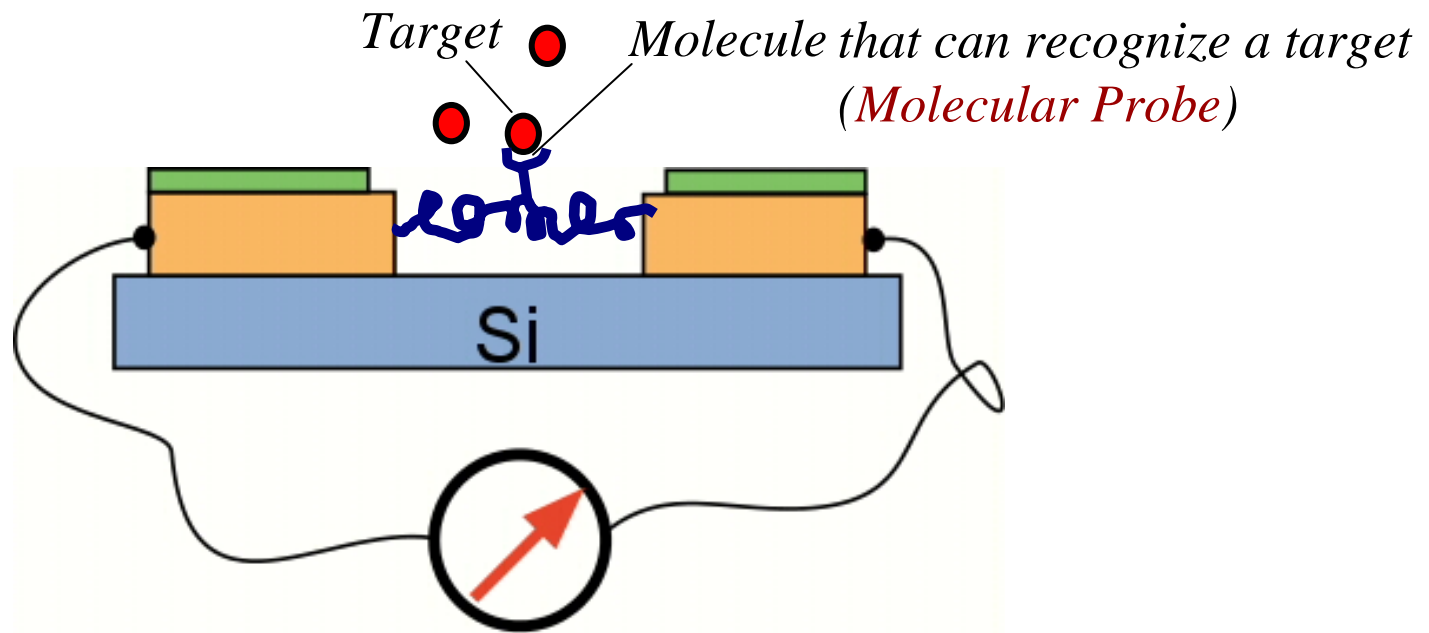


Based on the AFM images, the number of Cyt C molecule adsorbed onto the SWNT is ~30-40.

