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Environmental Applications in Nanotechnology

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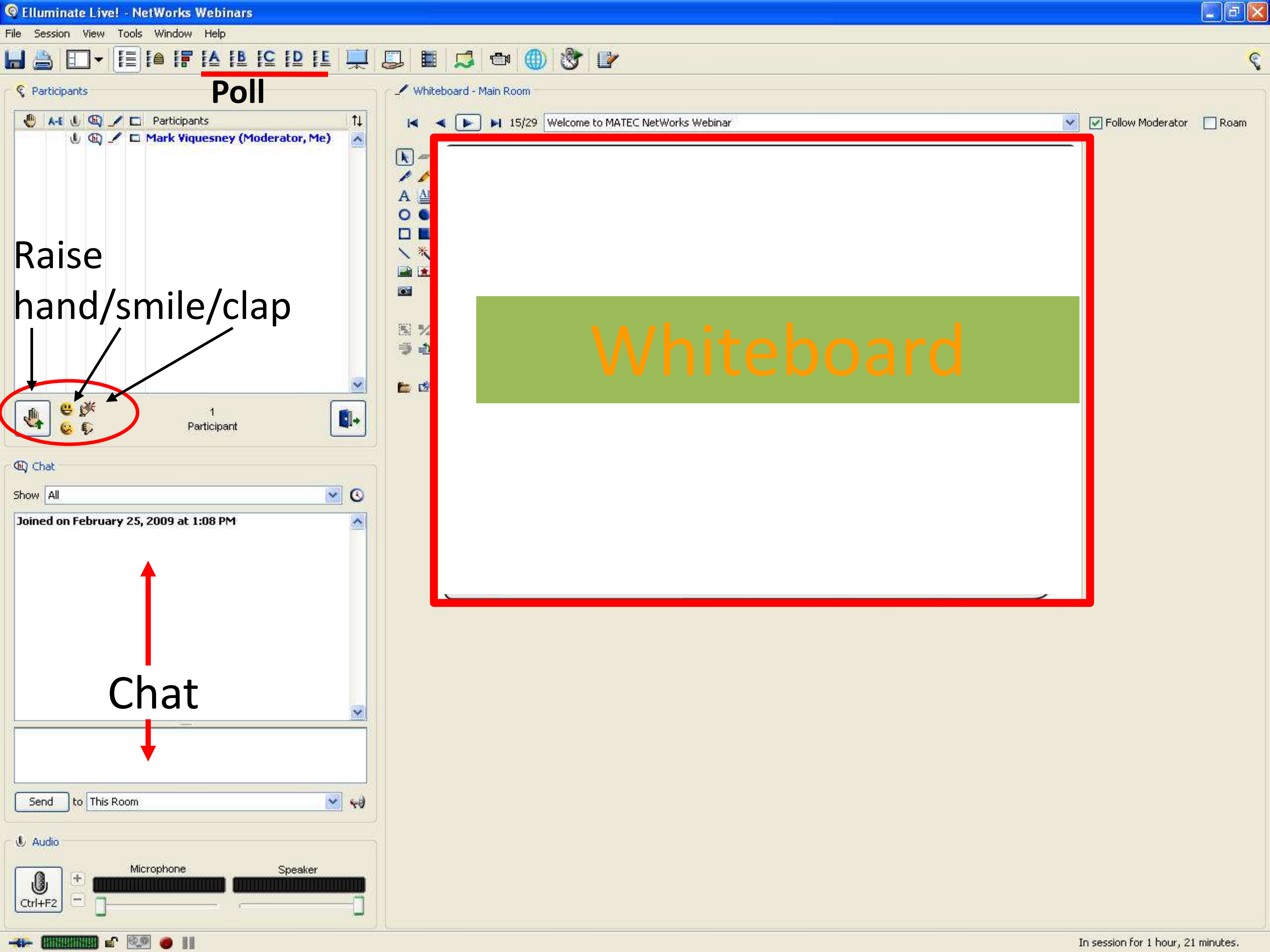

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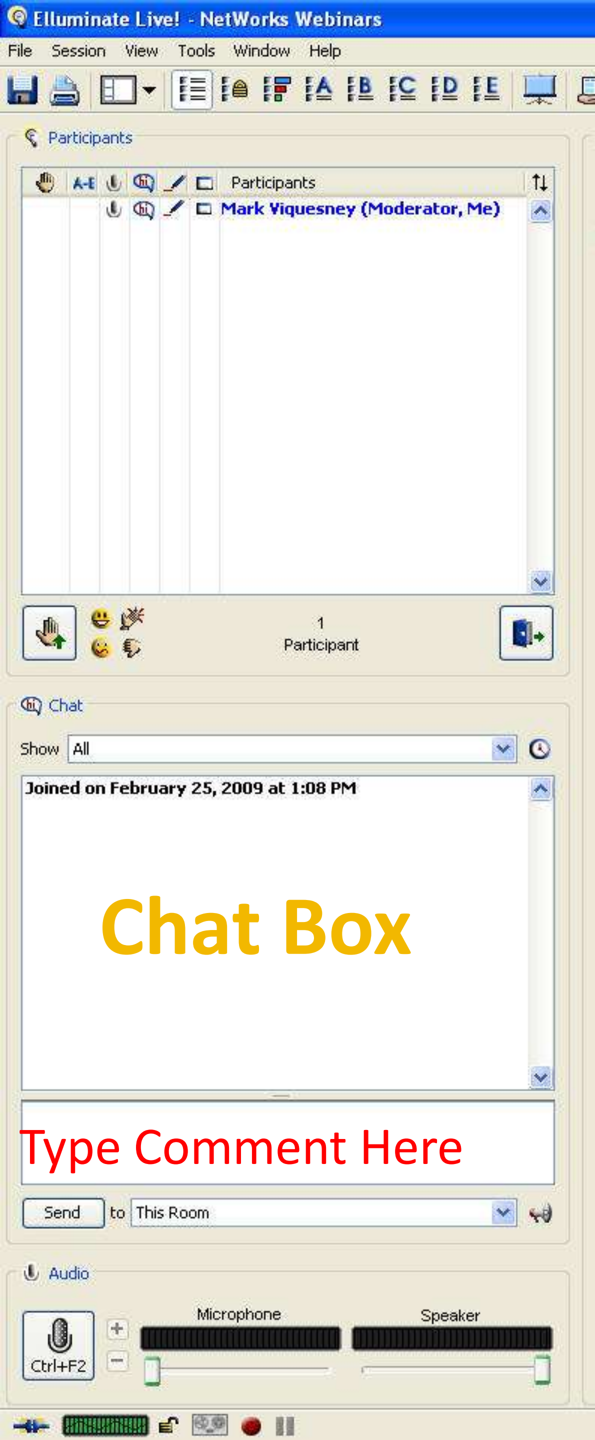

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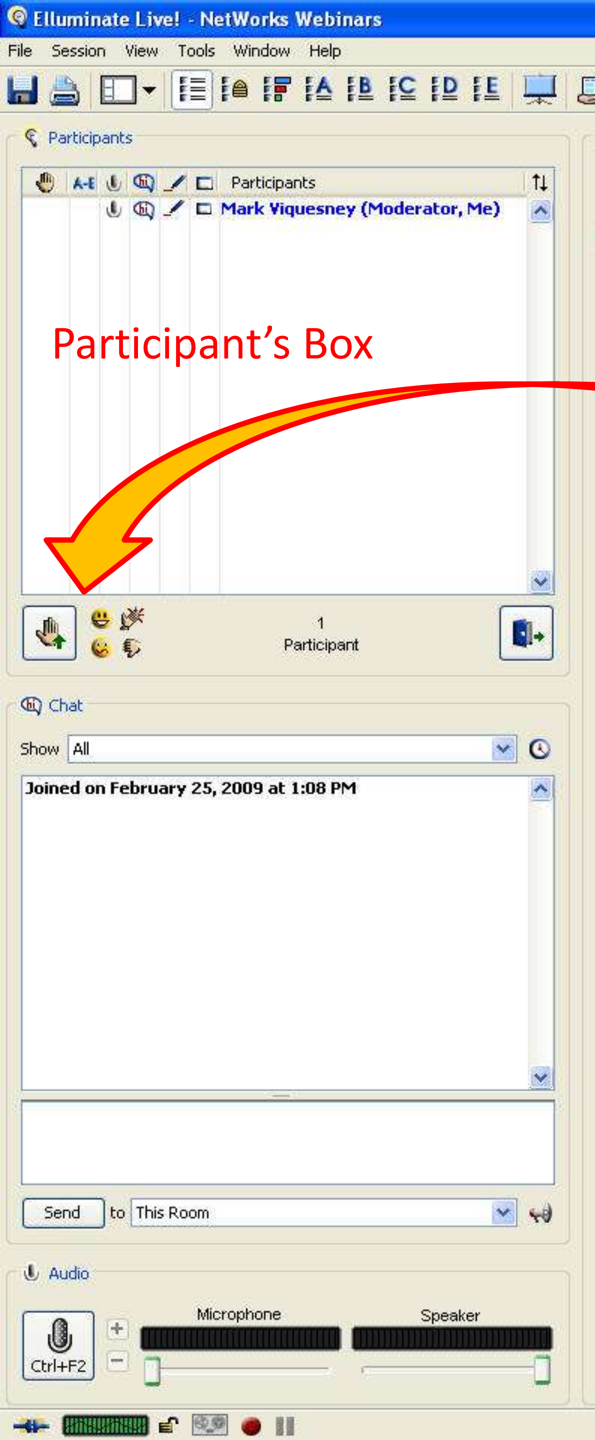

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NACK's Webinar Presenter

Presented by Prof. Arturo A. Keller

Bren School of Environmental Science & Management

UC Center for Environmental Implications of Nanotechnology

University of California, Santa Barbara

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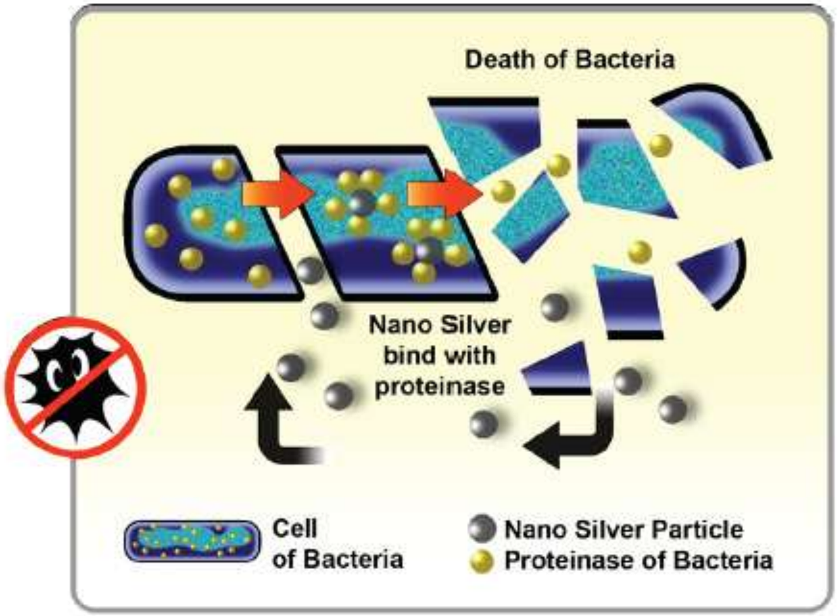
Challenging Environmental Issues

- Legacy Pollutants
  - Chlorinated Solvents
  - PCBs, PAHs, Chlorinated Pesticides (e.g. DDT)
  - Lead, cadmium, chromium
- Emerging Contaminants
  - Pharmaceuticals & Personal Care Products
  - Newer pesticides
  - Engineered Nanoparticles & their by-products?
- Common water constituents
  - Salinity, hardness

Possible applications of NMs

- As reactants
  - Nano Zero Valent Iron
  - Nano Silver
- As catalysts
  - Nano TiO2
  - Nano CeO2
- As adsorbents
  - Carbon Nanotubes (CNTs)
  - Mag-PCMAs
- As sensors
  - CNTs

