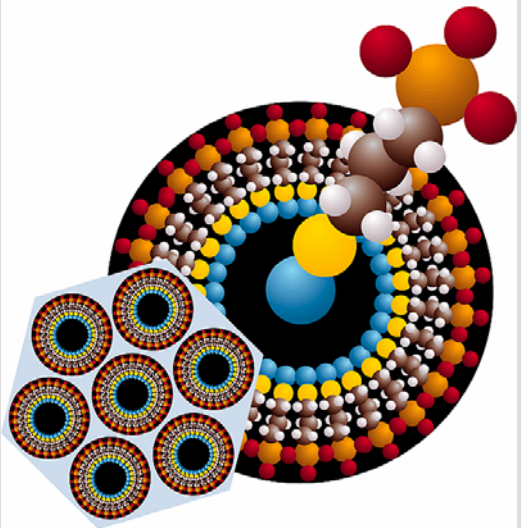
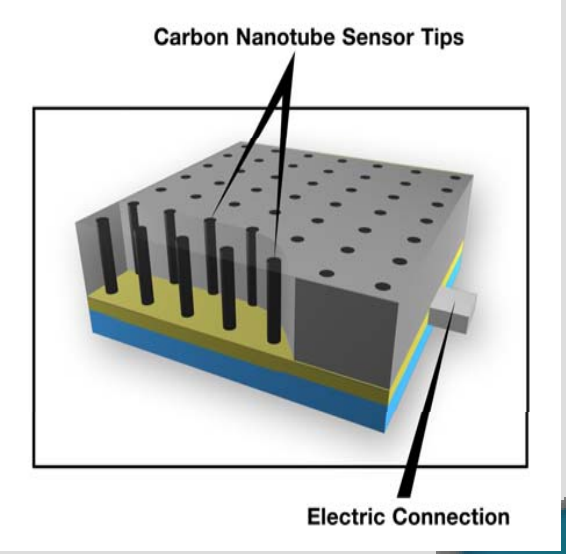
# Electrochemical Sensors and Biosensors Based on Functional Nanomatrials for Environmental Monitoring


Yuehe Lin
Chief Scientist
yuehe.lin@pnl.gov
Environmental Technology Division
Pacific Northwest National Laboratory



# Electrochemistry & Nanotechnology Lab

## Environmental Molecular Sciences Laboratory (EMSL)

**EMSL**

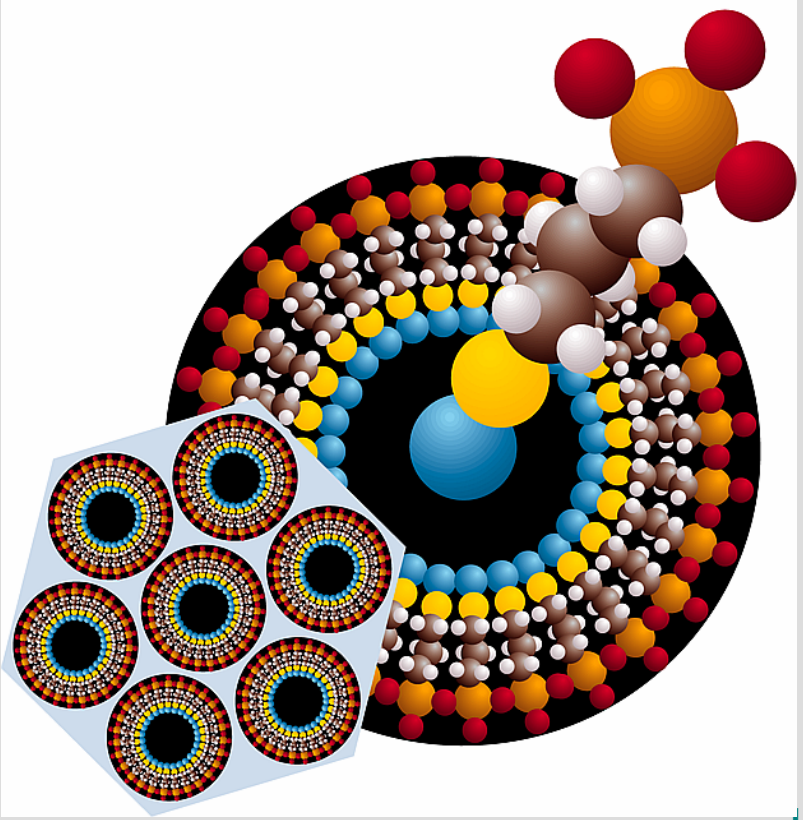
**DOE User Facility**

Nanotechnology & Electrochemical Sensors and Biosensors

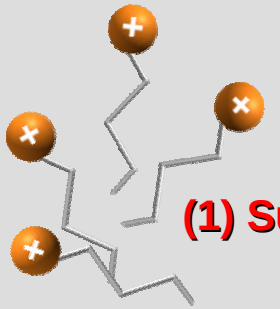
* ***functionalized nanoporous silica***
* ***carbon nanotubes***
* ***nanoparticle labels/immunosensors and DNA sensors***

# I. Electrochemical Sensors Based on *SAMMS* for Detection of Toxic Metals and Radionuclides

*SAMMS: Self-Assembled Monolayer on Mesoporous Silica*

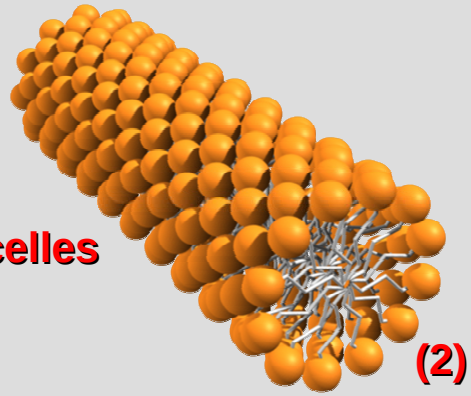


# Nanostructured Mesoporous Silica



Micelles

(1) Surfactants form micelles

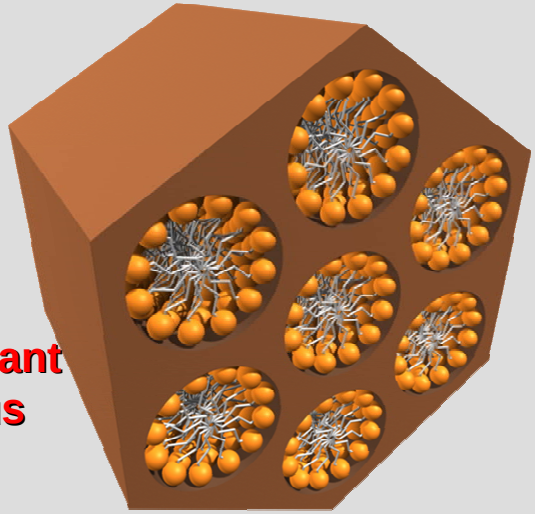


Surfactants

$R\text{-}N^{+}\text{-}(CH_3)_3X^{-}$

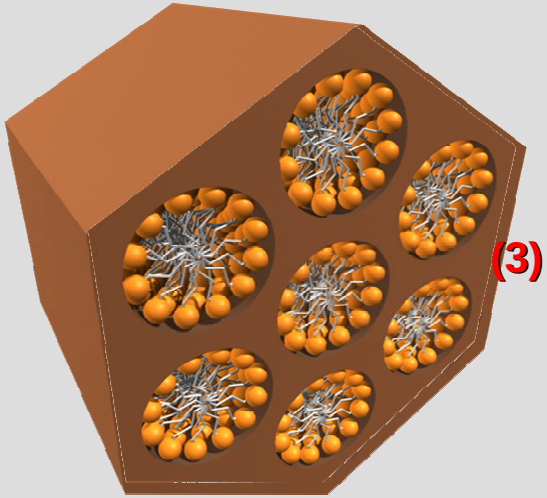
(2) Ceramic precursor binds to head groups and form a condensed ceramic phase

Sol-gel



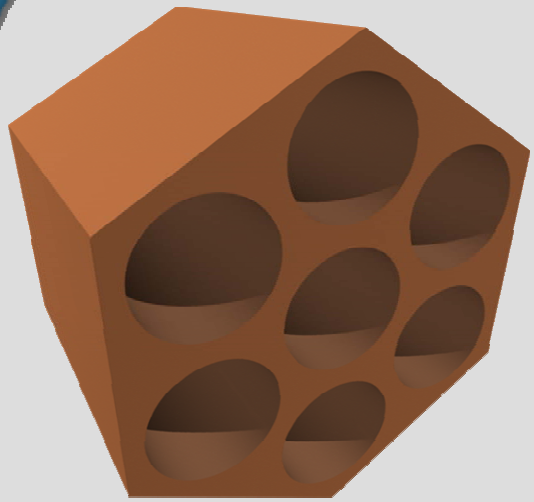
Template removal

(3) Removal of surfactant to form mesoporous materials

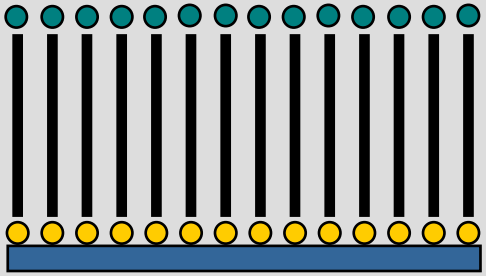


# Synthesis of SAMMS

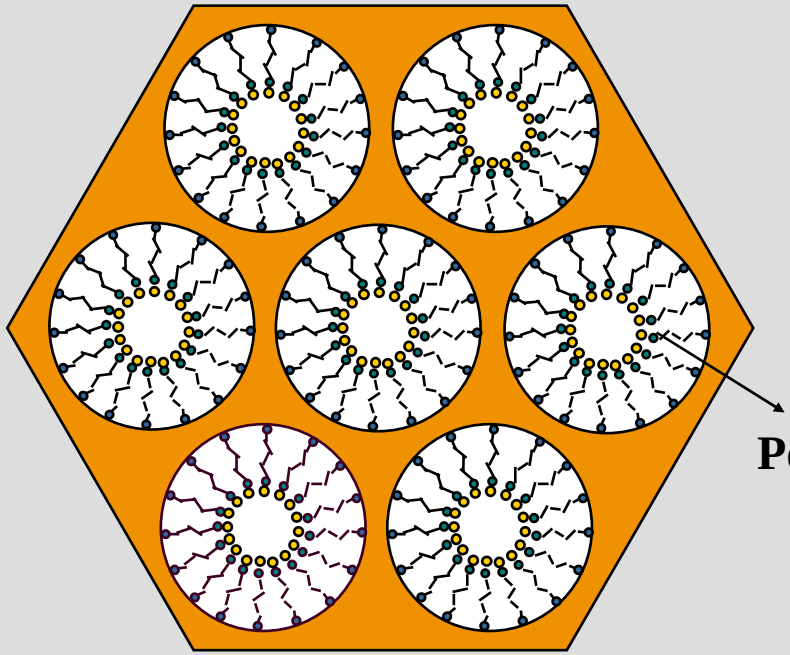
A. Ordered mesoporous silica



B. Self-assembled monolayers



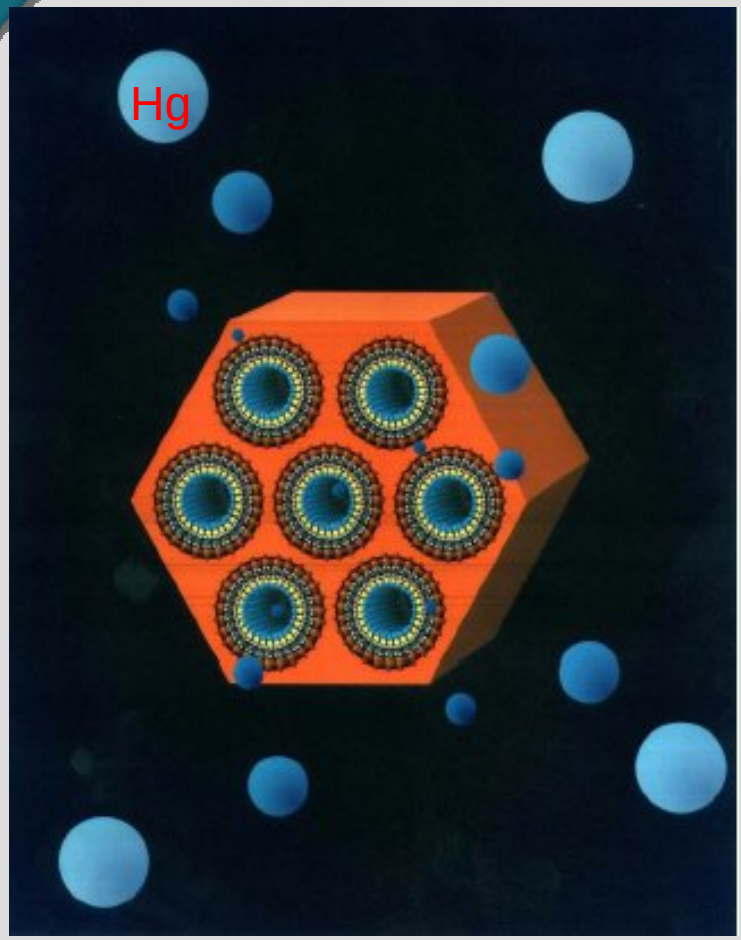
C. Self-assembled monolayers on mesoporous supports (SAMMS)