Arrays of Electrically Wired Nanosensing Elements

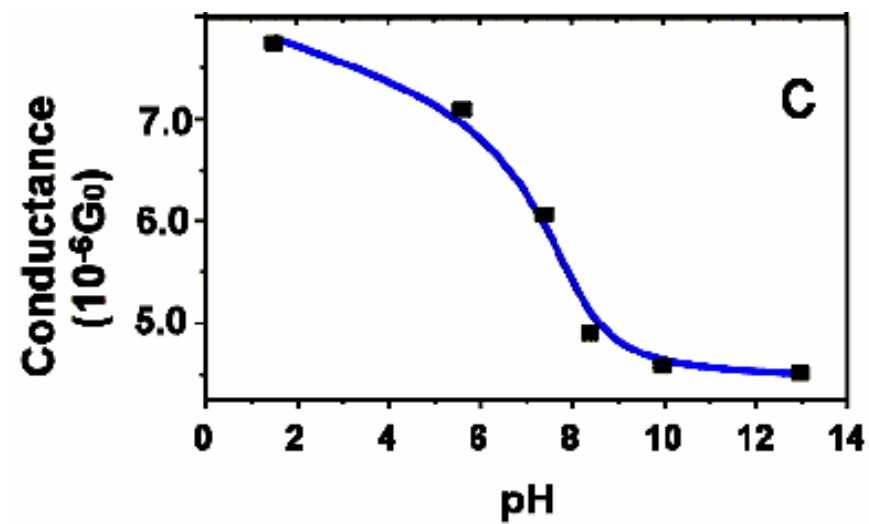
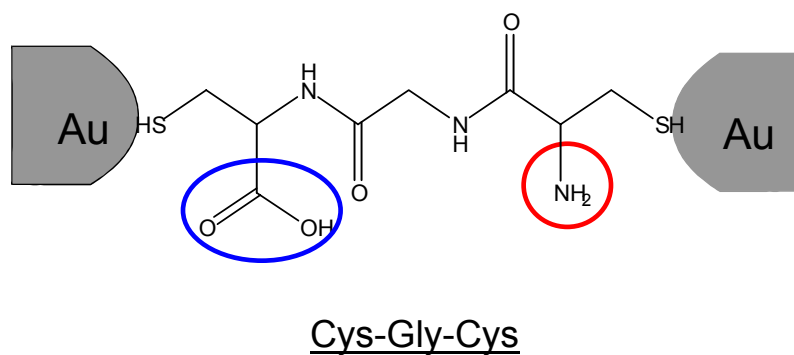


Molecular Junction Sensor



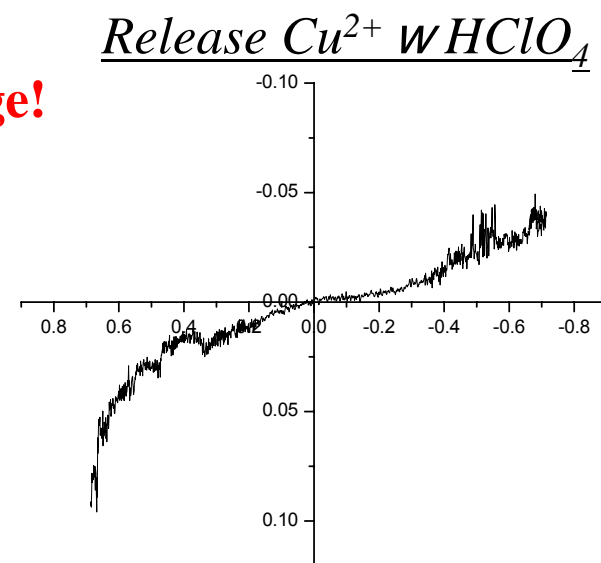
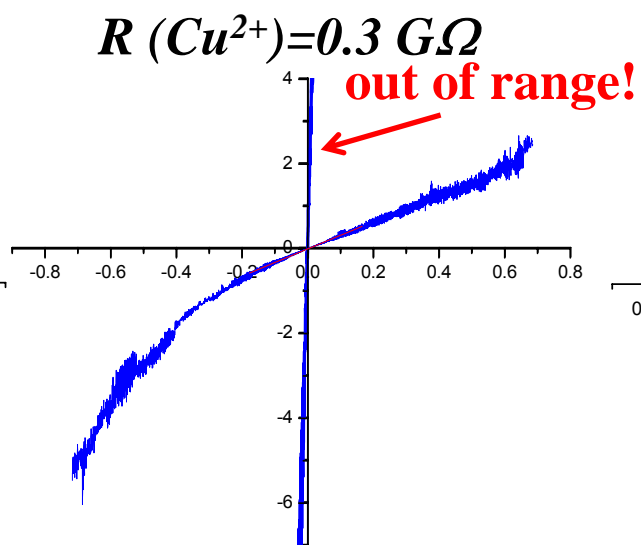
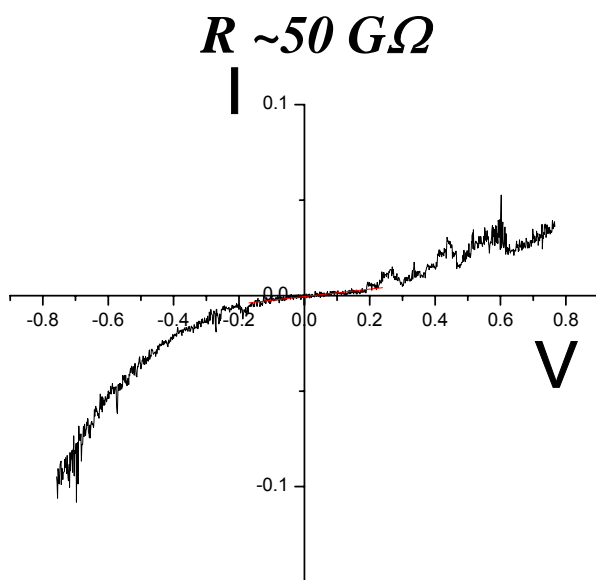
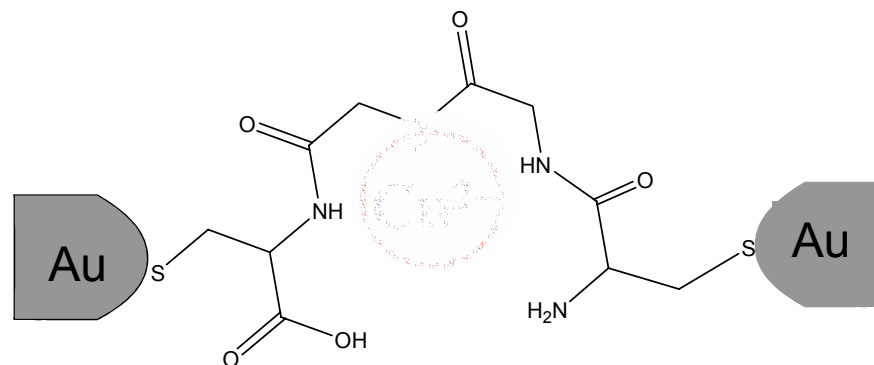
- ✓ Direct approach
- ✓ Single molecule detection