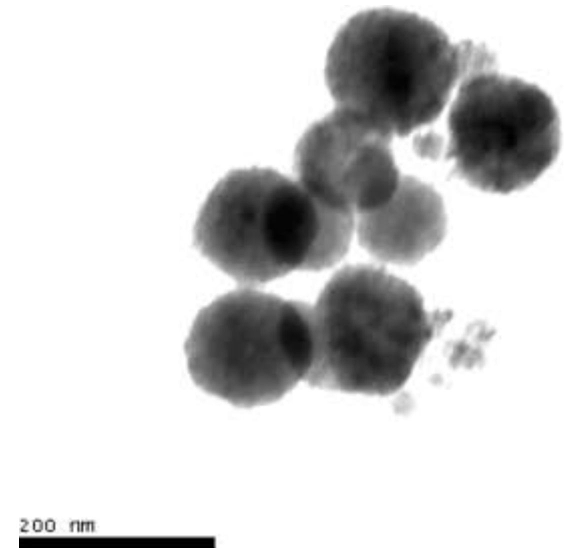


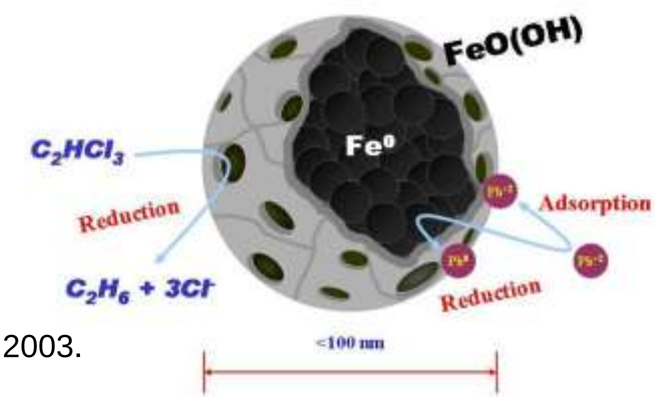
Nanoparticles as Reactants



Nanoscale Zero-Valent Iron Particles

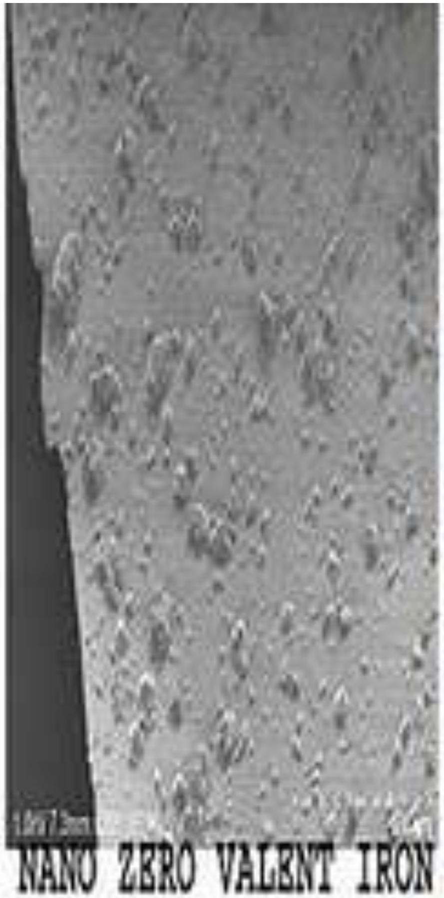
- Zero-Valent Iron (ZVI) has been proposed as a metallic reducing agent for environmental applications:
  - Abundant
  - Relatively low cost
  - Effective as a reductant
- nZVI has been evaluated for in-situ remediation:
  - halogenated solvent spills (DNAPLs)
  - Cr(VI) & As(III) contaminated soils or aquifers



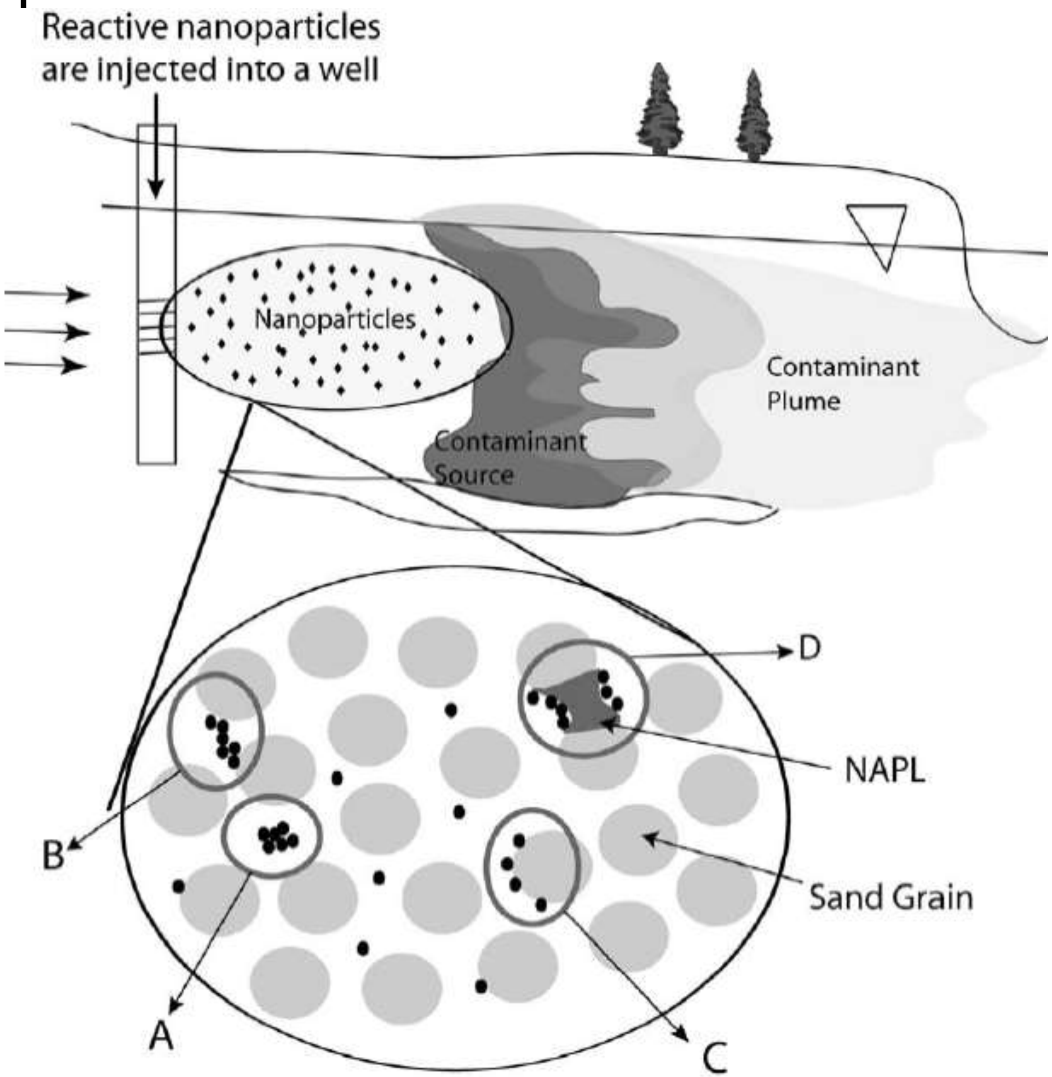


Bigg and Judd, 2000; Tratnyek et al., 2003.

Nanoscale Zero-Valent Iron Particles



ZVI for source zone treatment



A: Aggregation

B: Straining

C: Attachment

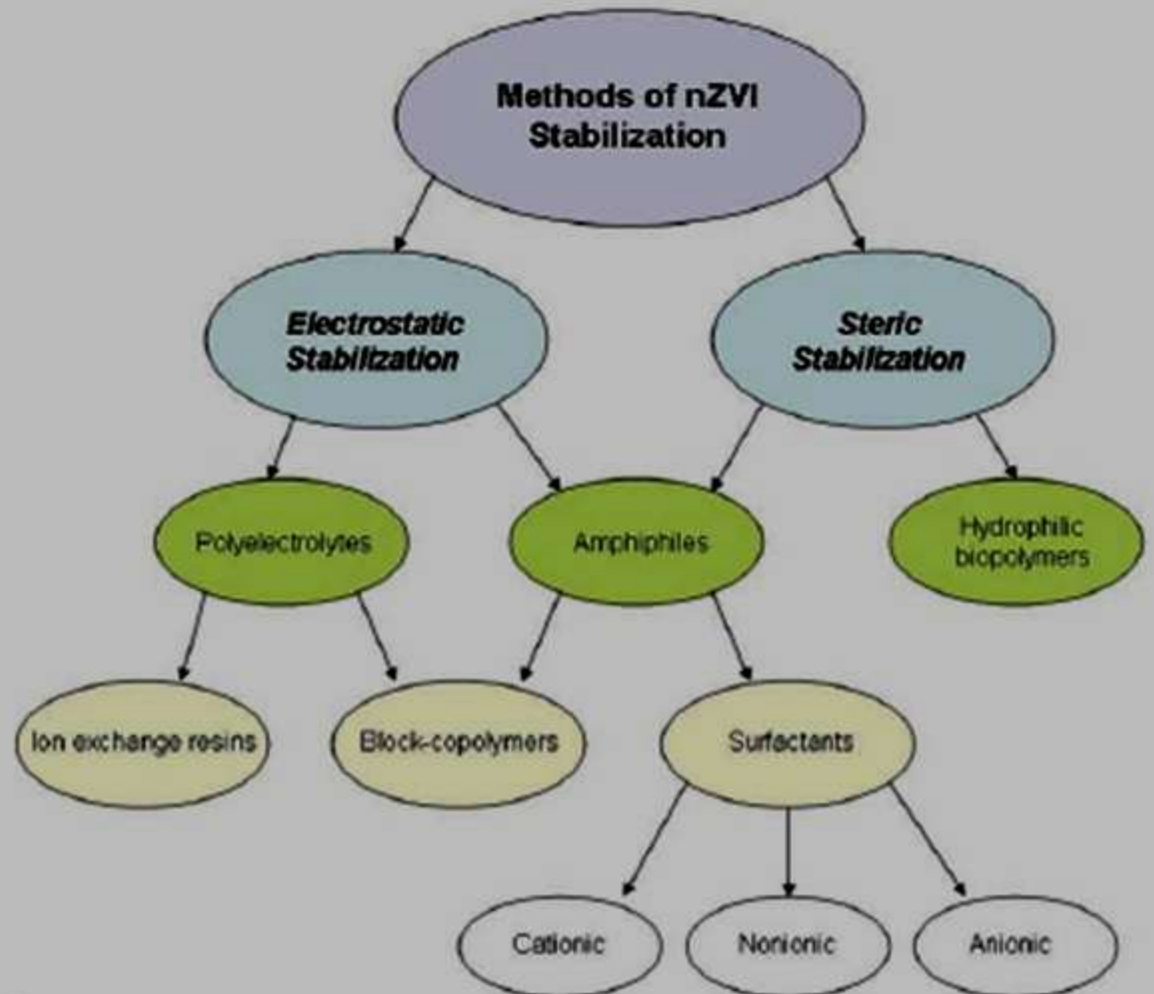
D: NAPL Target

Loss of ZVI is significant due to A, B and C interactions.

Research focus on inhibiting aggregation of ZVI and thus increase ZVI's mobility in aquifer

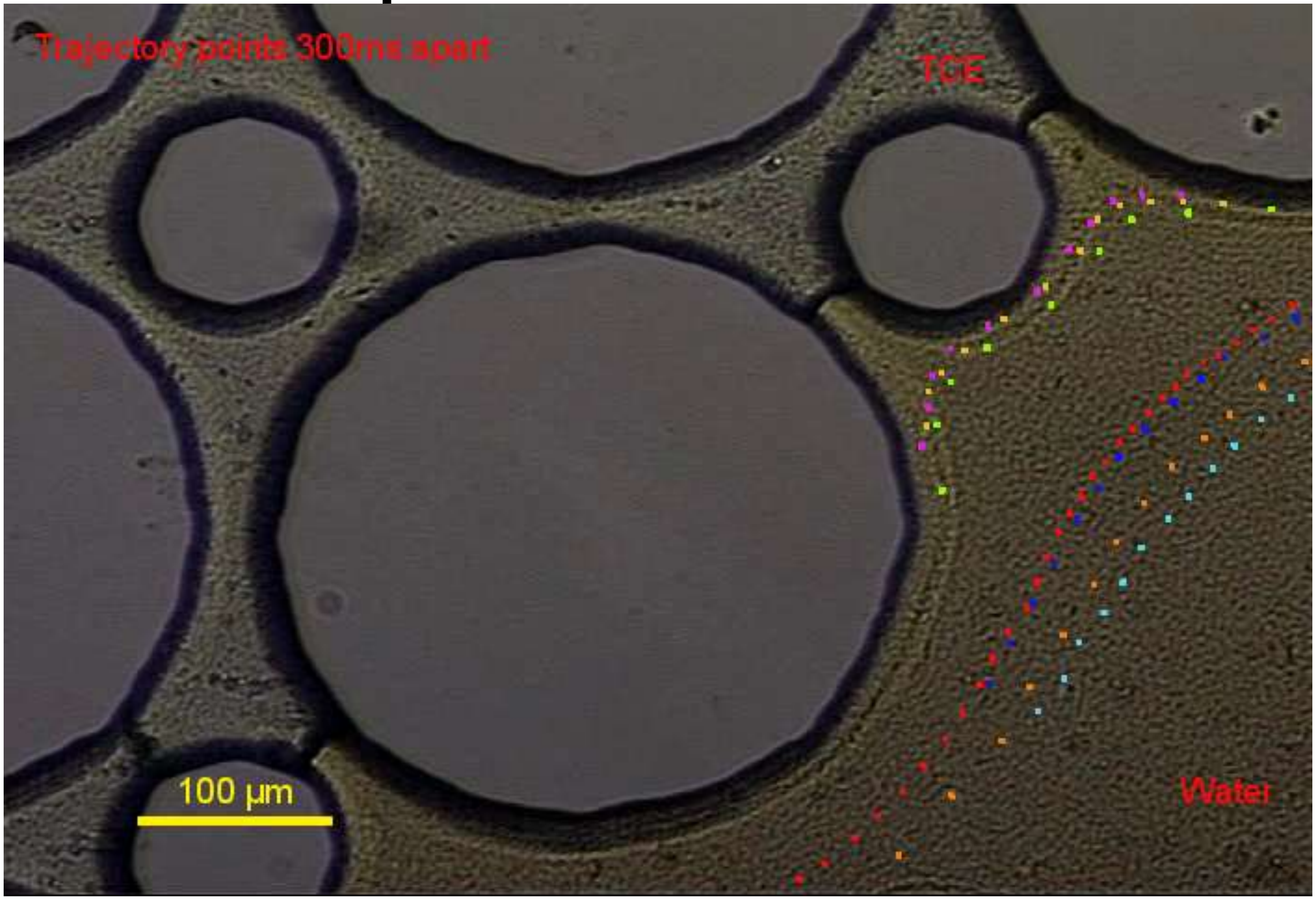
nZVI Particles

Figure 3-5. *Possible methods of nZVI stabilization*



Source: Kustov et al. 2009

Transport in streamlines



nZVI for source zone treatment

- Dechlorination of TCE takes place in 3 steps:

1. $C_2HCl_3 + Fe^{o} + H_2O \Rightarrow C_2H_2Cl_2 + Cl^- + Fe^{2+} + OH^-$

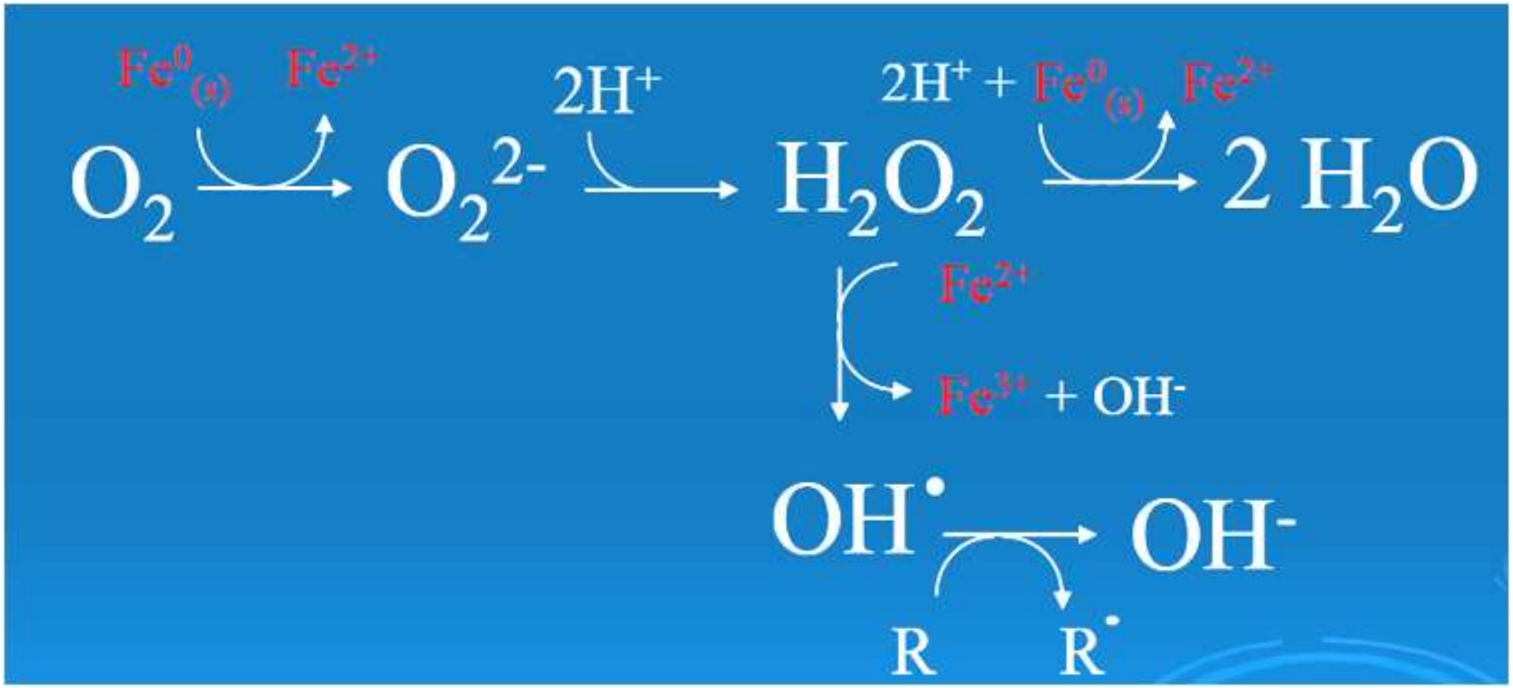
2. $C_2H_2Cl_2 + Fe^{o} + H_2O \Rightarrow C_2H_3Cl + Cl^- + Fe^{2+} + OH^-$

3. $C_2H_3Cl + Fe^{o} + H_2O \Rightarrow C_2H_4 + Cl^- + Fe^{2+} + OH^-$

Consumptive use of Fe^{o} and significant effect on pH…!

Nanoscale Zero-Valent Iron Particles

- nZVI can also be used for oxidation:



Joo et al. ES&T (2005)



nZVI Particles

Table 1-1. *Common environmental contaminants that can be transformed by nanoscale iron particles*

Chlorinated methanes	**Heavy metal ions**	**Other polychlorinated hydrocarbons**
Carbon tetrachloride	Mercury	PCBs
Chloroform	Nickel	Dioxins
Dichloromethane	Silver	Pentachlorophenol
Chloromethane	Cadmium	
Chlorinated benzenes	**Organic dyes**	**Other organic contaminants**
Hexachlorobenzene	Orange II	N-nitrosodimethylamine
Pentachlorobenzene	Chrysoidine	TNT
Tetrachlorobenzenes	Tropaeolin O	
Trichlorobenzenes	Acid Orange	
Dichlorobenzenes	Acid Red	
Chlorobenzene		
Pesticides	**Chlorinated ethenes**	**Inorganic anions**
DDT	Tetrachloroethene	Dichromate
Lindane	Trichloroethene	Arsenic
Trihalomethanes	*cis*-Dichloroethene	Perchlorate
Bromoform	*trans*-Dichloroethene	Nitrate

Nanoscale Zero-Valent Iron Particles

- Concerns
  - Large amounts required given that it is consumed
  - Non-specific reduction or oxidation, resulting in additional consumption
  - Mobility and potential direct toxicity
  - By-products of degradation (mobility, bioavailability, toxicity)



Nanoscale Zero-Valent Iron Particles

- Current research on:
  - Coatings to reduce aggregation and attachment until nZVI reaches target contaminants
  - Surfactants can also reduce initial aggregation
  - Maintain reactivity until the point of use
    - Avoid formation of oxide layer on surface
    - Early disappearance of Fe(0)
  - Potential toxicity of Fe(0), Fe(II) and Fe(III) when groundwater discharges into a surface water
  - Adding catalysts to the surface of nZVI (Pt, Pd)

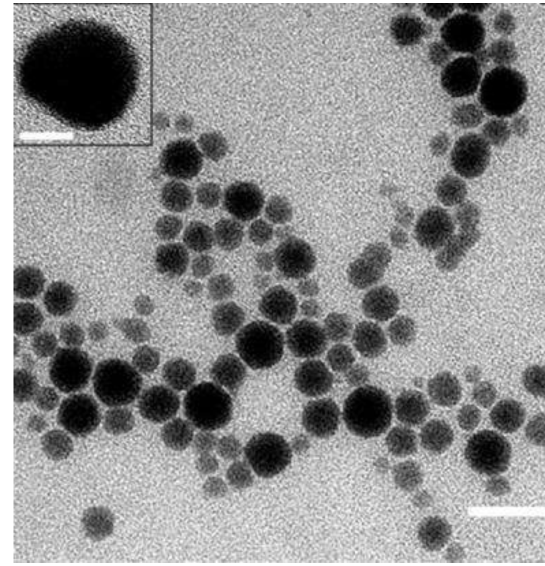


Poll

- Based on the current information, do you feel we should use nZVI for environmental remediation?
  - A: definitely
  - B: probably
  - C: not sure
  - D: don't think the benefits are there
  - E: too much risk

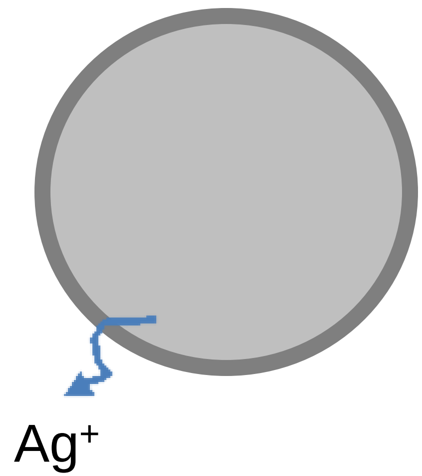
Nano Silver

- Antimicrobial & antifungal
- Applications in
  - Textiles
  - Surface coatings
  - Food preservation



Nano Silver

- Elemental silver, Ag(0) at core of nanoparticle
- Nanosilver particles typically coated with an organic molecule to avoid aggregation
- Slow dissolution of nanosilver, shedding Ag^+
- Biocidal function due to Ag^+
- Relatively non-toxic to humans
  - Long-term exposure effects unknown



Nano Silver

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Nano Silver

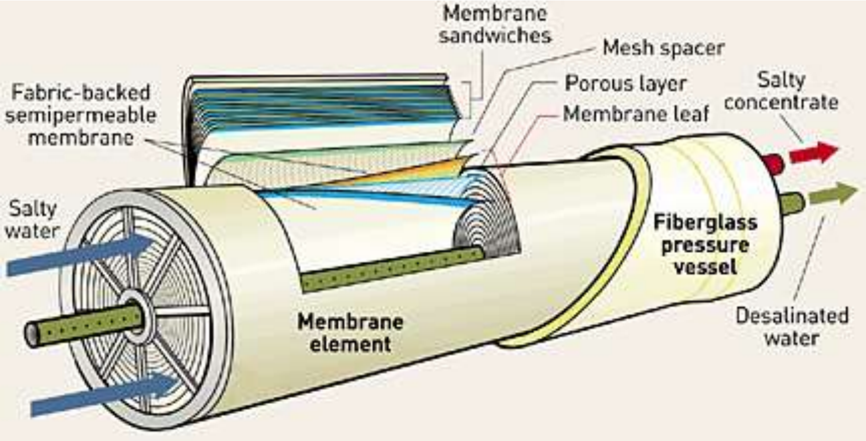

Nano Silver
Toothpaste

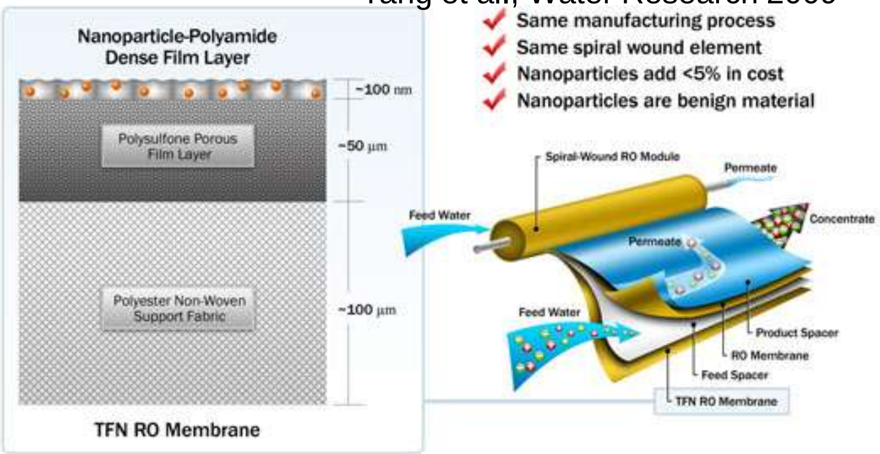

NanoSilver(Ag+)
Sterilization
99.9%
Ag+
Applied to the brush
■ Bristles:
PBT + Nano Silver Powder
■ US Patent No.6,660,058BI

Nano Silver

- Application of nanosilver surface modification to RO membrane
  - mitigating biofouling in seawater desalination

Yang et al., Water Research 2009







Quiz

- What is the key factor controlling nZVI effectiveness in remediation
  - A: amount applied
  - B: straining in the media
  - C: aggregation
  - D: reaching the target pollutants
  - E: all of the above