**One end group of the functionalized monolayers is covalently bonded to the silica surface and the other end group can be used to bind metal ions**

*Feng, Fryxell, Wang, Liu, Kemner, Science 276, 923 (1997)*

# Advantages of SAMMS for Sensing




- **High sensitivity**

  *High capacity due to high surface area (1000 $m^2/g$) and high-density of functional groups*

- **High selectivity**

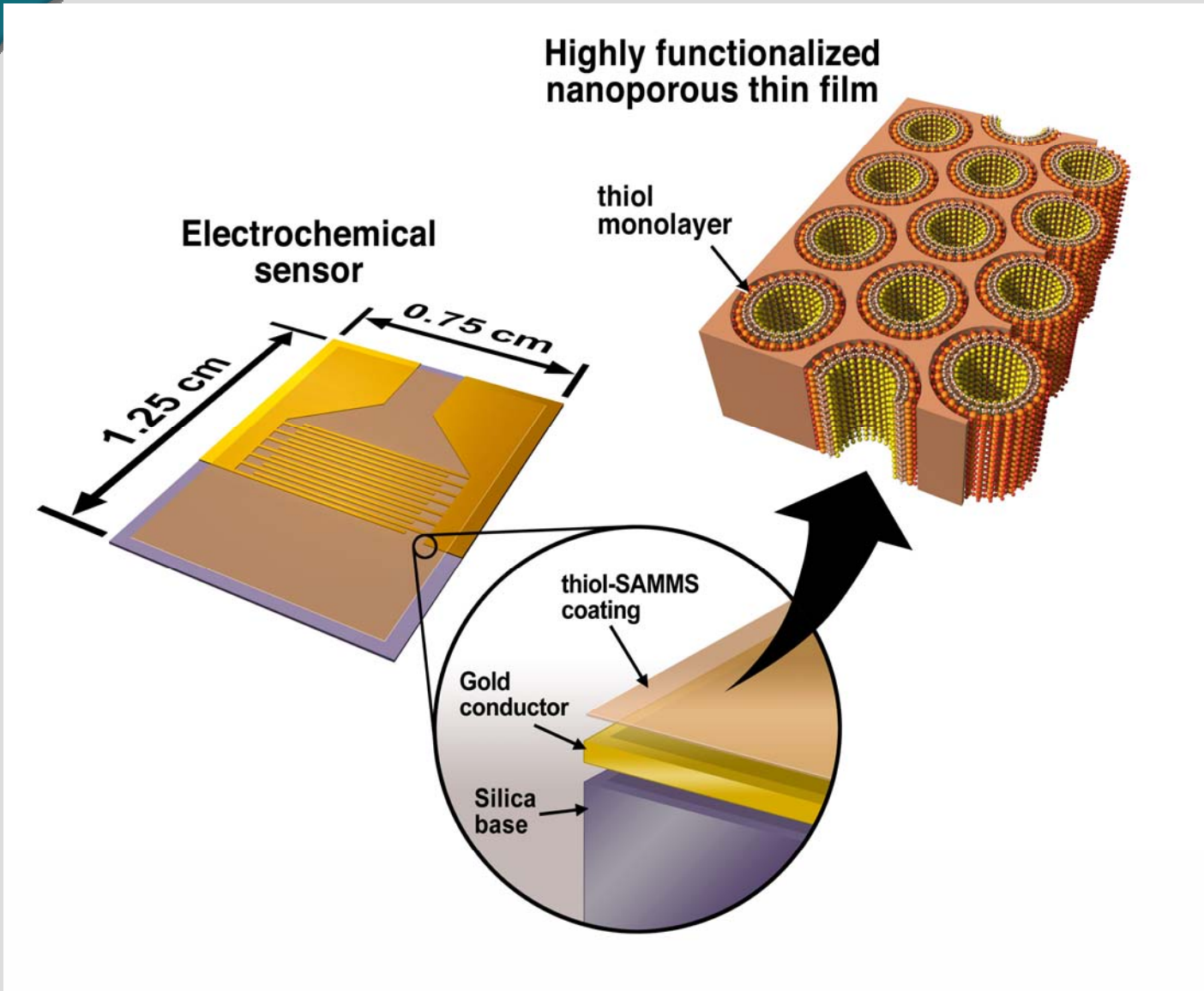
  *The interfacial chemistry can be easily tuned for binding different metal ions*

- **Fast Response**

  *Open pores for fast adsorption/fast response for sensing*

Lin*, Yantasee, Fryxell, "Electrochemical Sensors Based on Functionalized Nanoporous Silica." ***Ency. Nanoscience & Nanotechnology,*** pp. 1051-1061. Marcel Dekker, 2004

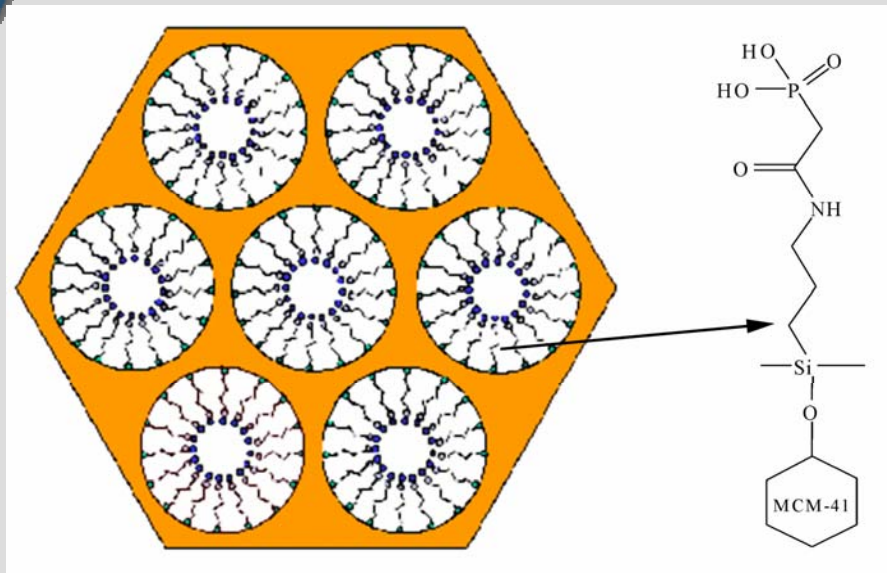
# Electrochemical Sensors Based on SAMMS Thin-Film



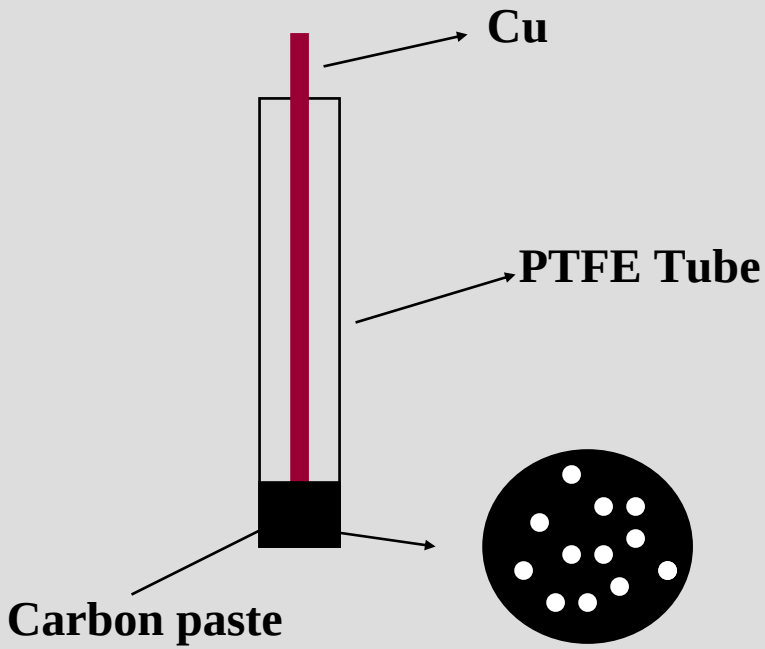

*Yantasse, Lin*, Li, Fryxell, Zemanian, Viswanathan, Analyst, 128, 899-904, 2003*

# Electrochemical Sensors Based on Carbon Paste Electrode:

***Directly embed SAMMS particles in conductive carbon paste matrix***




**Ac-Phos SAMMS**




**20% SAMMS particles in carbon paste matrix**

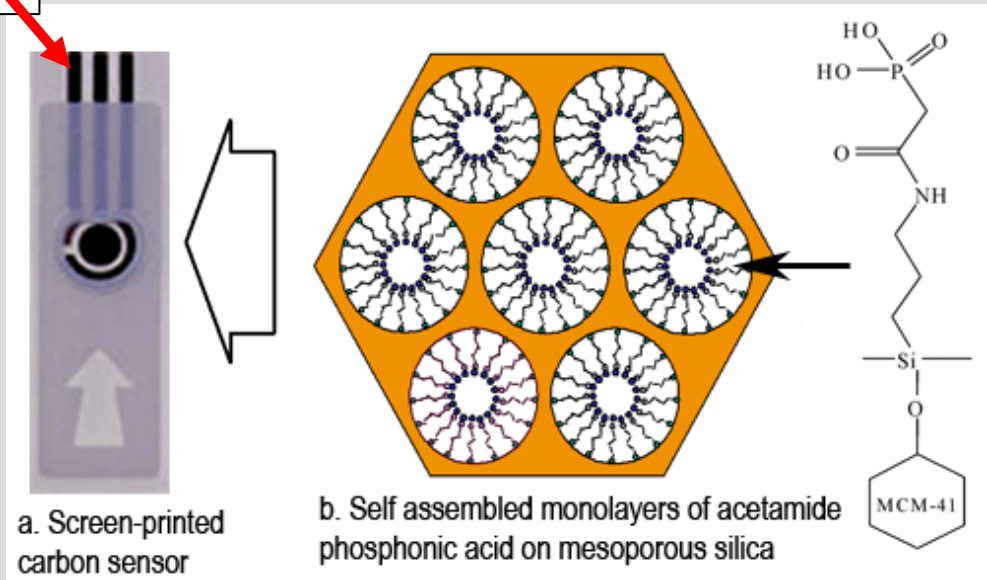
## Carbon Paste Electrode

*Yantasee, Lin*, Fryxell, **Electroanalysis**, 16, 870 (2004)*

*Yantasee, Fryxell, Lin*, J. Nanosci. Nanotech., 5, 1537(2005)*

# Electrochemical Sensors + Hand-held Detector

- **On-site monitoring of toxic metal ions**
- **Biomonitoring of Children's Pb poison**