pH Sensor



Xiao XY, Xu BQ, Tao NJ, JACS 126 (17): 5370-5371 MAY 5 2004

Metal Ion Detection

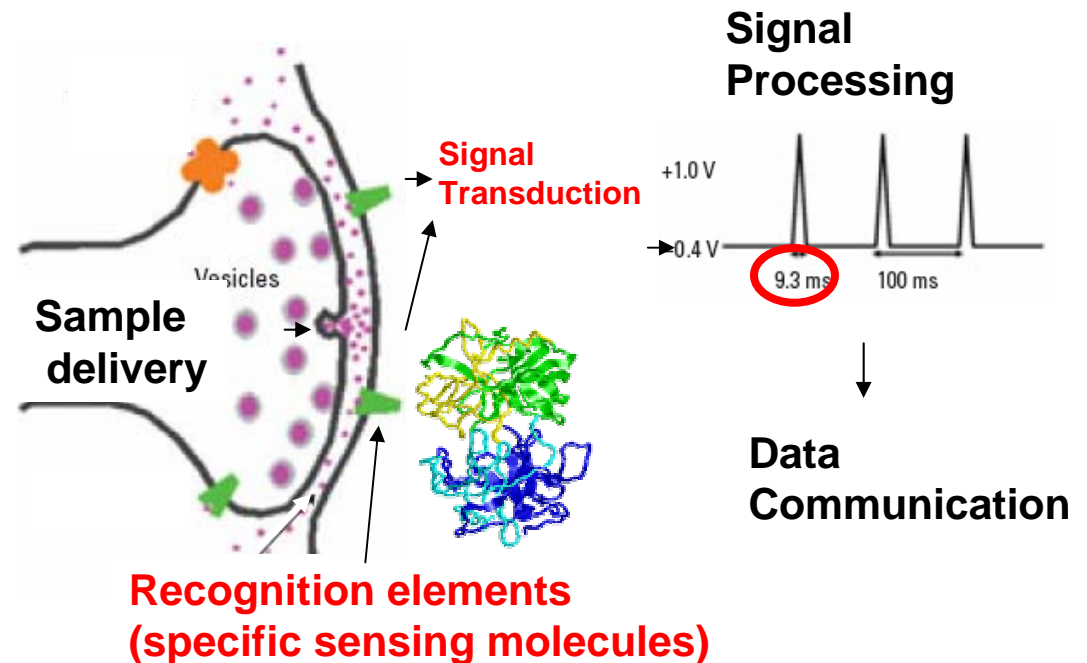


- ✓ Conductance increases upon Cu^{2+} binding
- ✓ Metal ion dependence (Cu^{2+} vs. Ni^{2+} ions)

300 higher for Cu^{2+} , 100 higher for Ni^{2+}

Xiao XY, Xu BQ, Tao NJ, Angew. Chem. (asap) 2004

What is the progress achieved to date trying to emulate nature ?