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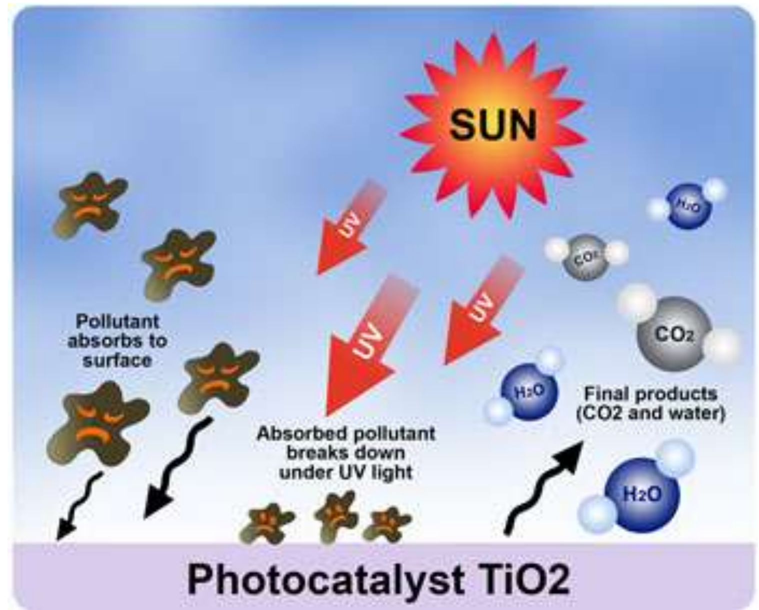
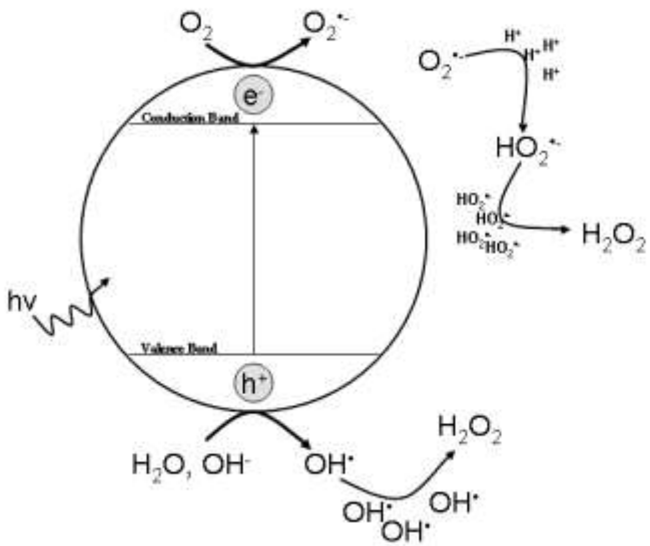
Nanoparticles as Catalysts

Nano Titania

- TiO_2 has been used as a photocatalyst for decades
- Nanotitania has several orders of magnitude more photoactive surface area than micron-sized particles
- Also has antimicrobial properties



Nano Titania



Bennett and Keller, 2010

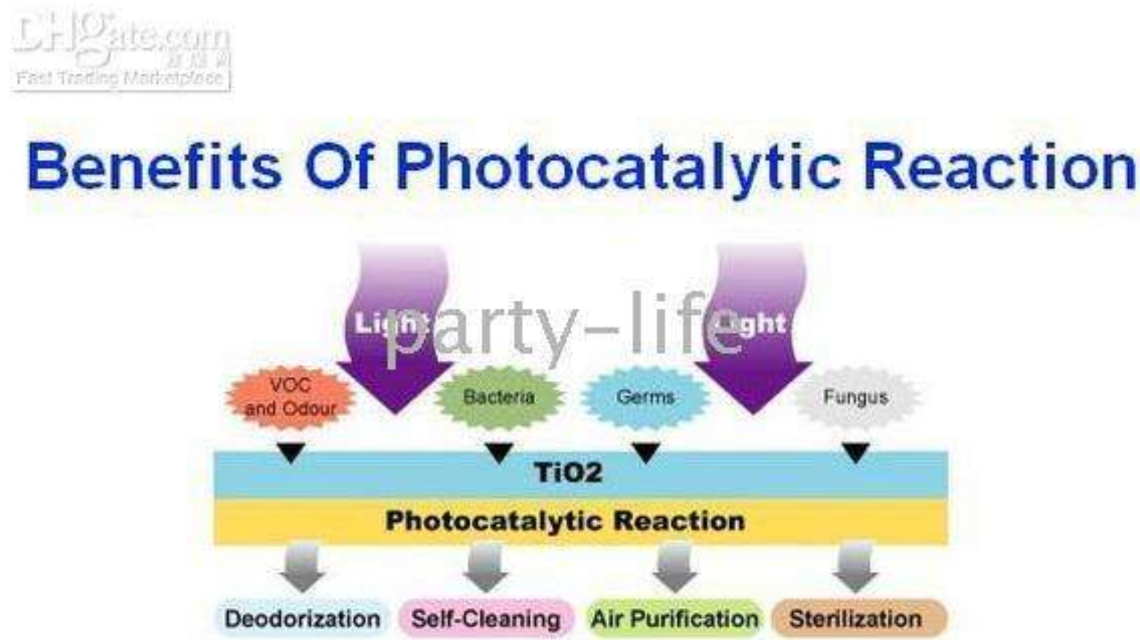
- Titania is very effective in capturing UV photons and promoting electrons
- Generates reactive oxygen species
- Catalyzes oxidation of pollutants (and microbes)

Nano Titania

- Functions of a photocatalyst
  - Sterilization of surfaces
    - Self-cleaning
  - Air Purification
    - NOx
    - VOCs
    - Cigarette smoke
  - Water Treatment
    - VOCs
    - PPCPs
    - Pathogen inactivation

Green Earth Nano Science Inc.

Nano Titania



Poll

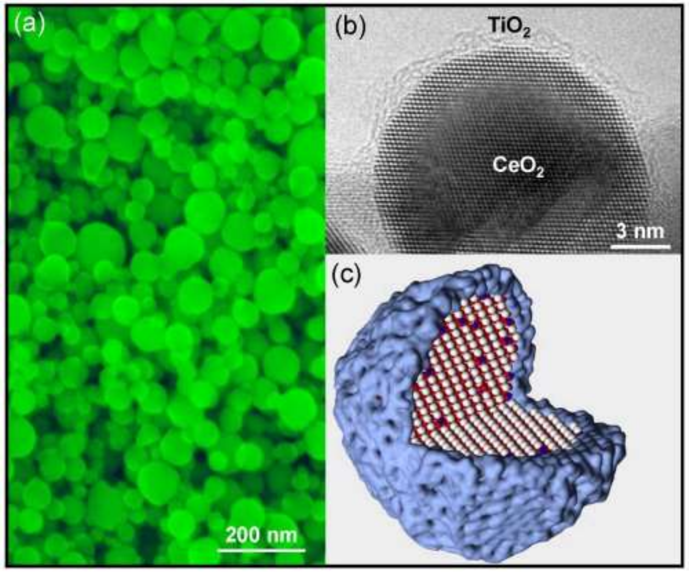
- Have you used sunscreen with titania or zinc oxide nanoparticles
  - A: Yes
  - B: Maybe
  - C: Don't know
  - D: How would I know?
  - E: Does it matter?

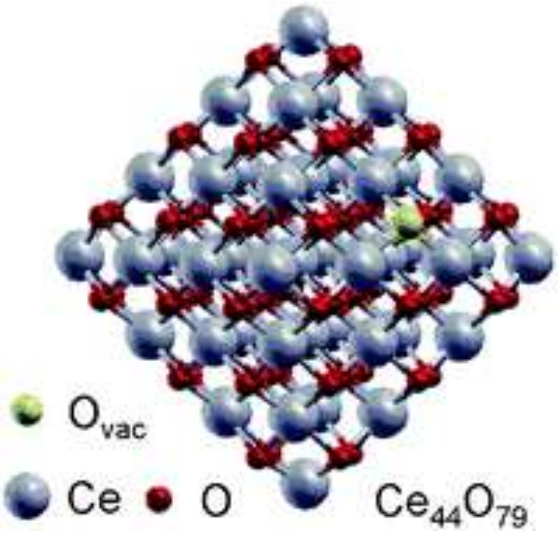
Nano Ceria

- Ceria (cerium oxide) may lead to catalytic converters that are better at cleaning up auto exhaust
- In a catalytic converter, ceria acts as a buffer
  - absorbs or releases oxygen depending on the conditions of the engine
  - maintains catalyst in its optimum operating condition

Nano Ceria

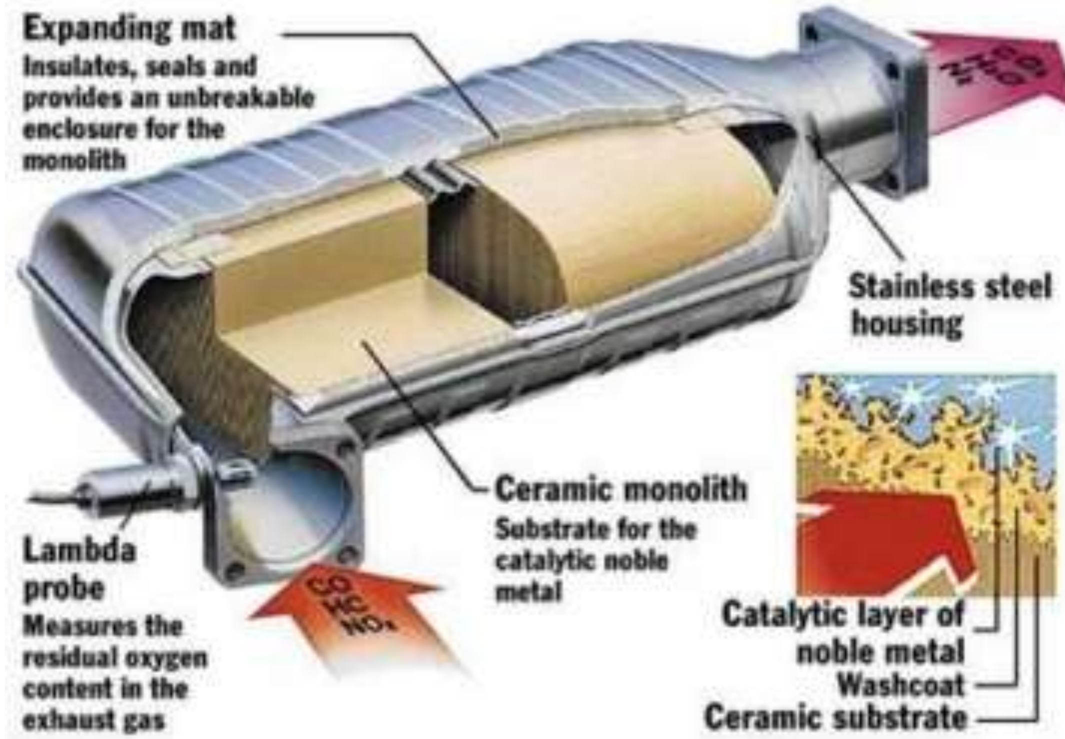
- Cerium has two important redox states:
  - Ce(III) and Ce(IV)
  - Can easily go from one to the other
  - Good "place holder" for oxygen
  - Promotes oxidation and reduction reactions
- Ceria nanoparticles have much better performance, higher chemical reactivity, than the bulk form

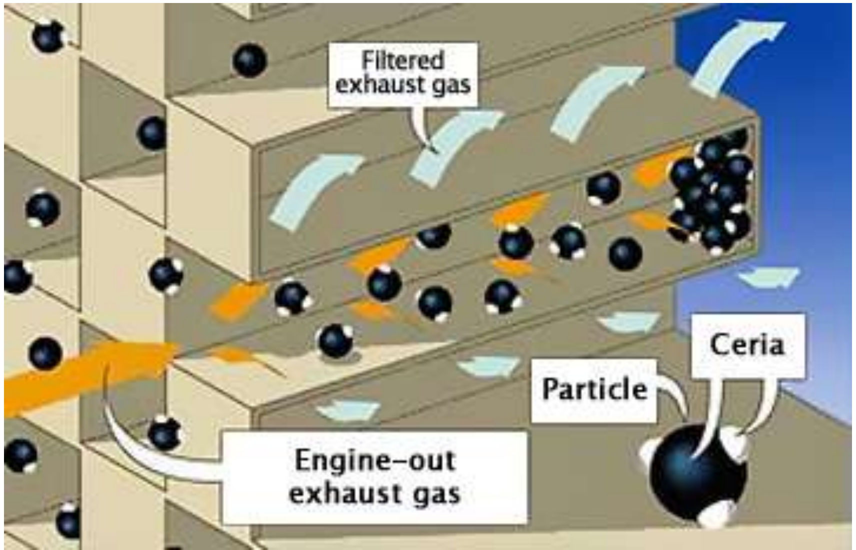




Nano Ceria

- Ceria converts emissions of
  - carbon monoxide
  - nitrogen oxides
  - VOCs (HCs)
- Output is carbon dioxide, water and nitrogen gas
- Reduces/eliminates need for Pt and Pd in catalytic converter





Nano Ceria

- Used as a catalyst for producing ammonia (NH_3) from N_2 gas
  - Current process use lots of energy
  - Nano-iron and ceria catalysts can cut energy costs by 40-50%