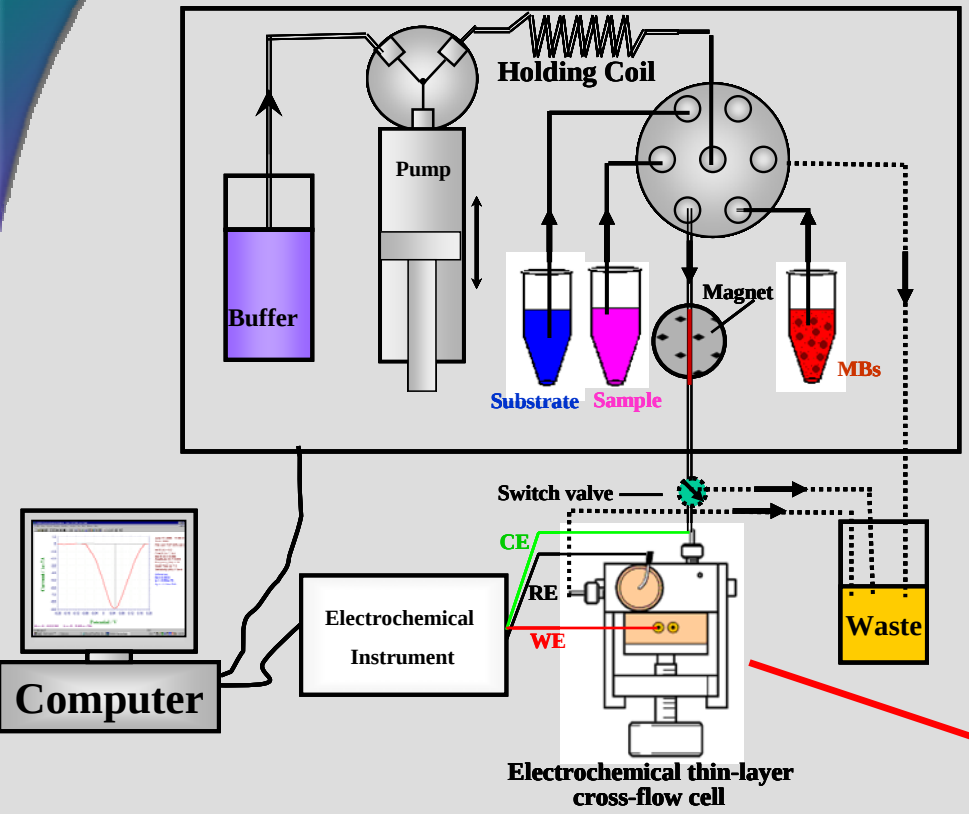



a. Screen-printed carbon sensor

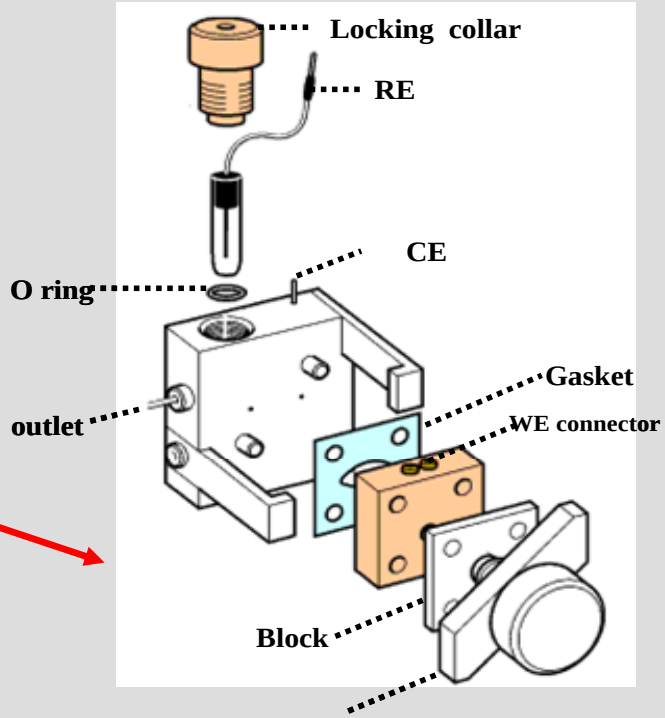
b. Self assembled monolayers of acetamide phosphonic acid on mesoporous silica

Yantasee, Fryxell, Lin*,
***Electrochemistry Communications,***
7, 1170-1176, 2005

# Electrochemical Sensors + Automatic Sequential Injection Analytical System for On-Line Process Monitoring



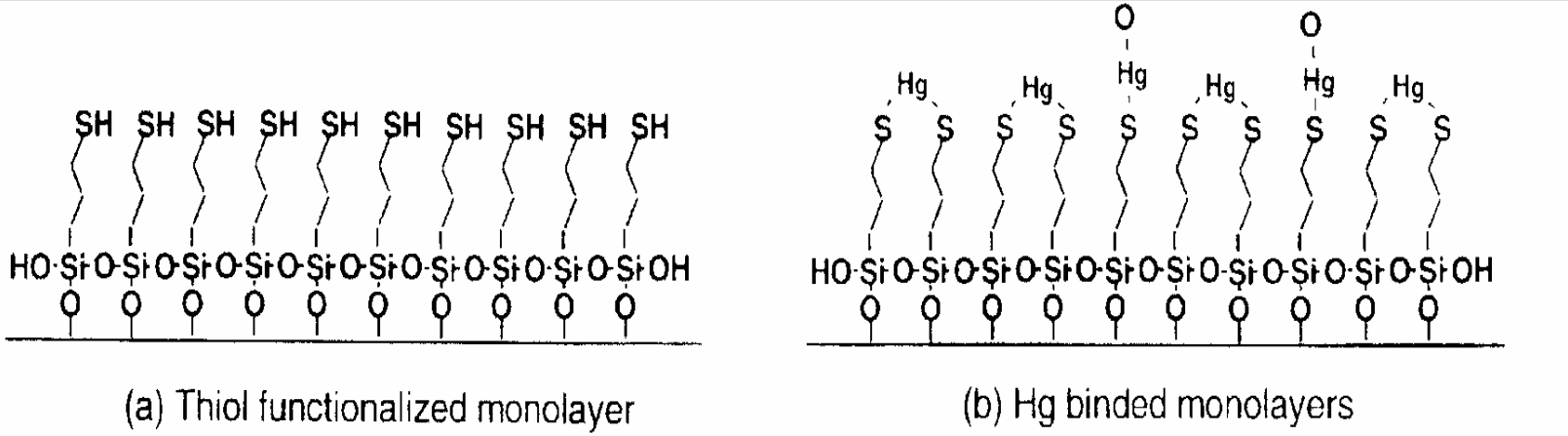

(A)




(B)

Yantasee, Fryxell, Lin*, ***Talanta***, 68, 256 (2005)

# Thiol-SAMMS for Mercury




» **Surface coverage of monolayers up to 76%**

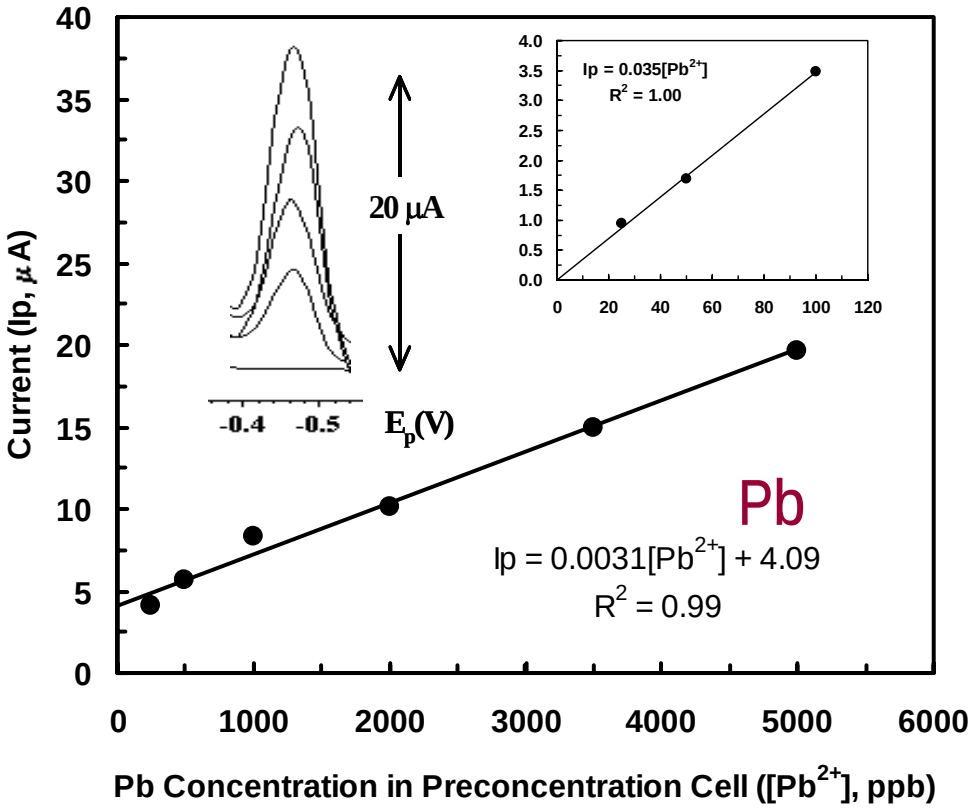
» **High affinity for Hg (Kd up to 340,000)**

» **Fast Hg-binding kinetics (0.5 ppm to 0.5 ppb; < 2 min)**

» **Loading capacity for Hg: 0.64 g/g**

*Feng, Fryxell, Wang, Liu, Kemner,*
*Science 276, 923 (1997)*

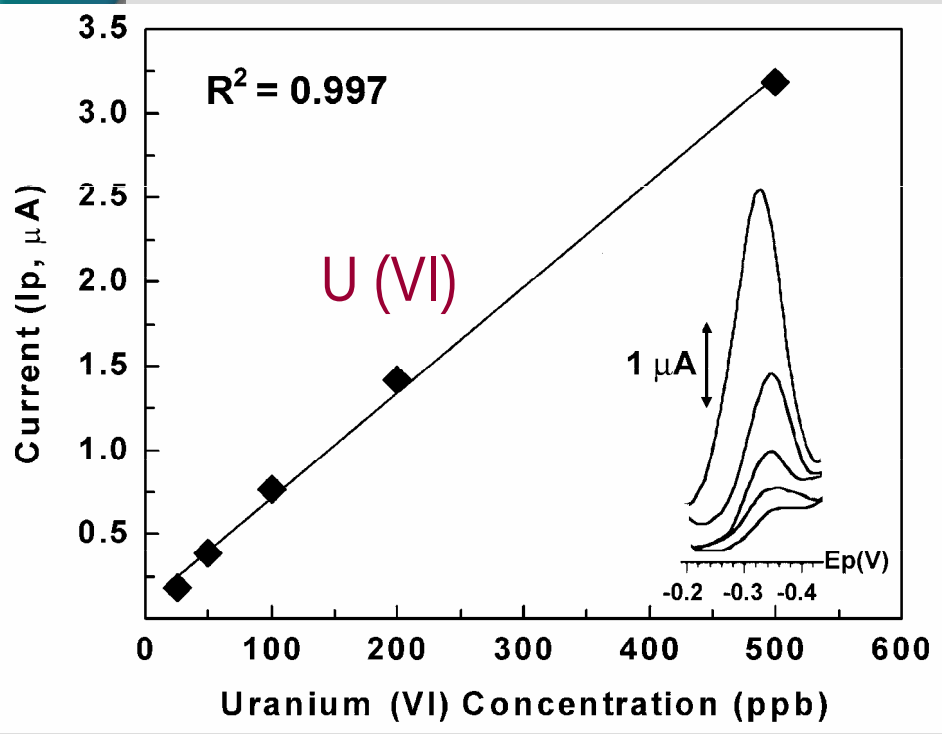
# Electrochemical Sensors Based on SAMMS Thin-Films for Detection of Toxic Metal Ions

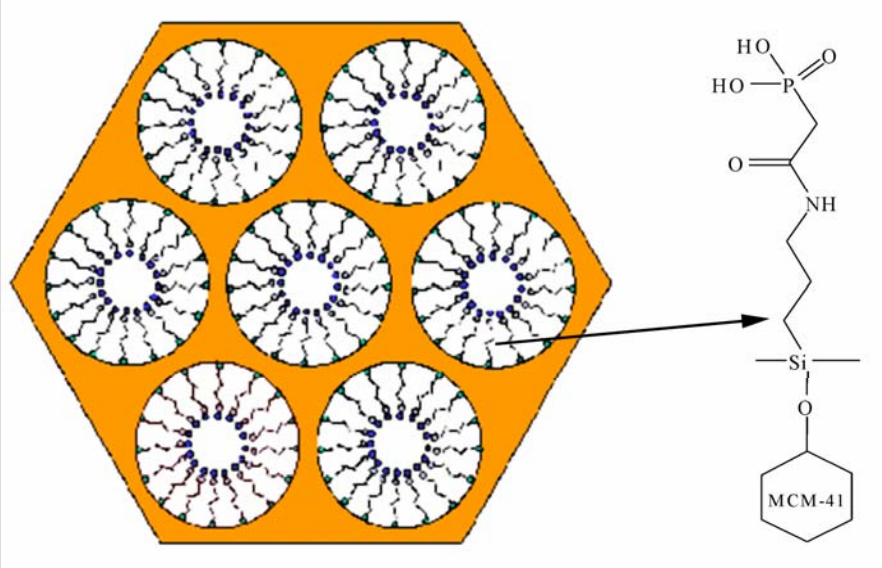



- High sensitivity, 0.5 ppb
- High selectivity
- Pb, Hg, Cd

*Yantasse, Lin*, Li, Fryxell, Zemanian, Viswanathan, Analyst, 128, 899-904, 2003*