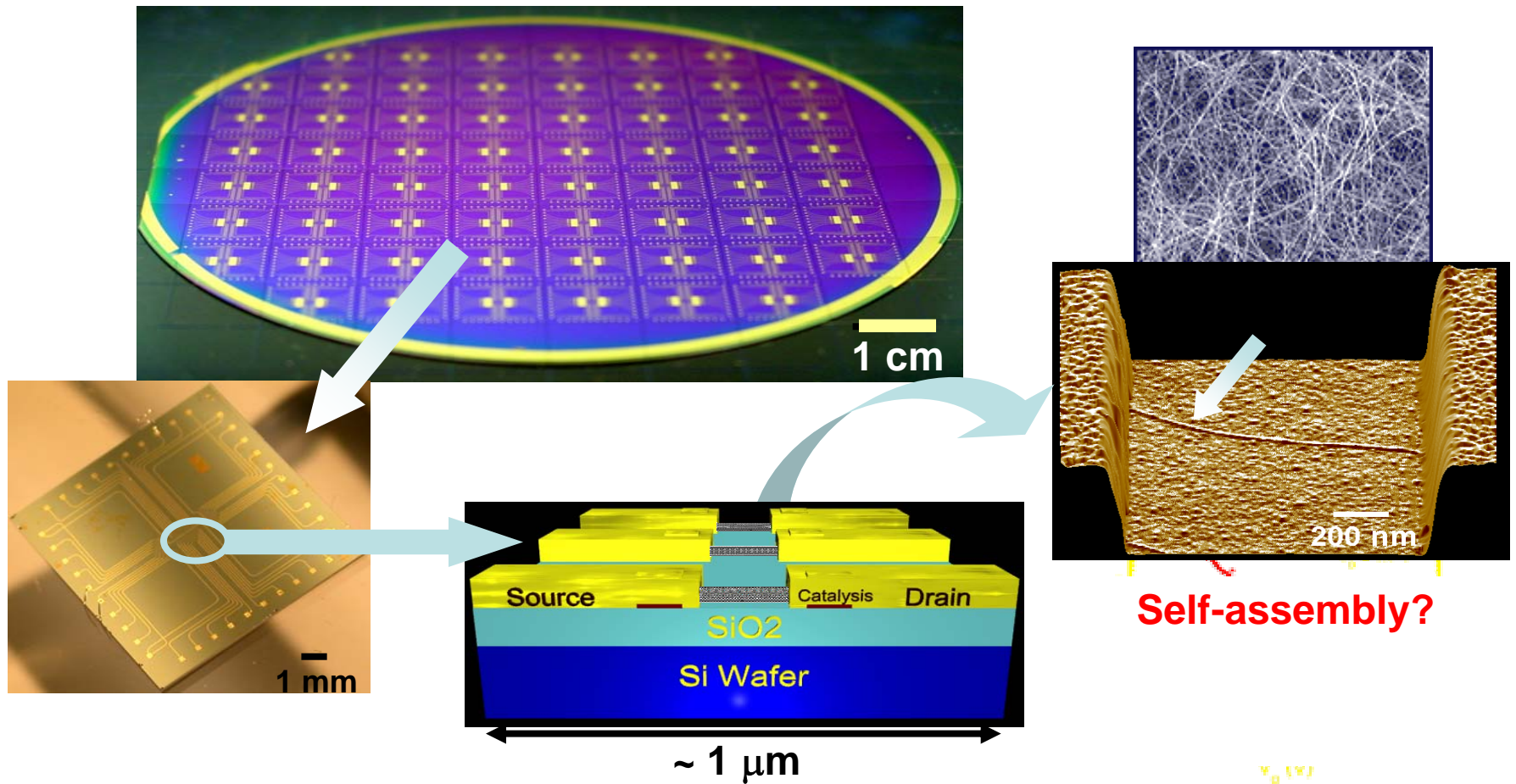
An Integrated Nanosensor for Simultaneous Detection of A Range of Species