Nano Ceria

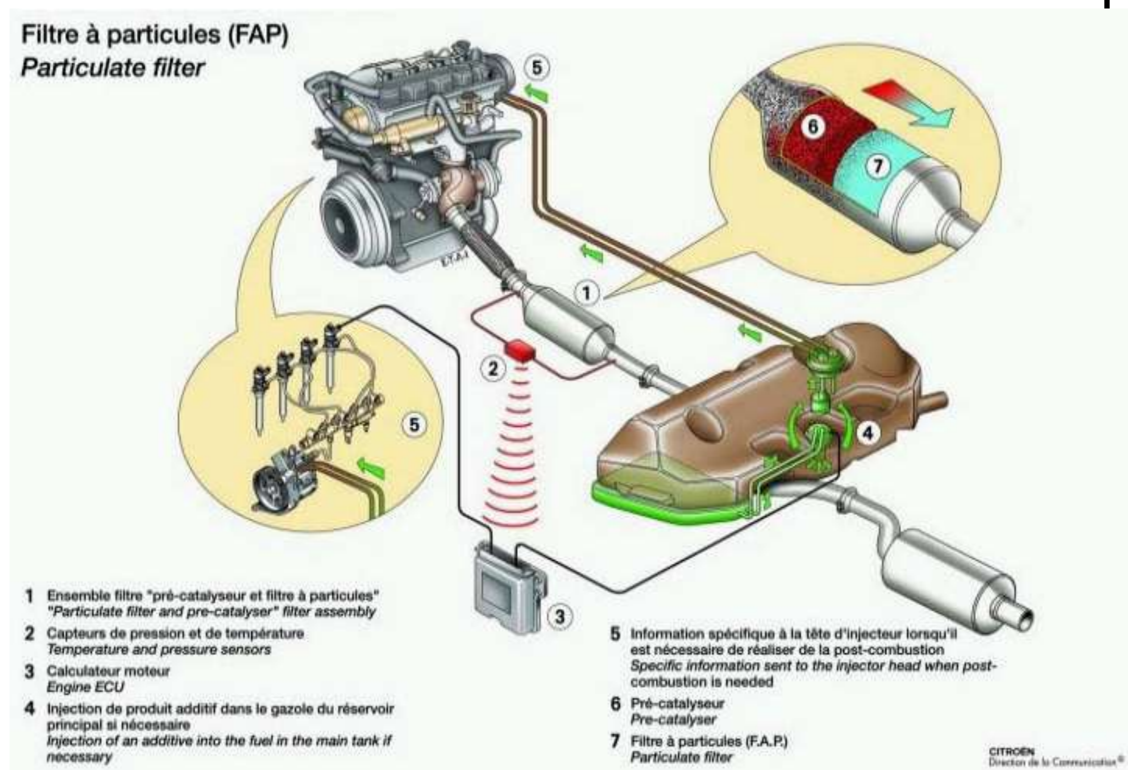
- Ceria also used for producing hydrogen (H_2) at low temperature (water-gas shift process)

Nano Ceria

- Can potentially produce H_2 from
  - Ethanol (from sugar cane, beets, switch grass or corn)
  - Methanol (from natural gas)
- Do the conversion in a fuel cell so the H_2 is used almost immediately
  - No storage of H_2
  - No risky fueling

Nano Ceria

- Nano ceria also being used as a fuel additive
  - Can decrease particulate (ash/soot) production from diesel fuel
  - Also decreases CO
  - Dosed at 10-25 ppm



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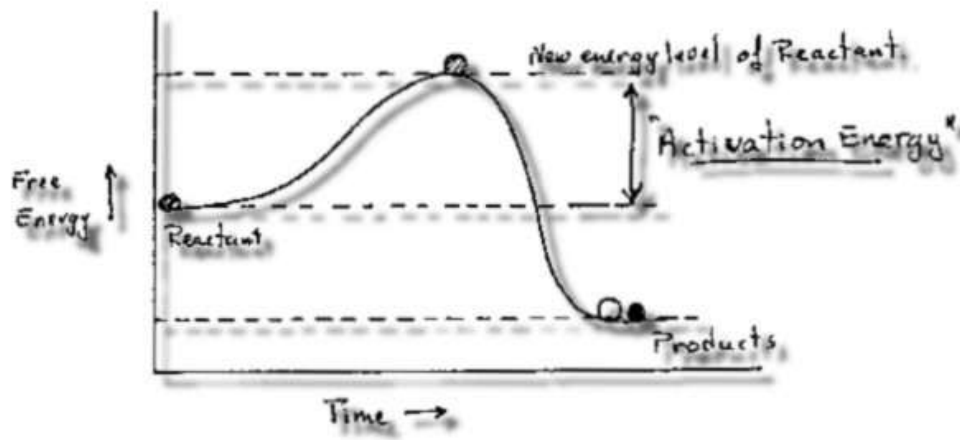
Nano Ceria

More than 500,000 vehicles equipped to date

(750,000 vehicles by the end of 2003)

Poll

- Nanoparticles as Catalysts or Reactants? What makes more sense?
  - A: Catalysts
  - B: Reactants
  - C: Not sure
  - D: Depends on the application
  - E: Neither one



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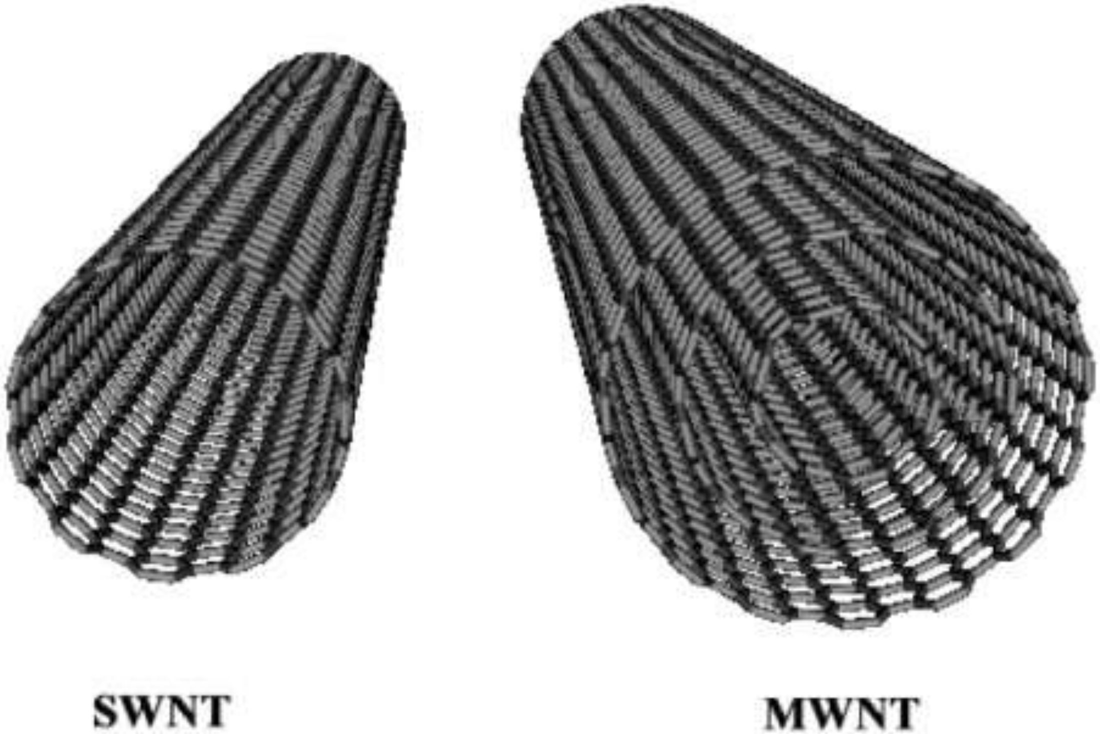
Nanoparticles as Adsorbents

Carbon Nanotubes as adsorbents

- Organic dye elimination
- Volatile Organic Compounds
- Pesticides
- PAHs
- Wastewater treatment





Carbon Nanotubes as adsorbents

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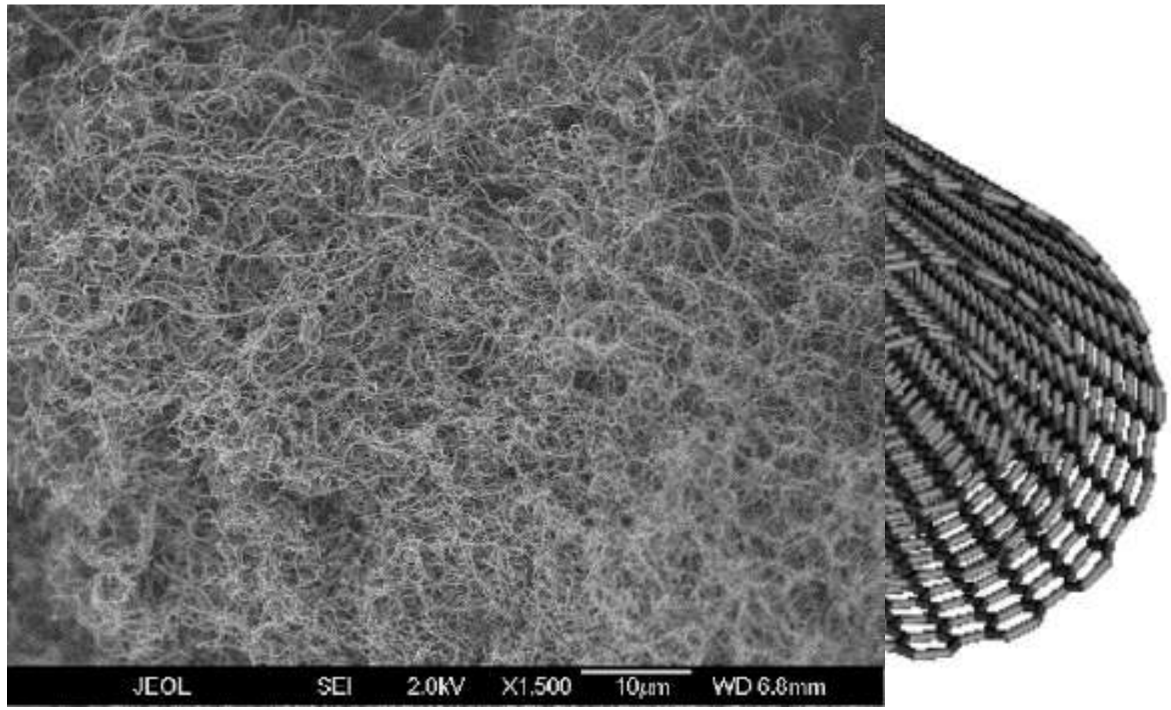
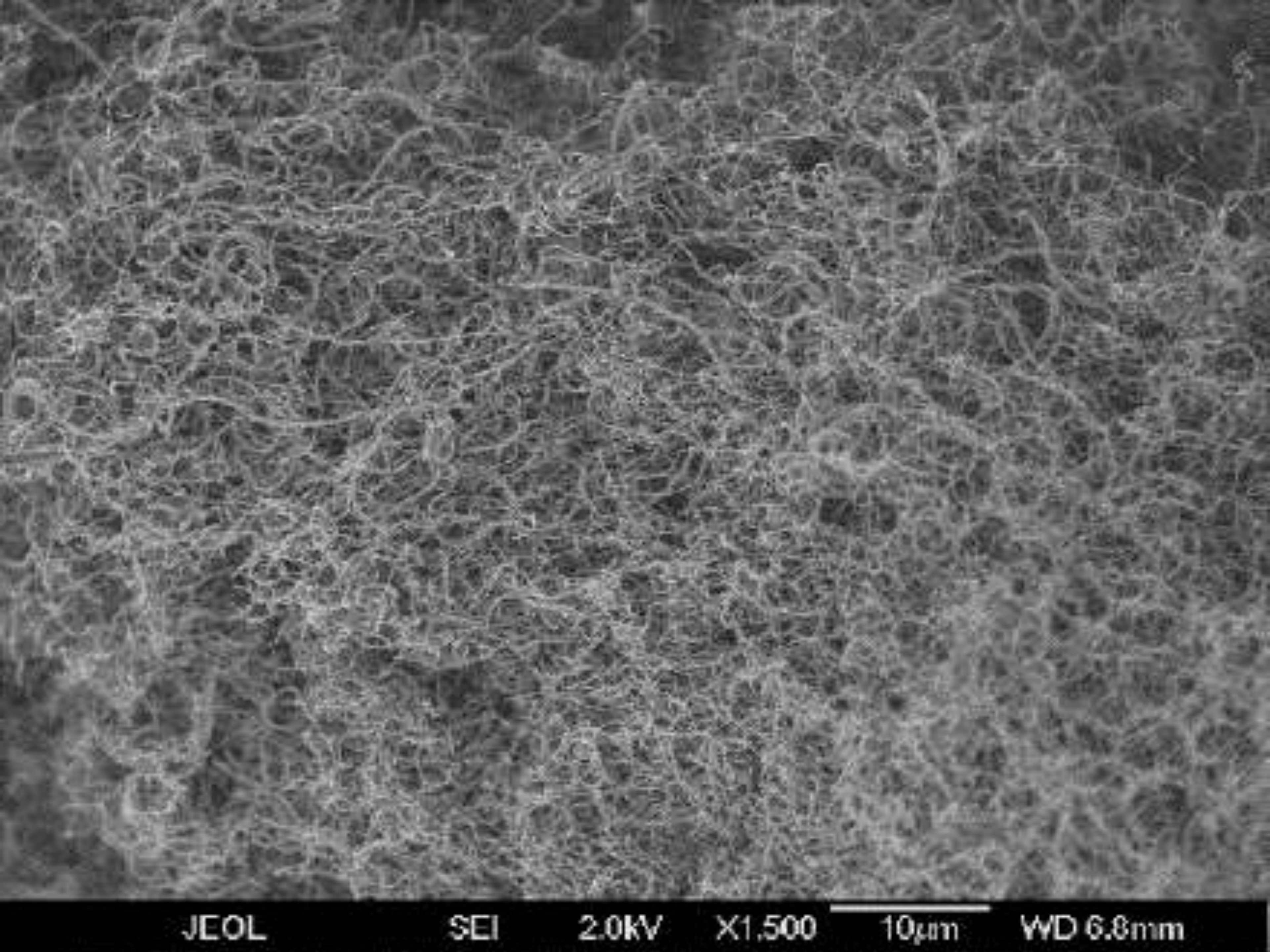