# Electrochemical Sensor Based on Phosphonic Acid SAMMS for Detection of U(VI)




**Ac-Phos SAMMS**

**Detection limit: 1 ppb**

*Yantasee, Lin*, Fryxell, Electroanalysis, 2004, 16, 870-873*

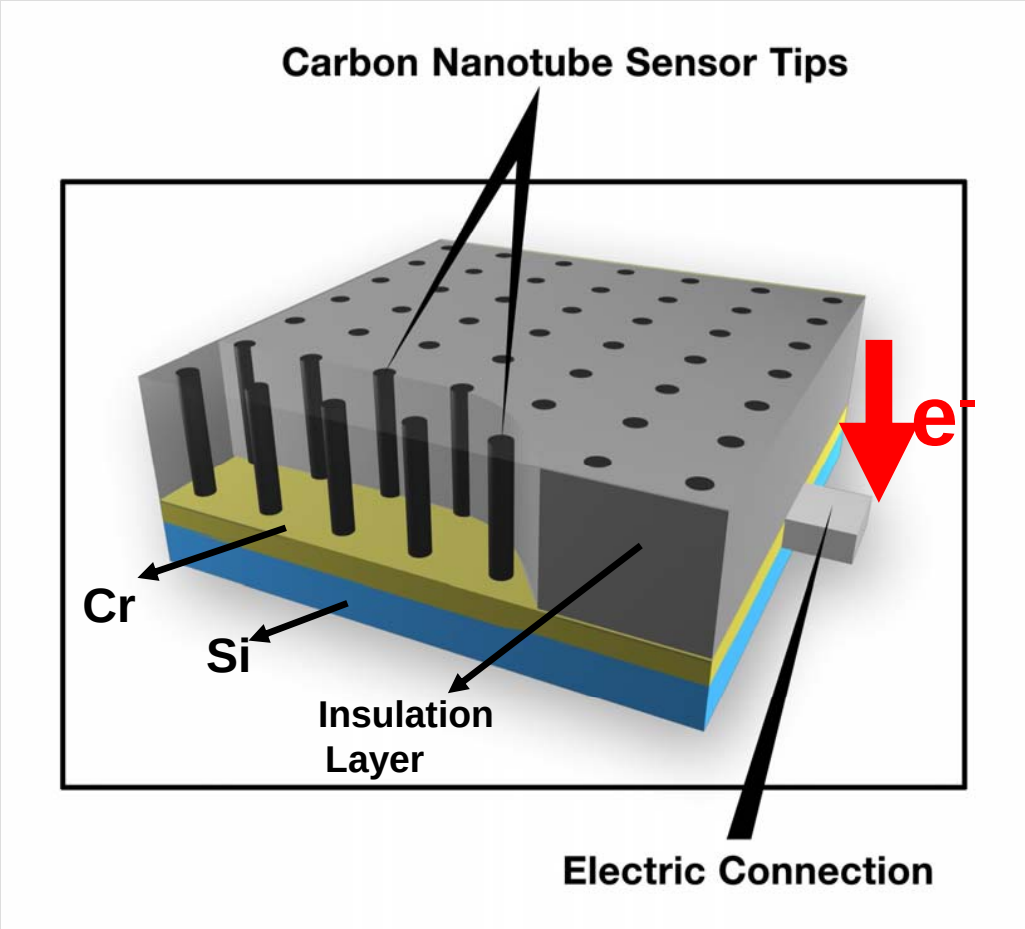
*Fryxell, Lin,Fiskum, Birnbaum, Environ. Sci. & Technol., 2005 39,1324-1331.*

*Lin et al. Environ. Sci. & Technol., 2005,39, 1332-1337.*

# Summary on SAMMS-Sensors

- Developed a new class of nanoengineered sorbent, SAMMS. The materials have fast sorption kinetics, high selectivity and loading capacity for adsorption of heavy metals and U(VI)
- Successfully developed two electrochemical sensors by embedding thiol- and phosphonic acid SAMMS on carbon paste electrodes. Demonstrated the enhanced sensitivity for monitoring of toxic metals and U(VI).
- Developed a nanoengineered electrochemical sensor by immobilization of functionalized nanoporous silica thin-film on surface of microchip-based Au microelectrode array. Demonstrated the sensitive detection of toxic heavy metals.

# II. Nanosensors Based on Carbon Nanotube Nanoelectrode Arrays



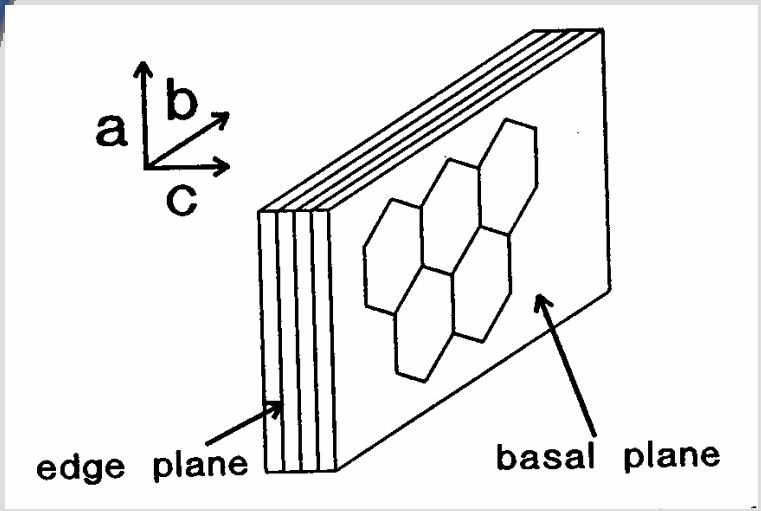

Lin et al, "Biosensors Based on Carbon Nanotubes." ***Ency. Nanoscience & Nanotechnology,*** pp. 361-374. Marcel Dekker, 2004

# Advantages of Carbon Nanotubes as Electrodes

- Good conductivity (similar to graphite, HOPG)
- Wide potential window
- Easy to be functionalized

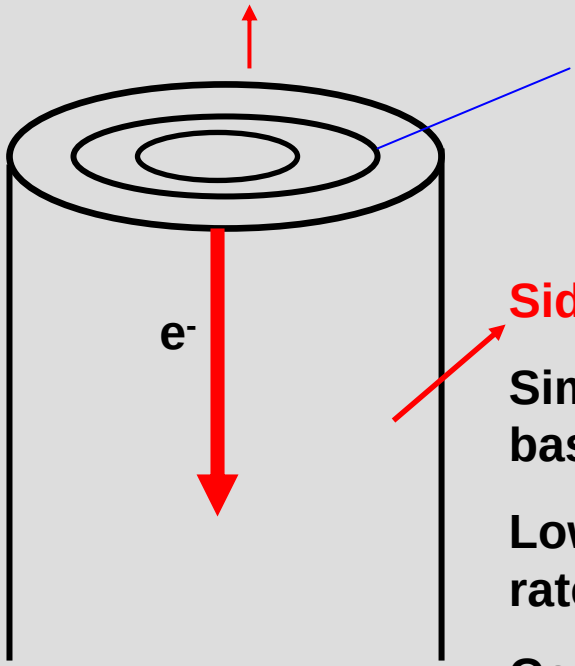
  Enzymes can be directly attached to ends of CNTs
- Ultra small size of CNTs (30-60 nm) for making nanoelectrode arrays

# Structures and Electron Transfer Rate of MWCNT




Highly Ordered graphite sheet

**Open-end:** similar to a graphite edge-plane, fast electron transfer rate




WMCNT

**Side-wall:**

**Similar to graphite basal plane.**

**Low electron transfer rate**

**Contribute to background current (capacitance)**

**To achieve the highest S/N, the side-walls need to be insulated to reduce the background.**

# Why Nanoelectrode Arrays

- **Single Nanoelectrode**
  - Single carbon nanotube (~ 50 nm)
  - Improved mass transfer
  - Fast response
  - High S/N ratio
  - But low current (pA), need expensive signal detection/amplification electronics.
- **Nanoelectrode array** (consists millions of nanoelectrodes)
  - Results in magnified signal, no need for expensive electronics
  - S/N improves 3-4 orders of magnitude compared with single nanoelectrode.

yl4 Yuehe Lin, 7/25/2004

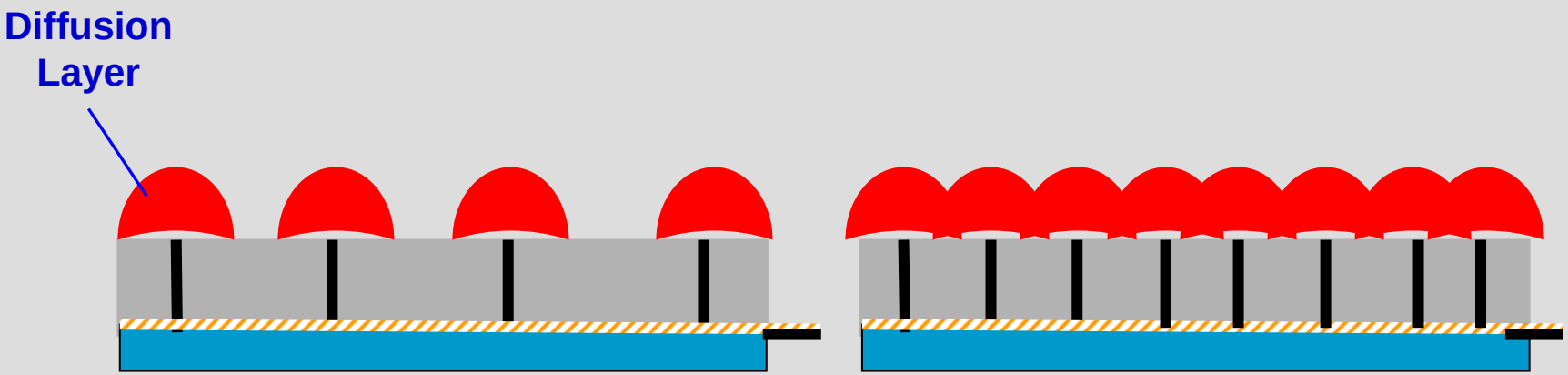
# Why Control the density of CNT electrodes

1. **Total current of nanoelectrode arrays ( 1-2 x $10^6$ CNT nanoelectrode) :**

   **Total** $I = n\,I_i$

2. **Density too high, diffusion layer overlap, loss the nanoelectrode property**

