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

NJ Tao

Arizona State University
Need of Environmental Sensors

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

By Justin Blum
Washington Post Staff Writer

Recent testing at 15 D.C. public school buildings found high lead levels in water from fountains at two of the 9

Youngsters, Fetuses Are Most Vulnerable

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 decline is about 54,000 kids, 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

What role will ‘NANO’ play?

An Integrated Sensor

• Sample Delivery
• Sensing Elements
• Signal Processing & Transmission

What role will ‘NANO’ play?

This will happen no matter what !!!
NANO-Solution?

Particle

Resonator

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

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

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).

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

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

Adding protein

\[ \Delta Q = C \Delta V \]

\[ C_{SWNT} = 4 \times 10^{-10} \ F/m \]

\[ L_{SWNT} = 1 \ \mu m \]

\[ Cytc = +10 \ e/\text{protein} @ pH 7 \]

\[ \# Cytc = \frac{4 \times 10^{-10} \ F/m \times 10^{-6} \ m \times 0.09 \ V}{10 \times 1.6 \times 10^{-19} \ C} \]

\[ \approx 20 \ Cytc \text{ molecules} \]
Based on the AFM images, the number of cytc molecule adsorbed onto the SWNT is ~30-40.
Pd Nanowire Hydrogen Sensor

Pd Nanowire Hydrogen Sensor

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

Response of the sensor to four gases

- 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: \( \gamma \) = peptides

20 amino acids:

<table>
<thead>
<tr>
<th>Gly</th>
<th>Ala</th>
</tr>
</thead>
<tbody>
<tr>
<td>Val</td>
<td>Leu</td>
</tr>
<tr>
<td>Ile</td>
<td>Pro</td>
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<tr>
<td>Pen</td>
<td>Tyr</td>
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</tr>
<tr>
<td>Asp</td>
<td>Glu</td>
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<tr>
<td>Apn</td>
<td>Gln</td>
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</table>

✓ 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

![Graphs a, b, c showing conductance vs. pH](image-url)
Metal Ion Detection

$R = 52 \, G\Omega$

$R \,(Cu^{2+}) = 0.3 \, G\Omega$

Release $Cu^{2+} \, wHClO_4$

out of range!
Metal Ion Detection - *Sequence Dependence*

<table>
<thead>
<tr>
<th>Peptides</th>
<th>Number of Ligands</th>
<th>Conductance of peptide</th>
<th>Conductance of Cu complex</th>
<th>Conductance ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cysteamine-Cys</td>
<td>2</td>
<td>$1.8 \times 10^{-4} G_0$</td>
<td>$1.9 \times 10^{-4} G_0$</td>
<td>$\sim 1.1$</td>
</tr>
<tr>
<td>Cysteamine-Gly-Cys</td>
<td>3</td>
<td>$4.2 \times 10^{-6} G_0$</td>
<td>$9.1 \times 10^{-6} G_0$</td>
<td>$\sim 2$</td>
</tr>
<tr>
<td>Cys-Gly-Cys</td>
<td>4</td>
<td>$5.3 \times 10^{-6} G_0$</td>
<td>$2.3 \times 10^{-5} G_0$</td>
<td>$\sim 4$</td>
</tr>
<tr>
<td>Cysteamine-Gly-Gly-Cys</td>
<td>4</td>
<td>$5.0 \times 10^{-7} G_0$</td>
<td>$1.6 \times 10^{-4} G_0$</td>
<td>$\sim 300$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Ni$^{2+}$: $5.5 \times 10^{-5} G_0$</td>
<td>$\sim 100$ (for Ni$^+$)</td>
</tr>
</tbody>
</table>

- 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

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
Acknowledgements

- Erica Forzani
- Xiaoyin Xiao
- Bill Xu
- Xiulan Li
- Win Ly
- Al Diaz
- John Zhang
- Larry Nagahara
- Islamshah Almani
- Ruth Zhang
- Ray Tsui