SWNT MWNT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10μm
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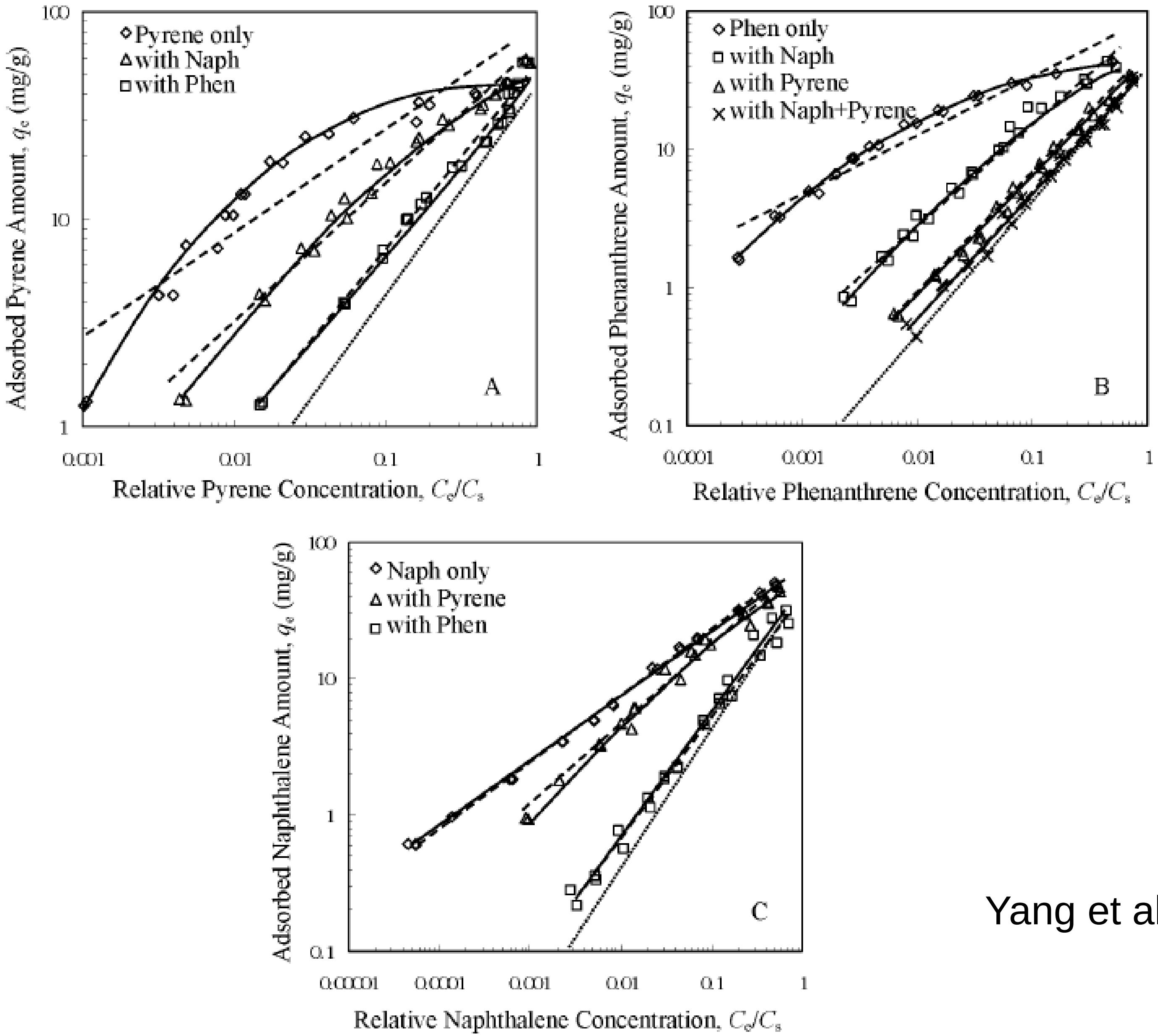
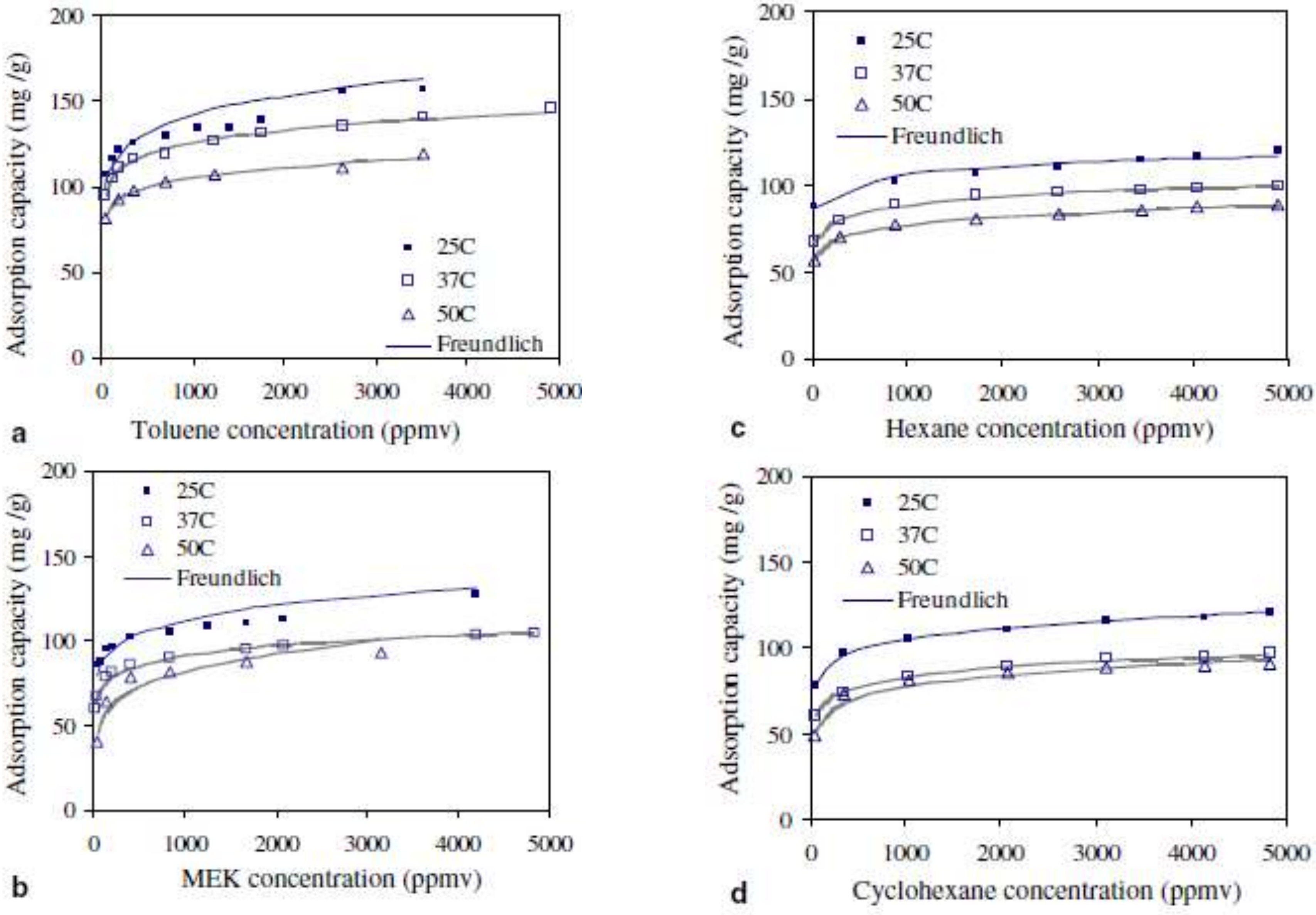


Yang et al. ES&T 2006

FIGURE 2. Sorption isotherms of PAHs on MWCNT15 without or with competitors at $C_e/C_s = 1$: (A) pyrene alone and with naphthalene or phenanthrene as competitor; (B) phenanthrene alone and with naphthalene, pyrene, or their mixture as competitors; and (C) naphthalene alone and with pyrene or phenanthrene as competitor. All isotherms were normalized by the primary solute solubility. Solid lines (——), the isotherms fitted by DA model; long dashed lines (– – –), the isotherms fitted by Freundlich model. Short dashed lines (-----) represent the limits of competition, computed using DA model with E = 5.71 kJ/mol, b =1, and Q_0 of single-solute isotherms. Phen and Naph represent phenanthrene and naphthalene, respectively.

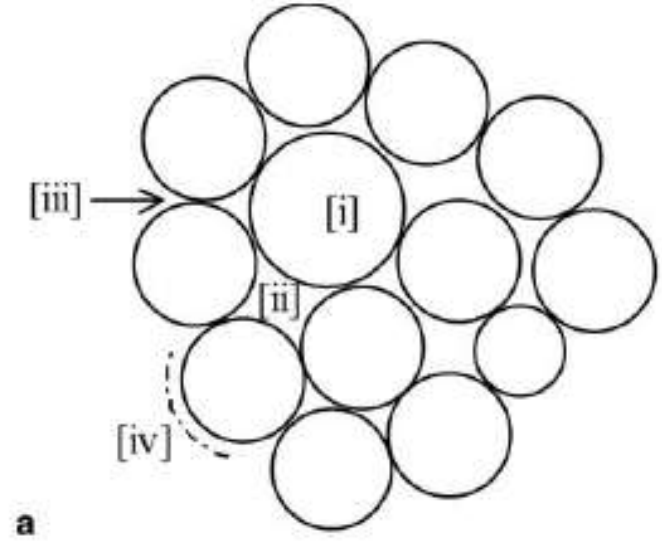
Agnihotri et al., Carbon 2005

Adsorption of solvents onto CNTs in gas phase



- Adsorption on SWNTs occurs
    i. in the hollow space inside nanotubes
    ii. in the interstitial spacing between three or more neighboring nanotubes
    iii. on the grooves present on the periphery of a nanotube bundle
    iv. on the curved surface on the periphery of a bundle

Agnihotri et al., Carbon 2005



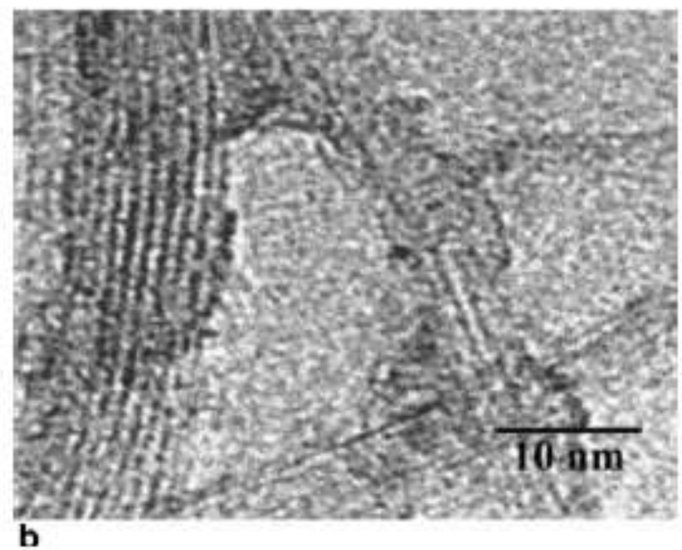


Fig. 4. (a) Cross-section of a SWNT bundle describing possible adsorption sites and (b) high resolution transmission electron image of sample EA95 [25]. Notice that multilayer adsorption on site [iv] would fill the void space between the SWNT bundles.