   Total $I < n\,I_i$




**Perfect Nanoelectrode Array**

**Distance/diameter ratio > 10**

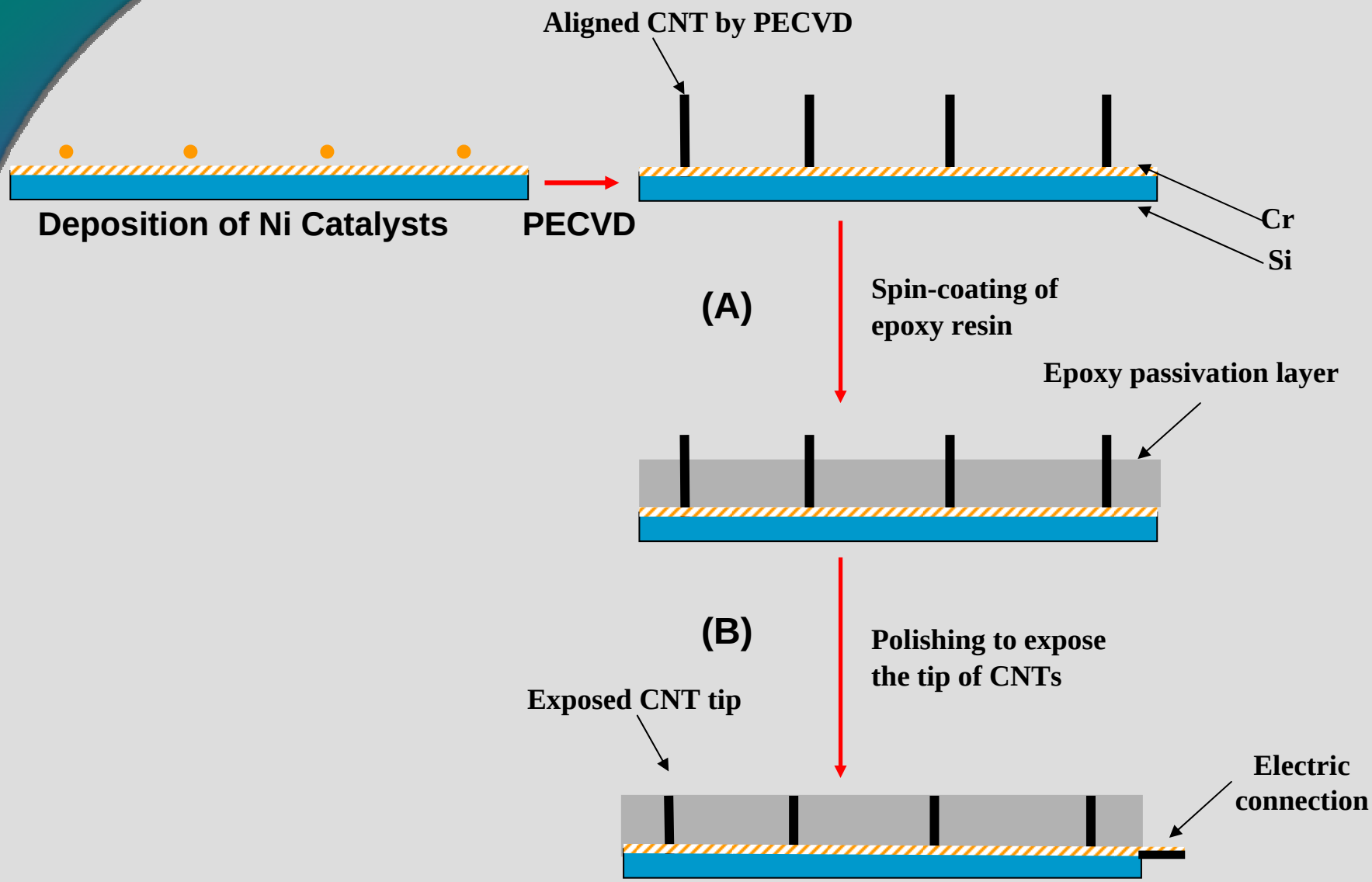
**Diffusion layers do not overlap**

**Nanoelectrode Array (high density)**

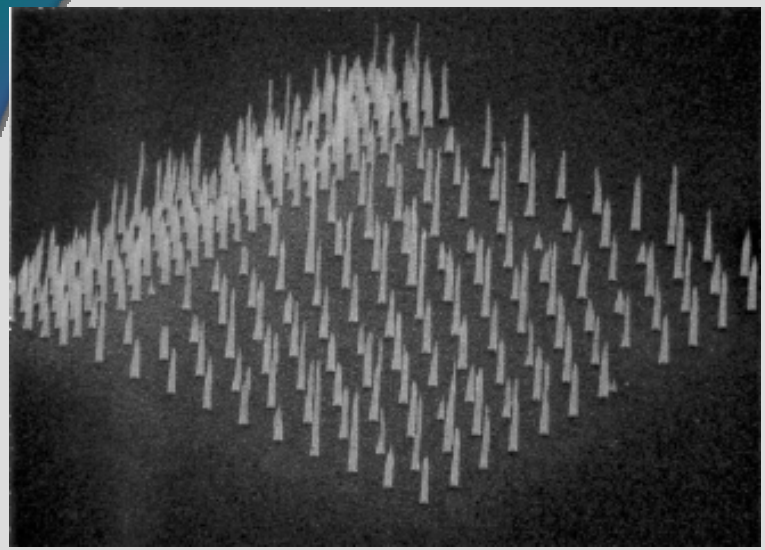
**Distance/diameter ratio < 10**

**Diffusion layers overlap**

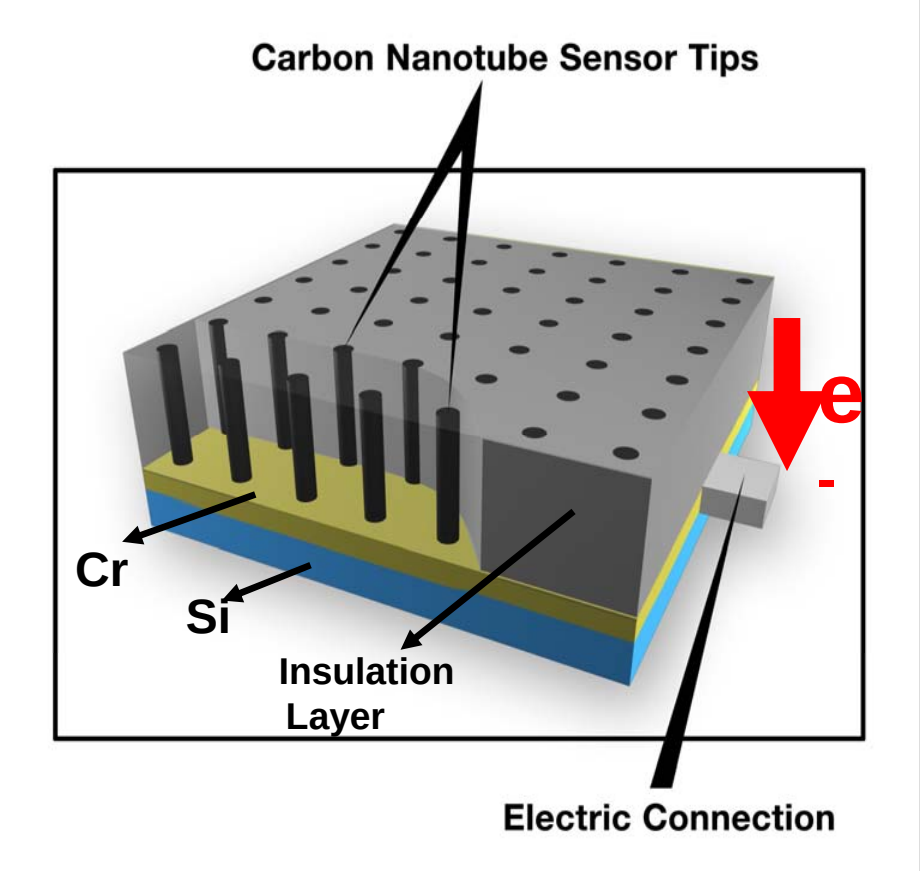
# Fabrication of CNT Nanoelectrode Array




Tu, Lin, Ren, *Nano Lett.* 2003, 3,107-109



Carbon Nanotube Arrays




Patent Pending

# Applications of CNT-NEAs

## I. *SW Stripping Voltammetric Analysis of Metal Ions*

- ***Stripping voltammetry is a sensitive analytical technique for metal analysis***
- ***$Pb^{2+}$*** **in sample is reduced and deposited on electrode surface**
- **After accumulation for 3 min, the potential of electrode is scanned from -1.0 V to 0 V**
- **Pb is oxidized to $Pb^{2+}$ and the oxidation current is proportional to the concentration of $Pb^{2+}$ in solution.**

- **Accumulation Step:**

  ***$Pb^{2+}$ + 2 e- ---> Pb  -1.0 V***

- **Stripping Step (measurement):**

  ***Pb ---> $Pb^{2+}$ + 2 e-  -1.0 V to 0 V***

# Applications of Nanosensors Environmental Monitoring

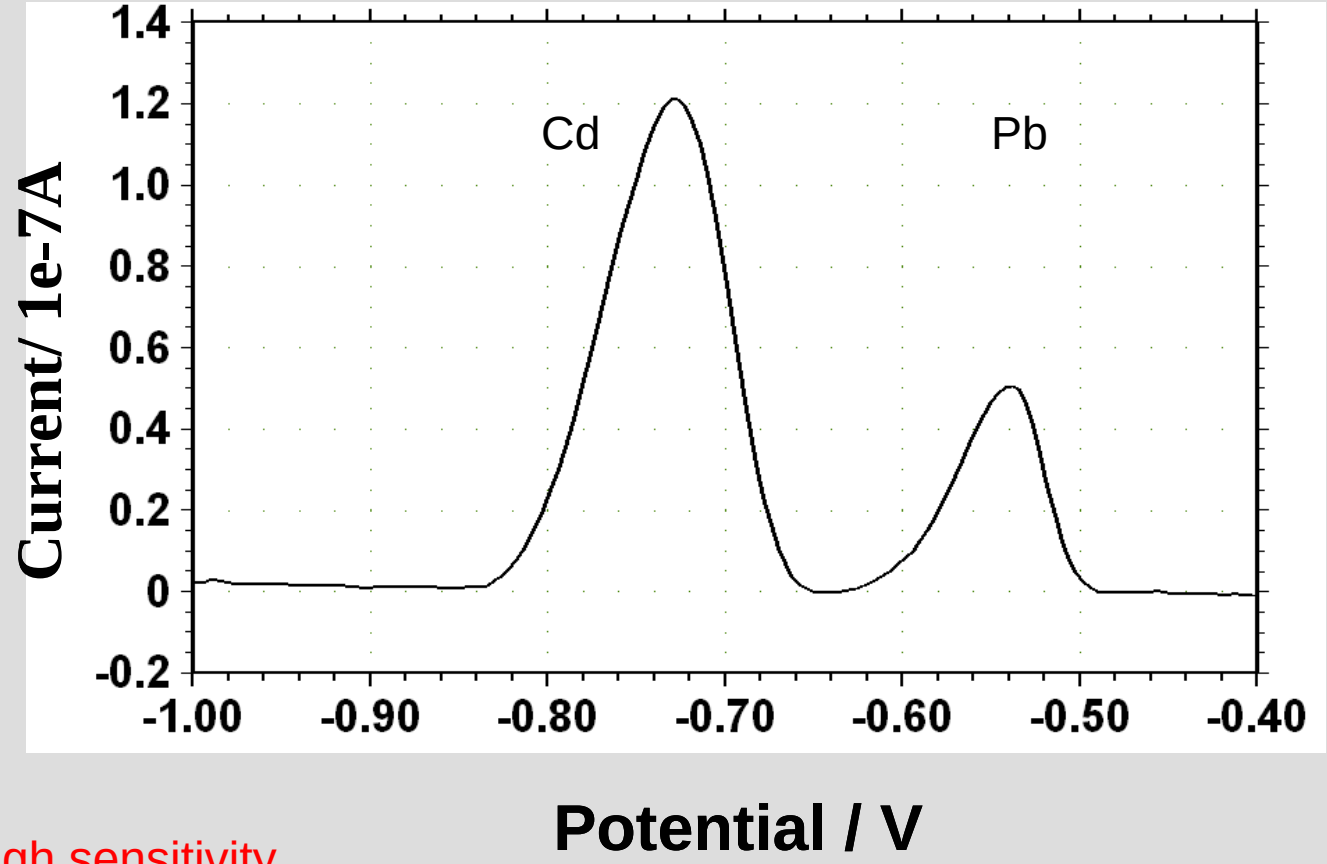
- **Nanosensors for toxic metal ions and radionuclides**

  Hg, Pb, Cd, Cr(VI), U

***Liu, Lin*, Analyst, 130,1098-1101,2005***

***Tu, Lin*, Yantasee, Ren, Electroanalysis, 17, 79-84, 2005***

# Nanoelectrode Arrays for Detection of Toxic Metal Ions: Square Wave Stripping Voltammetry

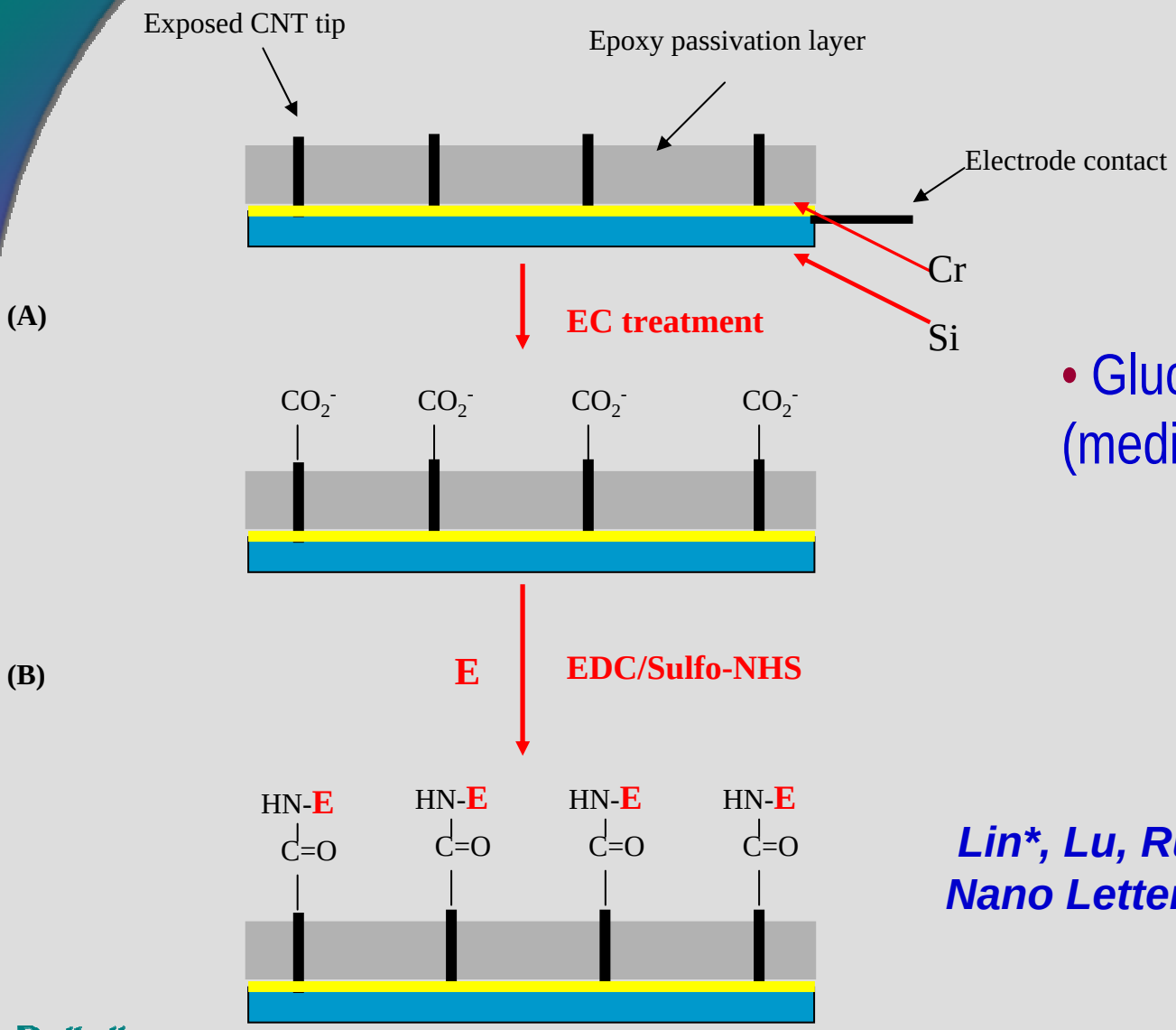



- High sensitivity
- Detection limits, 0.05 ppb for Pb and Cd
- Applications: groundwater monitoring; children's lead poison

