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

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Need of Environmental Sensors

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

District to Issue Warning on Lead

Youngsters, Fetuses Are Most Vulnerable

Studies Find IQ, Socialization Problems

Ammonia release, Feb. 1994
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
Emulating Nature…

Data processing, Action, (cm-m)

Brain (mm-cm)

Neurons (um)

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

Atoms of carbon

Spacing ~ 1.5 Å

macro

micro

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?
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

Nanocontacts

Nanotubes/Nanowires

Nanoparticles

Molecular Junctions

Conducting polymers

SiN

atomic scale

Au

Si
Recognizing element trapped on the junction

Conducting Polymer FET Sensors

- Polymer
- Gold pads
- Si$_3$N$_4$ window
- Gap smaller than 60 nm
Glucose Sensor

- 300 times faster
- 100 times more sensitive than similar sensors on 20 µm gap.

Time response: ~ 200 ms
Sensitivity: 1 nA/mM
Detection Limit: 1 µM
Why nanosensors are better than microsensors?

- Gap smaller than 60 nm
- Gap ~ (20 x 900) µm
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: \( \gamma \) = peptides

20 amino acids:

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✓ 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

Complexation of ions with peptides

Polyaniline - Peptide A

Working in parallel

Polyaniline - Peptide B

Polyaniline
Copper and nickel ion sensors

- Changes physical-chemical structure and electrical properties → Real time detection
- D.L.($\text{Cu}^{2+}$): 4 ppt, D.L.($\text{Ni}^{2+}$): 22.5 ppt
- Reusable device (6 times) for metal ion detection
- Drinking water analysis (Tempe): $(0.34 \pm 0.03)$ ppm. Result in agreement with AAS.

Comparison with 100 µm gap FET (polycarbazole):

✓ $4 \times 10^4$ times more sensitive
✓ 500 times faster

Other example of conducting polymer nanojunctions:

- Ammonia/HCl vapor detection:

![Graph showing current (I) vs. time (sec.) for 50 ppm HCl and 100 ppm HCl]

- 50 ppm HCl: 105 s (0.9 Rmax)
- 100 ppm HCl: 10 min (0.9 Rmax)

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

- **Nanocontacts**
  - SiN
  - Au
  - Si
  - atomic scale

- **Nanotubes/Nanowires**

- **Nanoparticles**

- **Molecular Junctions**

- **Conducting polymers**
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

H.J. Dai and co-workers
(http://www.stanford.edu/dept/chemistry/faculty/dai/group/hongjie.html)

R.M. Penner and co-workers (http://www.chem.uci.edu/people/faculty/mpenner/)

Nanowires

Z.L. Wang and co-workers
(http://www.nanoscience.gatech.edu/zwang/Research.htm)

Nanobelts

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

Protein Adsorption on bare carbon nanotubes

Adding protein

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

Boussaad S, Tao NJ, Zhang R, Hopson T, Nagahara LA
CHEM. COMM. (13): 1502-1503 2003
Conductance vs. Electrochemical Gate Potential

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

\[ \#_{\text{CytC}} = \frac{4 \times 10^{-10} \text{ F/m} \times 10^{-6} \text{ m} \times 0.09 \text{ V}}{10 \times 1.6 \times 10^{-19} \text{ C}} = \sim 20 \text{ CytC molecules} \]
Arrays of Electrically Wired Nanosensing Elements

- Nanocontacts
- Nanotubes/Nanowires
- Nanoparticles
- Molecular Junctions
- Conducting polymers
Molecular Junction Sensor

- Target
- Molecule that can recognize a target (Molecular Probe)

- Direct approach
- Single molecule detection
pH Sensor

Cys-Gly-Cys

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

R \approx 50 \, G\Omega
\frac{V}{I}

\begin{align*}
R (Cu^{2+}) &= 0.3 \, G\Omega \\
\text{Release } Cu^{2+} \text{ with } HClO_4
\end{align*}

- 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
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

Self-assembly?
Challenges Ahead
Microtechnology Meets Nanotechnology
- Sample Delivery

Microfluidic Device
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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