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



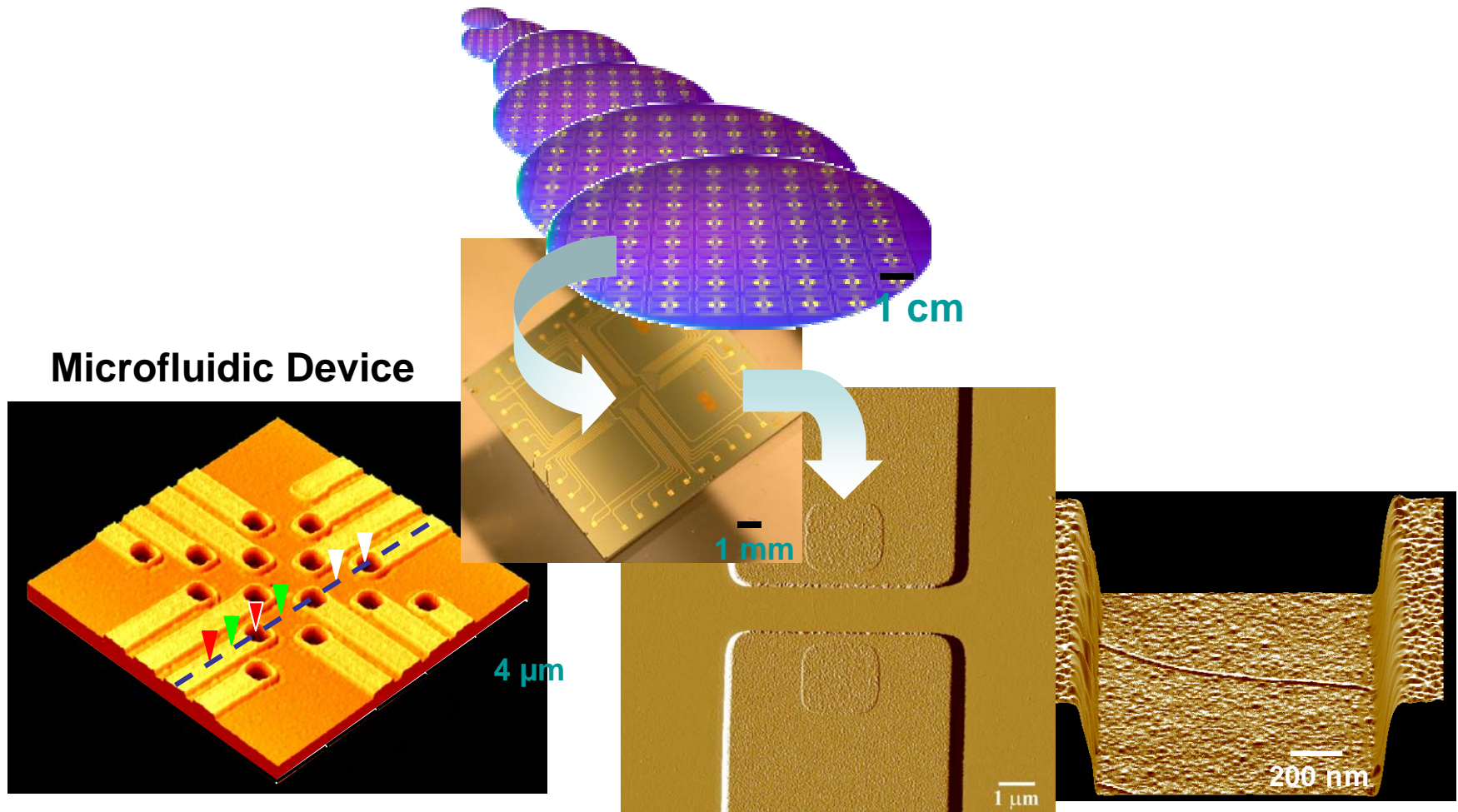
What are the challenges ahead ?

Microtechnology Meets Nanotechnology - Interconnection Issues

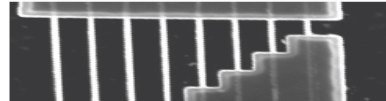
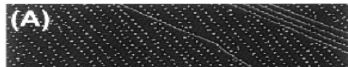


Challenges Ahead

Microtechnology Meets Nanotechnology - Sample Delivery



Nano-Solution to Big Sensor Problems?



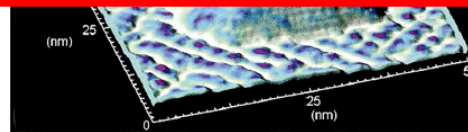
Unique Features:

- ✓ 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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