# Applications of Nanosensors

## II. Biosensor for Biomedical Monitoring

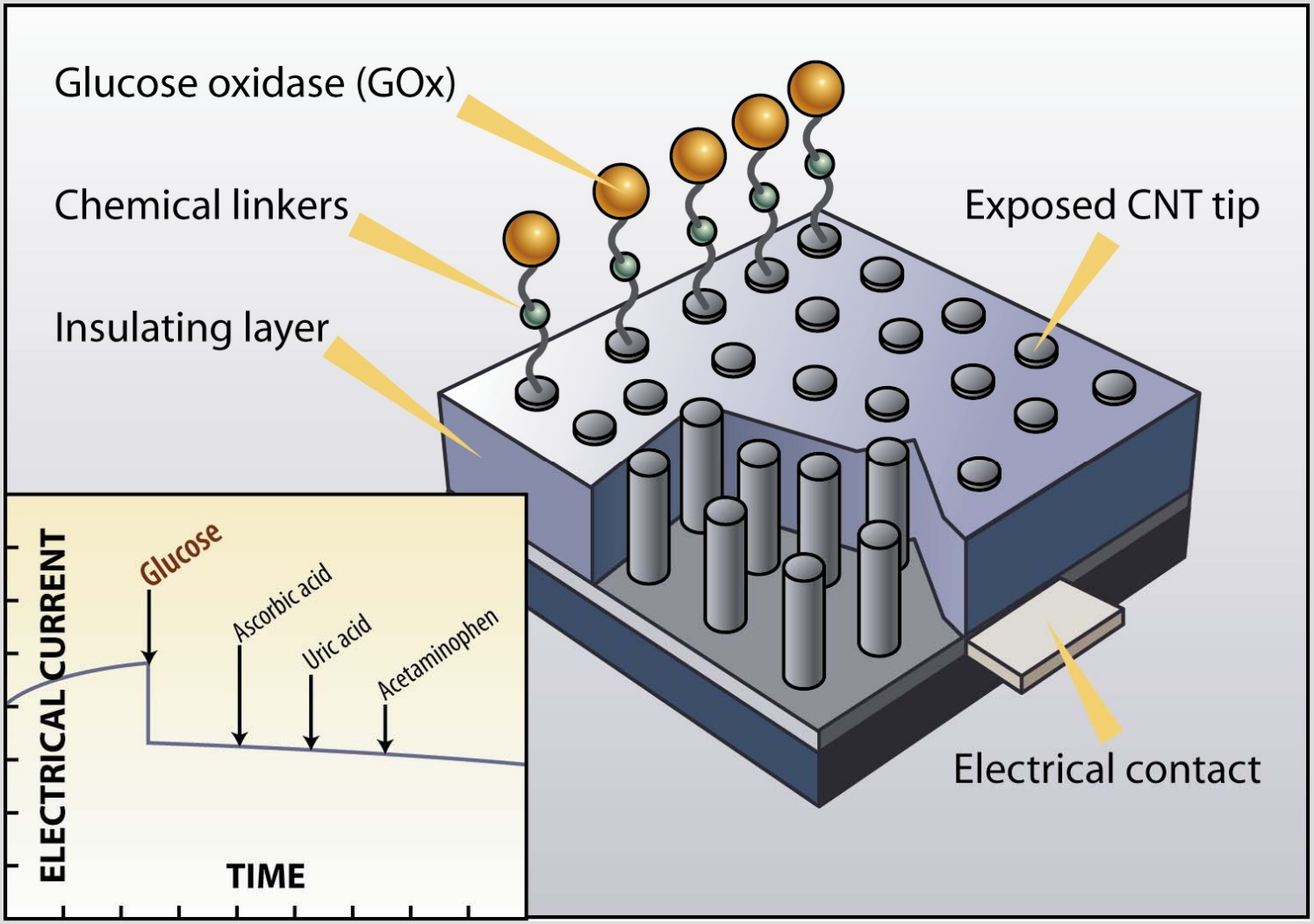
# Enzymes Immobilization on CNTs---Biosensors



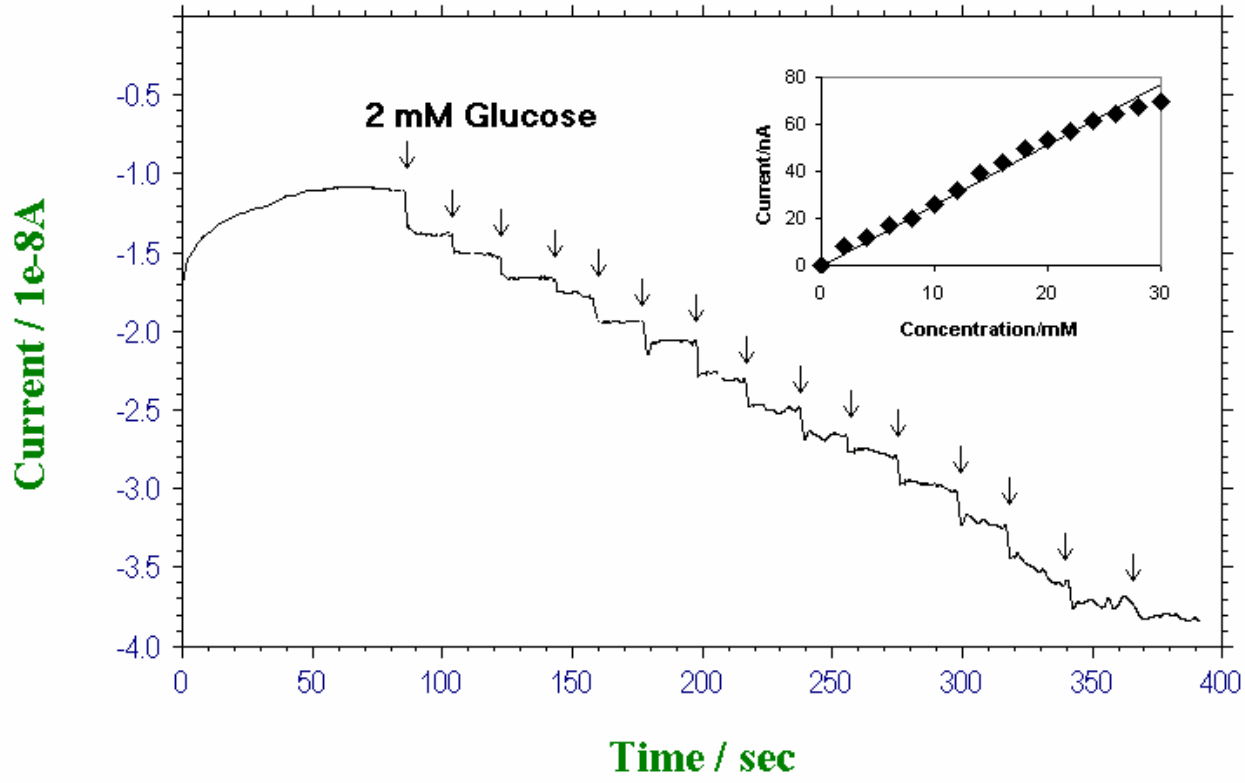

- Glucose biosensors (medical monitoring)

***Lin*, Lu, Ru, Ren,***
***Nano Letter, 4, 191-195, 2004***

# Glucose Biosensor



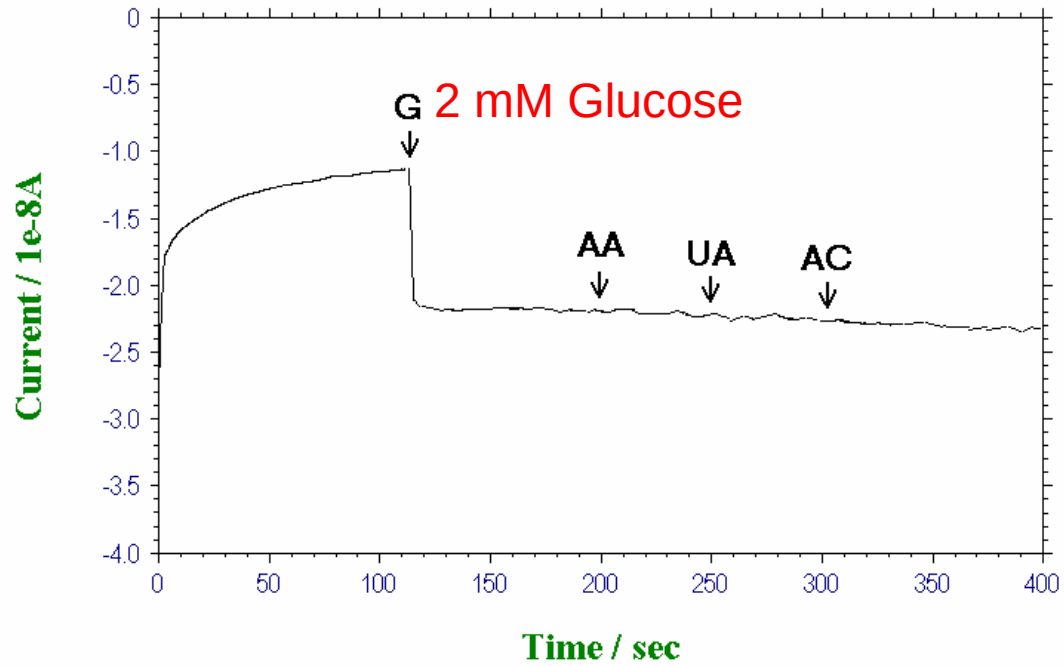
# Glucose Biosensor Based on CNT-NEAs




E = -0.20 V;  Detection limit, 0.08 mM

# Interference of Other Electroactive Species

*Amperometric responses of CNT-based glucose biosensor for relevant physiological levels of glucose (G, 2 mM), ascorbic acid (AA, 05 mM), uric acid (UA, 0.5 mM), and acetaminophen (AC, 0.5 mM)*