Adsorption on CNTs

- Sulfonyl urea herbicides
  - Similar performance compared to common adsorbent (C18)
  - Studied under a range of water conditions
    - Tap water
    - Reservoir water
    - Seawater
    - Well-water

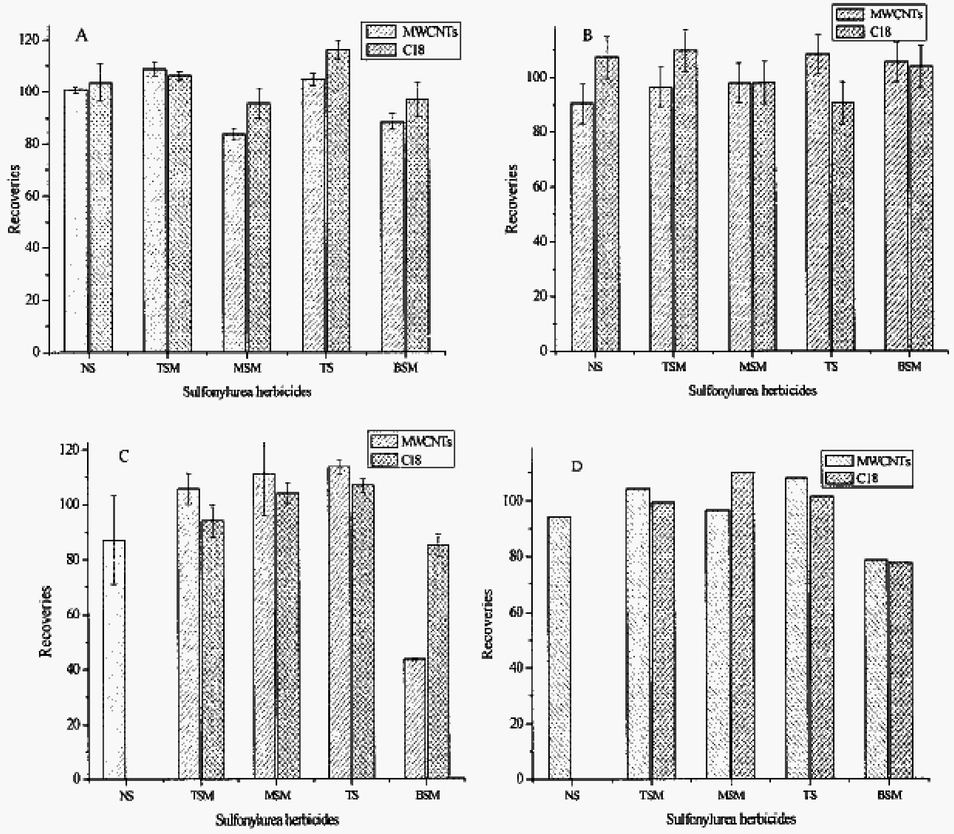


Fig. 1 Extraction performance of five sulfonylurea herbicides from spiked water samples with concentrations of 0.4 ng ml^{-1} nicosulfuron, thifensulfuron-methyl and bensulfuron-methyl, 0.2 ng ml^{-1} for metsulfuron-methyl and 0.8 ng ml^{-1} for triasulfuron using carbon nanotubes and C_{18}, respectively. A, Tap water samples; B, reservoir water samples; C, seawater samples; D, well-water samples. NS, Nicosulfuron; TSM, thifensulfuron-methyl; TS, triasulfuron; MSM, metsulfuron-methyl; BSM, bensulfuron-methyl.

Zhou et al. 2007

Adsorption on CNTs

- Acidic pesticides
  - Stronger adsorption onto CNTs than to other common adsorbents
    - Activated carbon
    - C18 sorbent
- Sorption is pH dependent, but for a wide range CNTs do better than common adsorbents

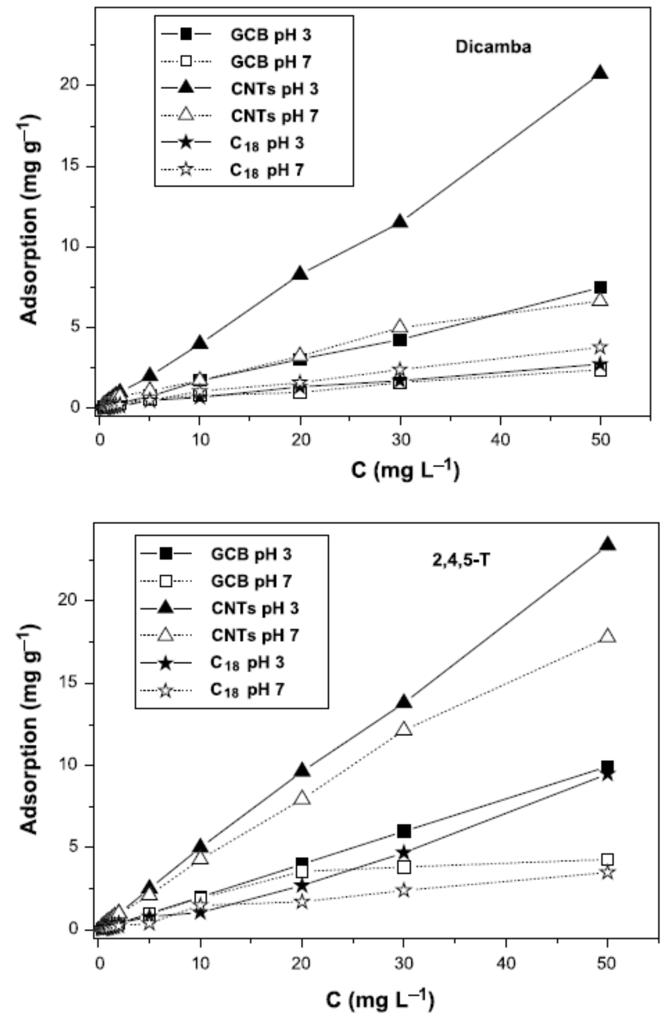


Fig. 3. Adsorption isotherms of dicamba and 2,4,5-T herbicides onto GCB, CNTs and C_{18} adsorbents

Biesaga and Pyrzynska, 2006

Adsorption on CNTs

Table 2. Results of Determination and Recoveries of Real Water Samples Spiked with Three Target Analytes

water sample	added (ng/mL)	found[a] (ng/mL)	recovery[b] (%)
tap water			
bisphenol A		nd[c]	
	0.40	0.36	89.8 ± 2.0
4-*tert*-octylphenol		nd	
	0.40	0.42	104.4 ± 2.5
4-*n*-nonylphenol		nd	
	0.40	0.37	93.5 ± 5.2
river water I			
bisphenol A		nd	
	0.40	0.41	101.4 ± 3.9
4-*tert*-octylphenol		nd	
	0.40	0.40	100.0 ± 4.4
4-*n*-nonylphenol		nd	
	0.40	0.39	98.4 ± 7.4
seawater			
bisphenol A		nd	
	0.40	0.41	102.8 ± 4.0
4-*tert*-octylphenol		nd	
	0.40	0.38	96.5 ± 3.3
4-*n*-nonylphenol		nd	
	0.40	0.39	98.6 ± 5.7
wastewater			
4-*tert*-octylphenol		nd	
	0.40	0.36	90.4 ± 1.9
4-*n*-nonylphenol		1.69	
	0.40	2.05	90.1 ± 6.7

[a] Mean for five determinations. [b] Mean and standard deviation for five determinations. [c] Not detected.

Adsorption on CNTs

- Adsorption of metals
  - Can achieve high recoveries
  - pH dependent
  - Affected by the presence of other water constituents
  - To date, mostly for analytical work

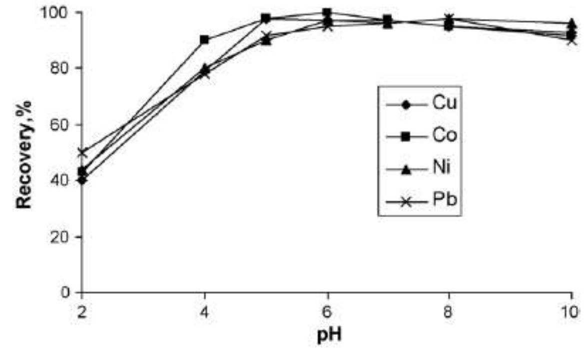


Fig. 1. Effect of pH on the recoveries of the metal ions on multiwalled carbon nanotubes ($N = 3$, eluent: $2.0\,mol\,l^{-1}$ HNO_3, amount of adsorbent: 200 mg).

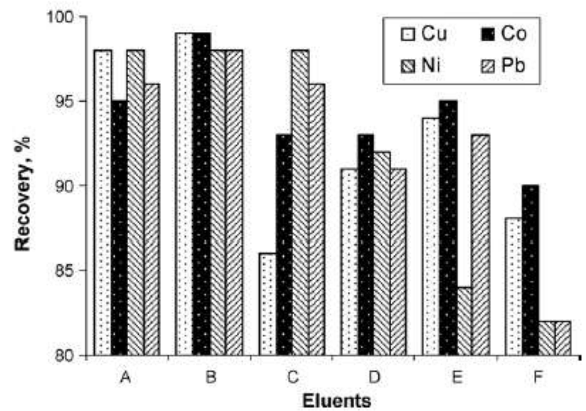


Fig. 2. Influences of some eluents on the recoveries of analyte ions (A: $1\,mol\,l^{-1}$ HNO_3, B: $2\,mol\,l^{-1}$ HNO_3, C: $3\,mol\,l^{-1}$ HNO_3, D: $1\,mol\,l^{-1}$ HCl, E: $2\,mol\,l^{-1}$ HCl, F: $3\,mol\,l^{-1}$ HCl).

Duran et al., J Haz Matl 2009

Sorption capacity of CNTs

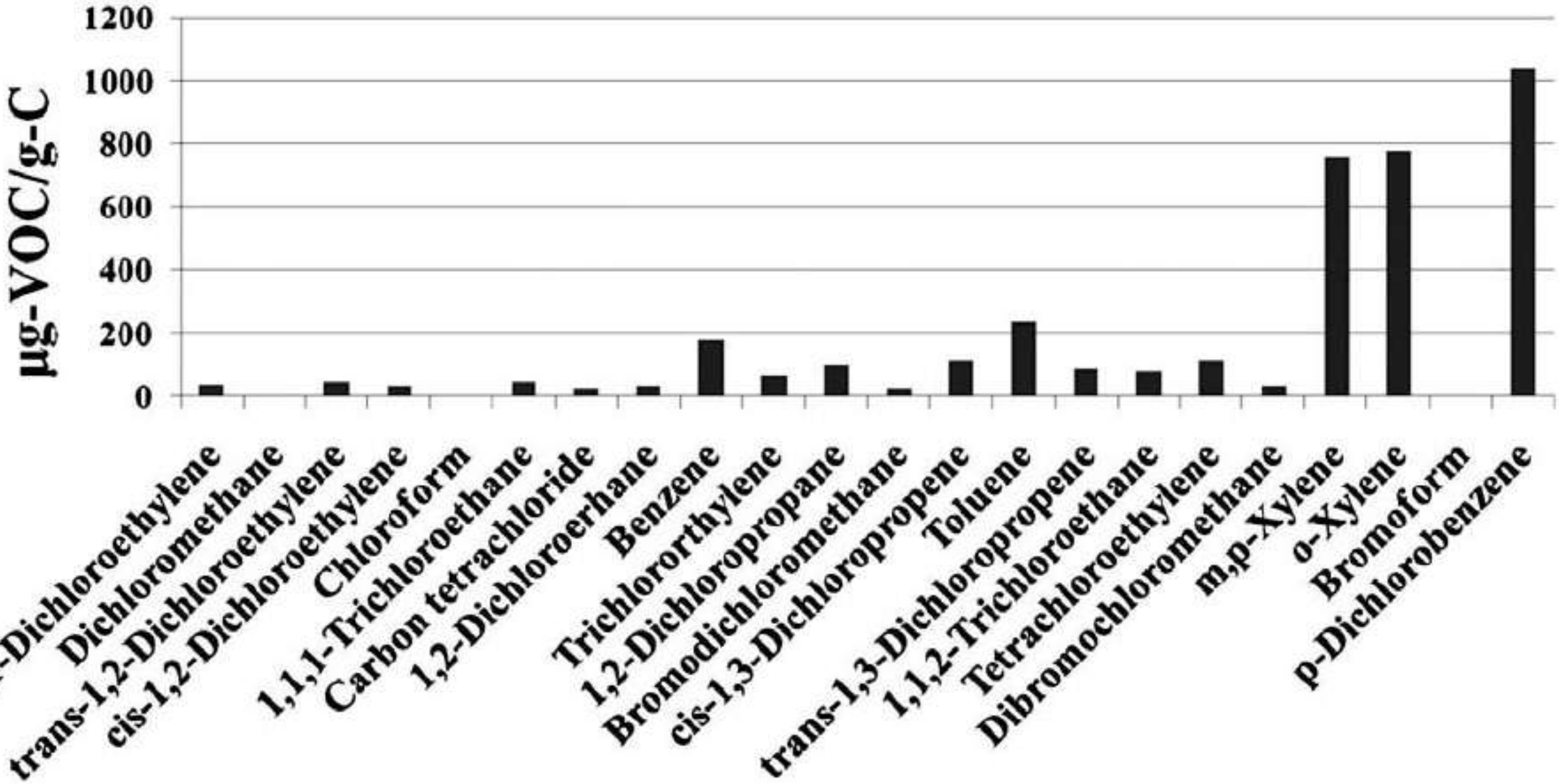


Fig. (2). Capacity of the HC-MWCNT-packed cartridges for adsorbing VOCs, expressed as micro-grams of VOCs per gram of HC-MWCNT (Adapted from [45]).