E = -0.20 V

***Lin*, Lu, Ru, Ren, Nano Letter, 4, 191-195, 2004***

# Biosensor for Organophosphorus (OP) Pesticides and Nerve Agents

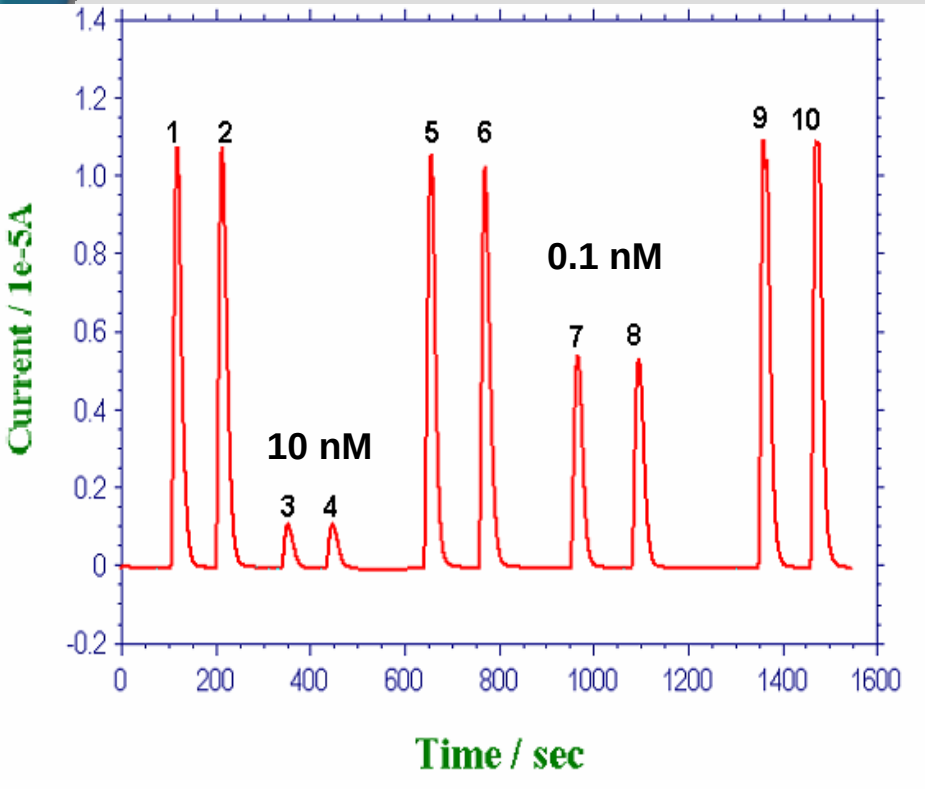
- OP compounds are known to inhibit the activity of acetylcholinesterase **(ACHE)**. Amperometric biosensor for OP compounds is fabricated based on immobilization of ACHE on CNT electrode.
- The enzyme ACHE hydrolyzes acetylethiocholine to thiocholine:

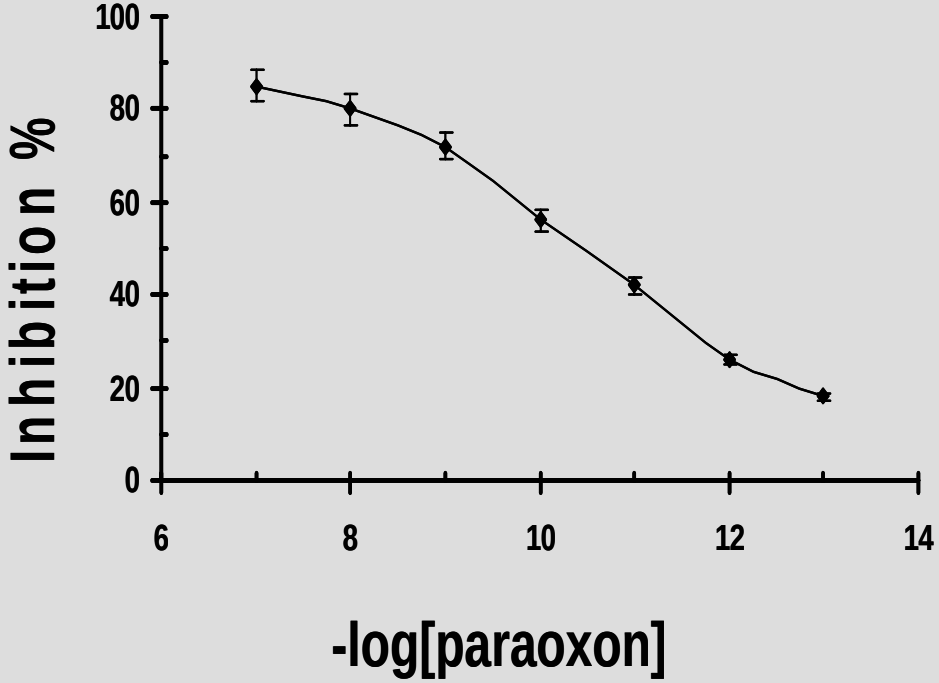
$$\textit{Acetylethiocholine} + H_2O \xrightarrow{\textit{ACHE}} \textit{Acetate} + \textit{Thiocholine}$$

- Thiocholine can be detected amperometrically.
- OPs are detected based on their inhibition effect on enzyme activity

# Flow Injection Analysis of Paraoxon Based on Inhibition Biosensor

**Detection limit, 0.4 pM**




*ACHE*

*Acetylethiocholine + $H_2O$ -----→ Acetate + Thiocholine*

# Summary on CNT Sensors

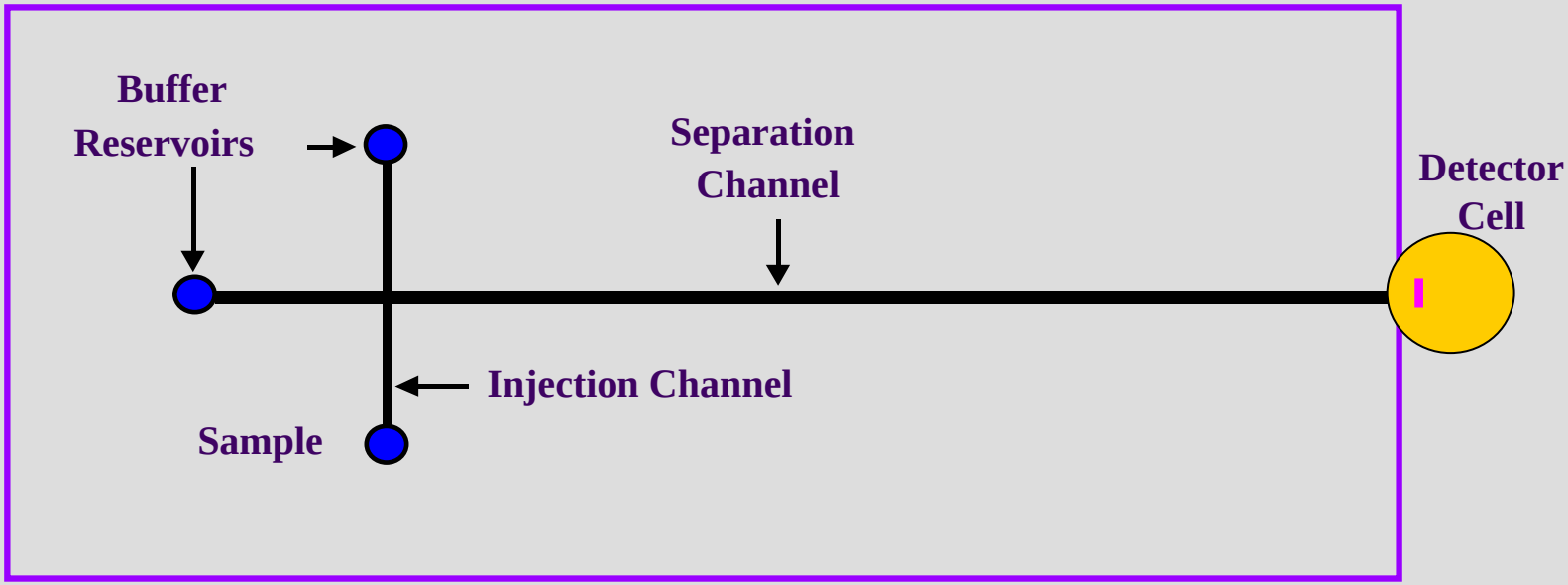
- Successfully fabricated the nanoelectrode arrays from millions of low-density aligned CNTs.
- Effectively insulated the side-wall, take advantages of high-electron transfer rate of open-end. Greatly improved S/N ratio
- Density of nanoelectrode arrays can be controlled precisely
- Successfully demonstrated the applications of CNT-NEAs for metal ion sensing and biosensing

# Integrated Microdevice Based on CE-Microchip with Electrochemical Detector for Monitoring of Organic Pollutants in Water

# TECHNICAL OBJECTIVE

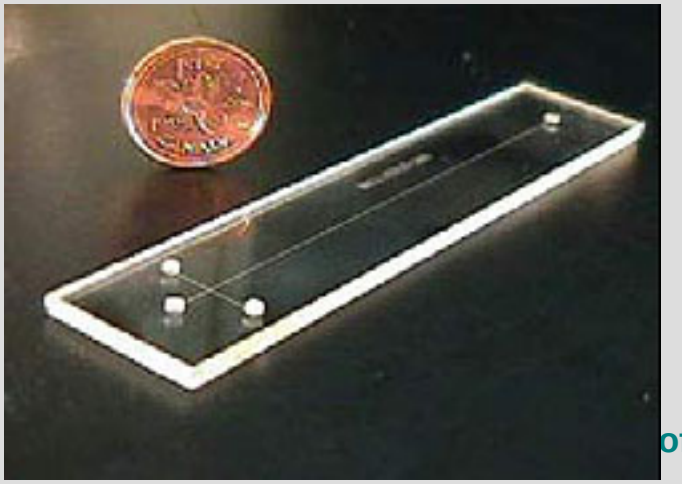
- **To develop a microanalytical system based on advanced "Lab-on-a-Chip" technology by integration of capillary electrophoresis (CE) microchip with electrochemical detector (ECD) for the real-time/ on-site detection of explosives and their degradation products in groundwater.**

# CE Microchip/Electrochemical Detector

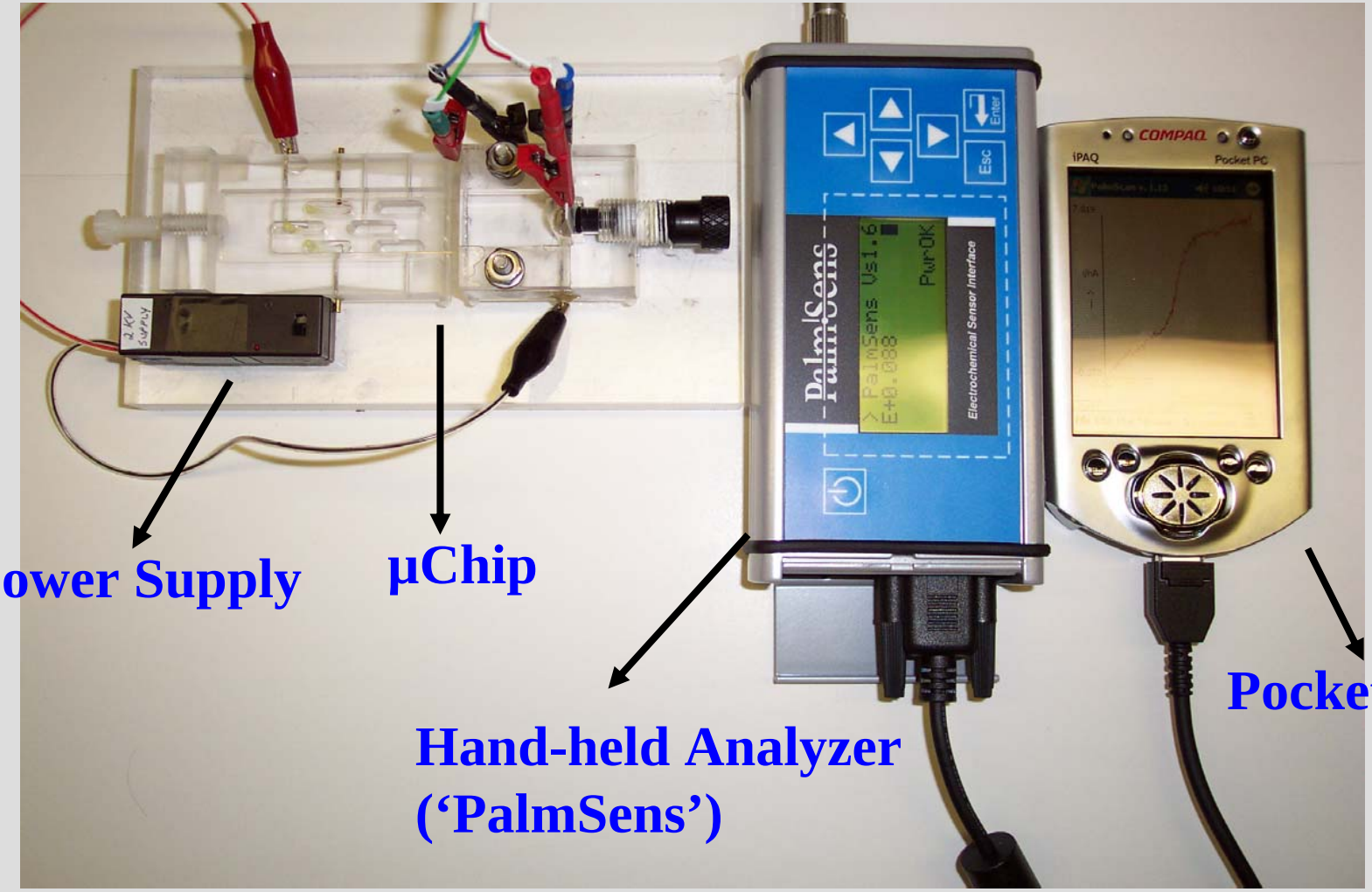



**Chip: 1.6 cm x 9 cm**

**Microchanels: 50 um x 20 um**

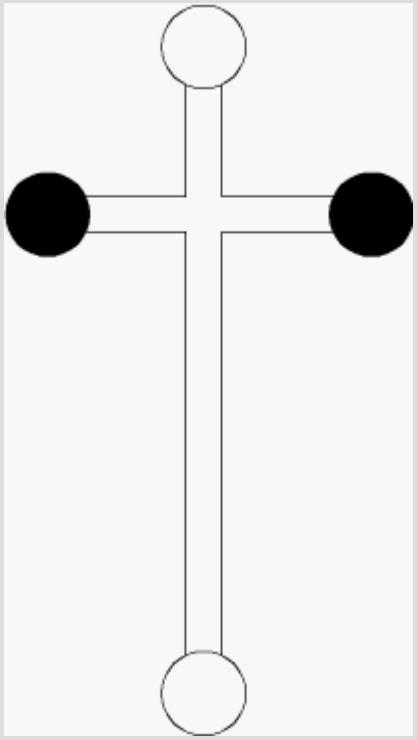


# ‘Lab-on-a-Chip’ Microanalytical System

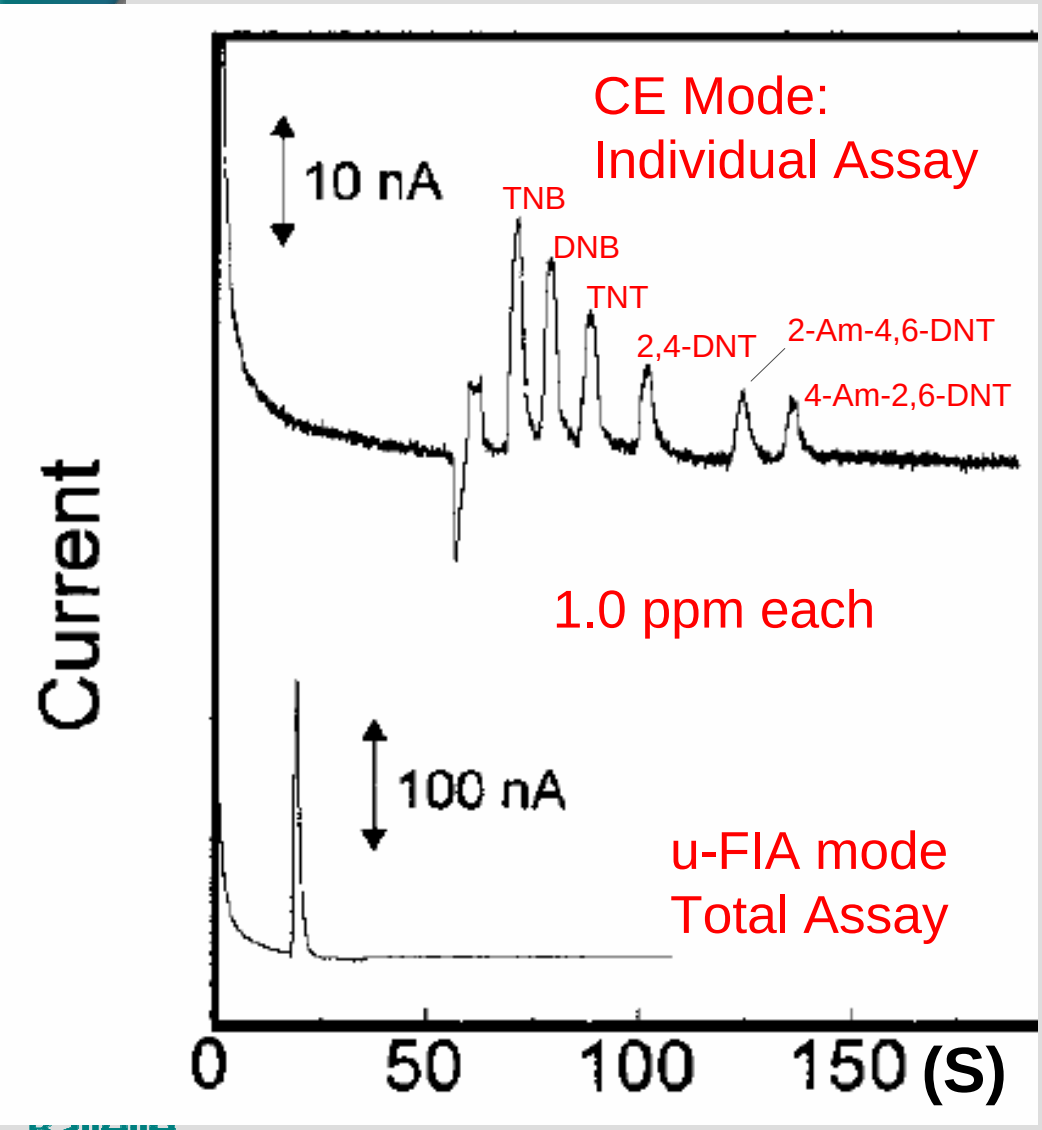


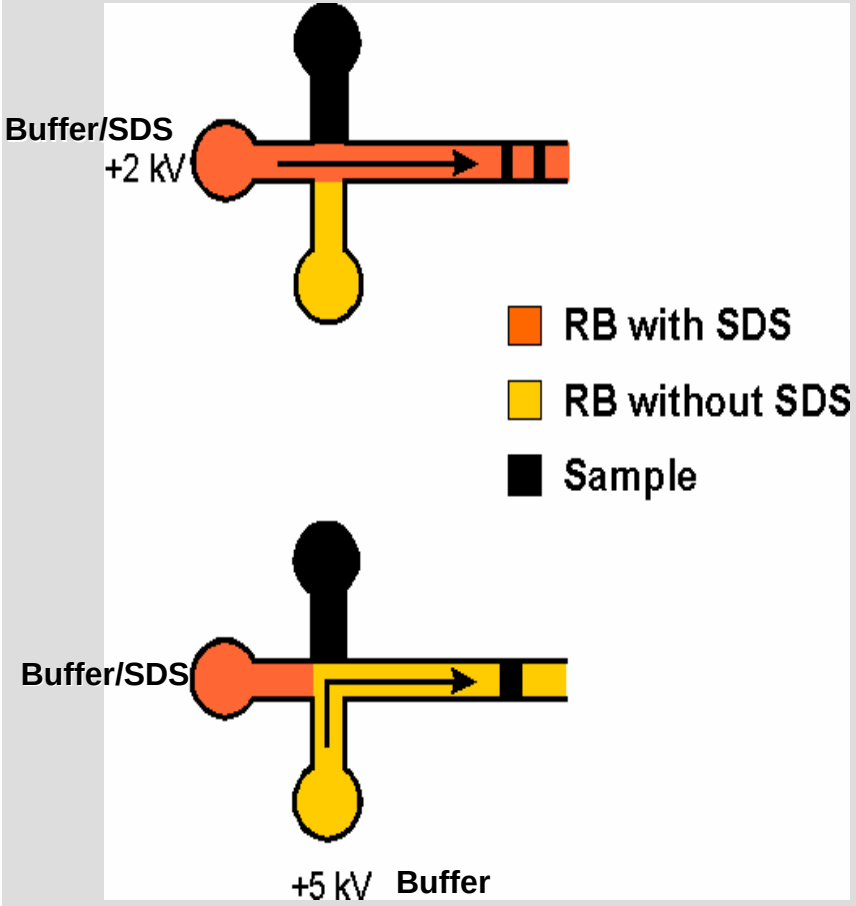
# Advantages of Microanalytical System Based on CE Microchip/ECD

- Capability to separate and quantitate mixtures of energetic explosives.
- Rapid separation times (< 2 min).
- Low reagents and sample consumption- little waste generation.
- Electrochemical detectors are sensitive, compact, and low cost. Compatible with microchip devices



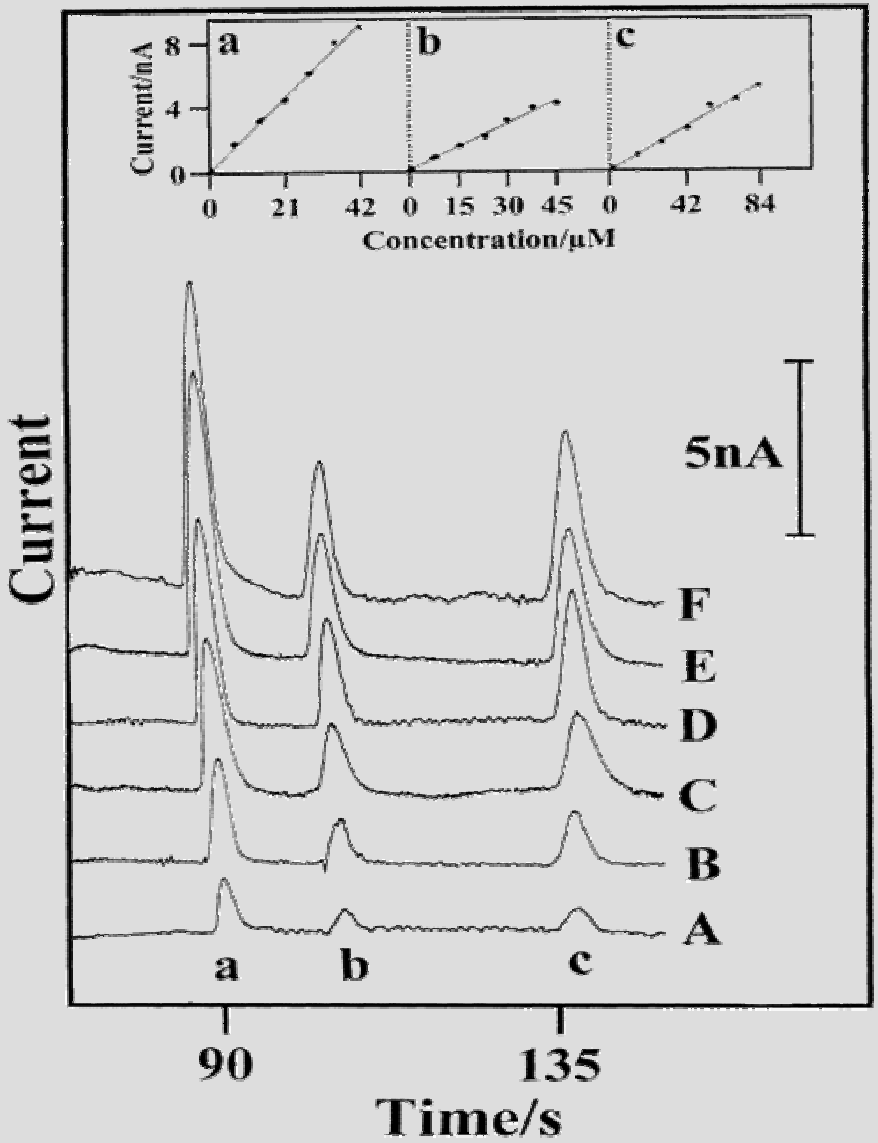
# Amperometric Microchip for Screening (u-FIA) and Identification (CE-mode) of Explosive Compounds

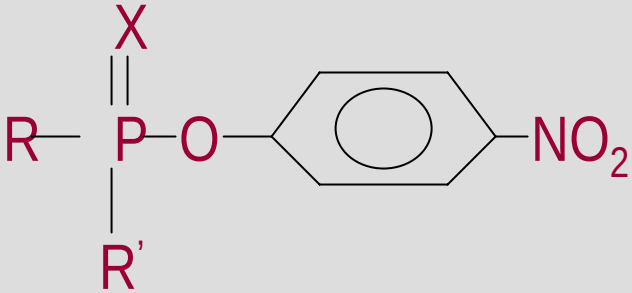


# Microchip CE/ECD for Detection of Organophosphate Pesticides

*Paraoxon (a), Methy Parathion (b), and Fenitrothion (c)*



# Summary (CE Microchip)

## Accomplishments

- Successfully integrated CE-microchips with electrochemical detector
- Systematically optimized the separation and detection processes
- Demonstrated the analytical performance for fast separation and detection mixtures of explosives and pesticides (< 2 min)

## Applications

Monitoring of explosives, phenols, pesticides, chemical agents in drinking water, waste water and groundwater

# Acknowledgements

- **PNNLTeam:**

  **Yuehe Lin, Guodong Liu, Jun Wang, Wassana Yantasee; Glen Fryxell**

  **Collaborator: Dr. Joseph Wang, ASU**

  **Dr. Z. F. Ren, Boston College**

- **Funding**

  **DOE-EMSP; SERDP; PNNL-LDRD**