Sone et al. Talanta 2008

Adsorption of Catalysts onto CNTs

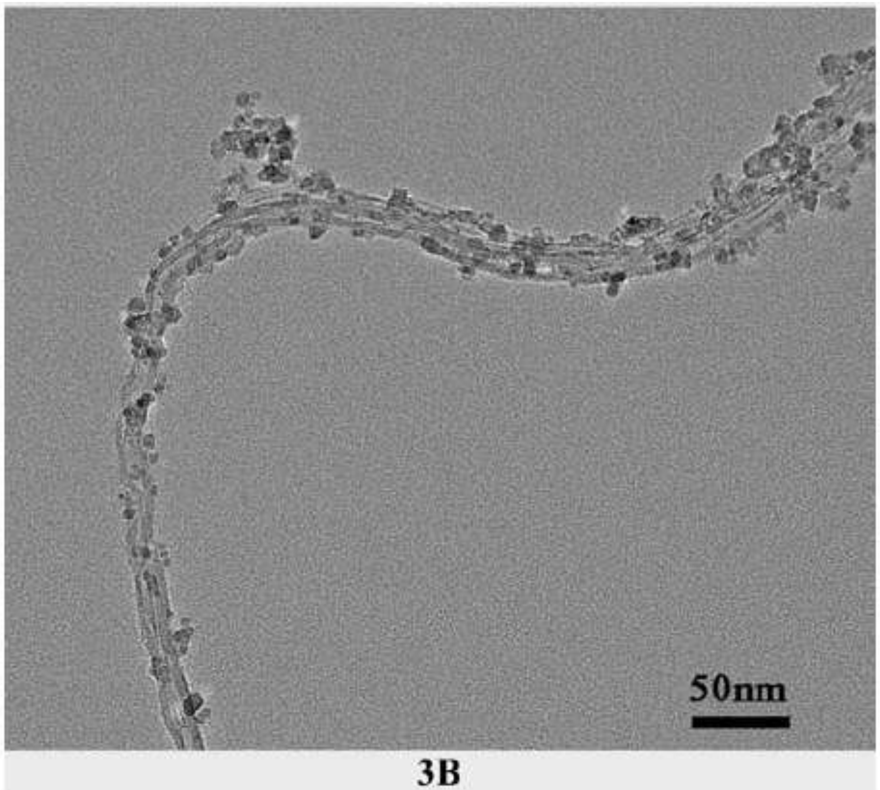


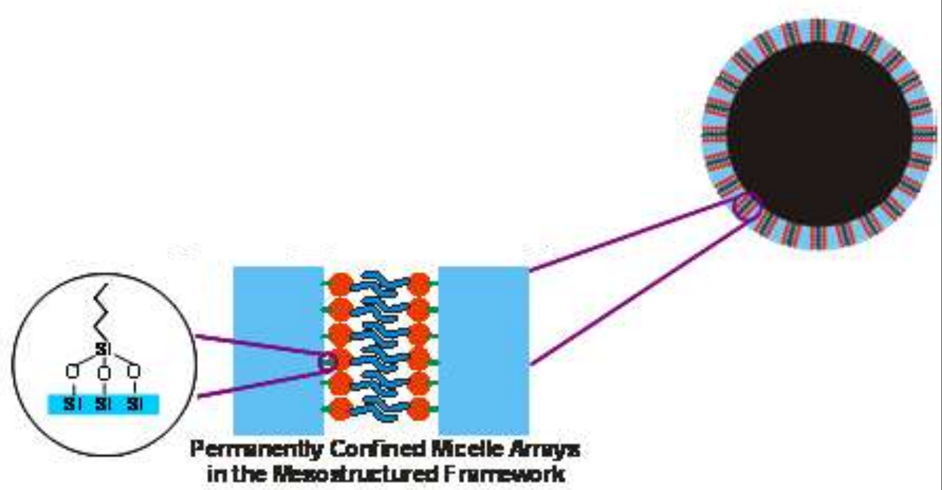
Fig. (3). Images of transmission electron microscopy (TEM) of TiO_2/MWNTs.

- Adsorption of TiO_2 onto CNTs
  - For potential oxidation of a wide range of compounds
  - CNTs serve as the "carrier" for the catalyst

Zhou et al., ***Recent Patents in Materials Science 2009***

Mag-PCMA as Adsorbent

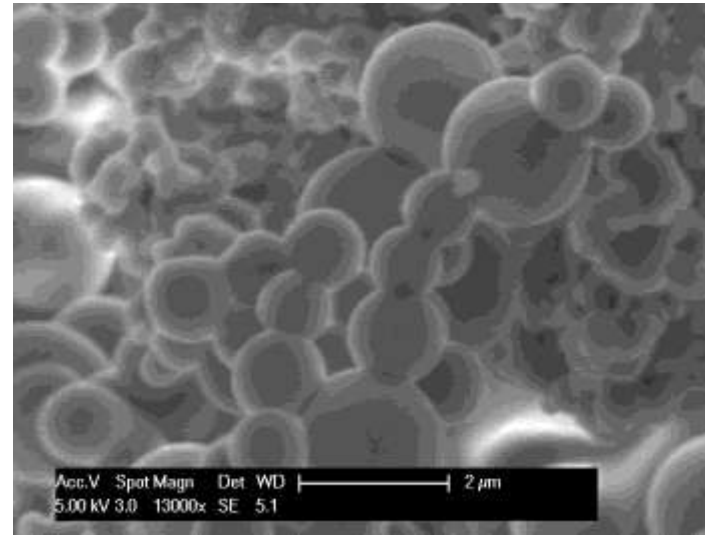
- Magnetic Permanently Confined Micelle Arrays
  - Magnetic nano-core
  - Mesoporous silica shell
  - Co-deposition of surfactant micelles covalently bonded to silica shell
- Can provide lots of sorption sites

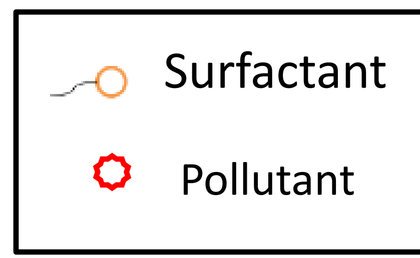


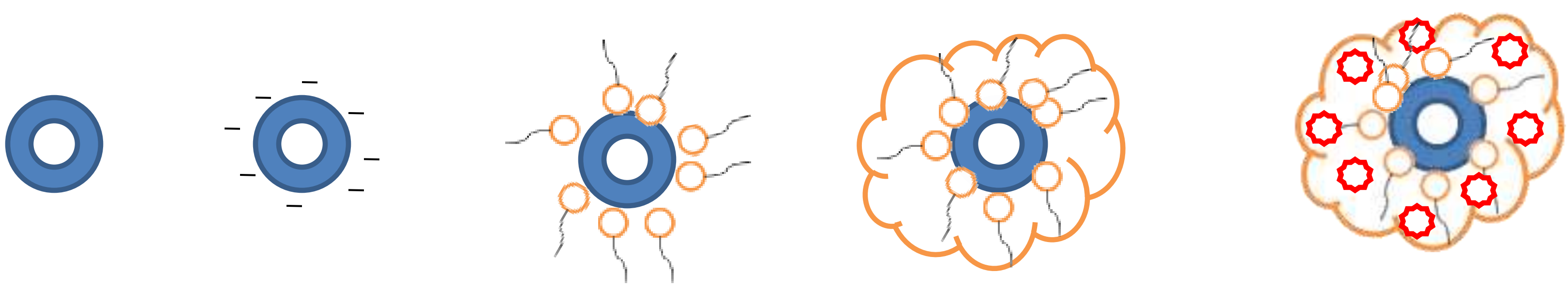
Wang, Keller et al., JACS 2008

Mag-PCMAs

- Starting material is a magnetic iron oxide nanoparticle
- A porous silica shell is used to encapsulate the core
- A surfactant is trapped permanently within the porous silica
- Pollutants have a strong affinity for the surfactant
- Saturated Mag-PCMAs can be removed using a simple magnet







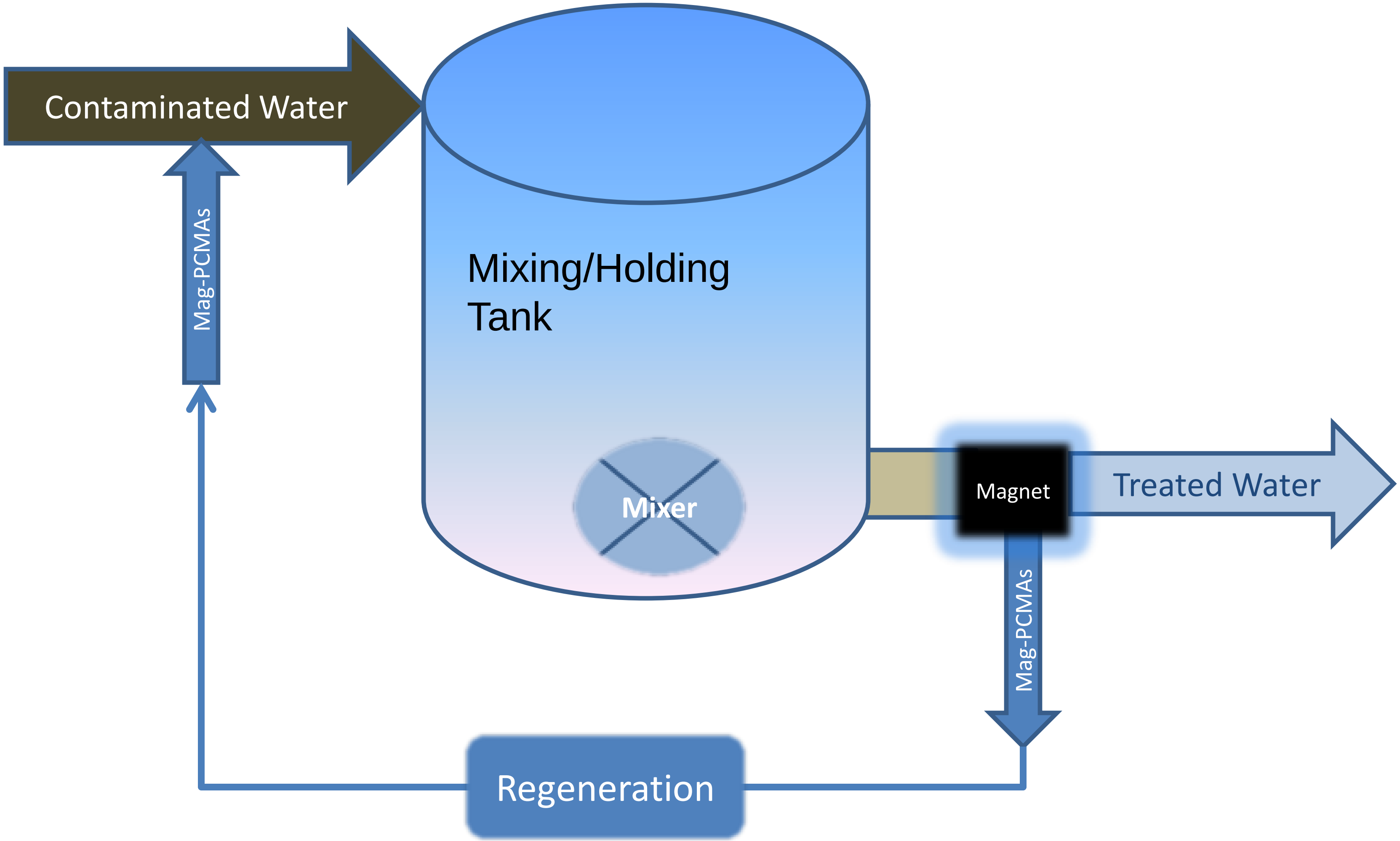
Removal of Mag-PCMAs with magnetic field

Planned treatment process

- Mag-PCMAs are added to the contaminated water
- Mixed thoroughly
- Allowed to sorb contaminants for 15 min
- Remove Mag-PCMAs with a magnet at the outlet of the treatment tank
  - May have a final polishing step to ensure no Mag-PCMAs are present in discharge
- Once the Mag-PCMAs are saturated with pollutants, remove and wash with ethanol to remove sorbed organics
  - Small volume of concentrated organics
  - Concentrated organics may have resale value
- Reuse Mag-PCMAs



Water Purification Process using Mag-PCMAs

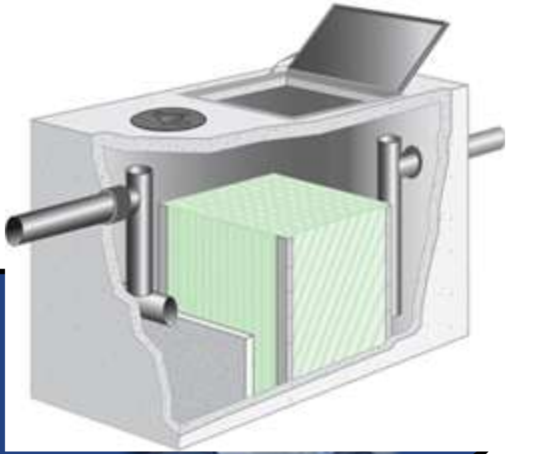


Possible applications of technology

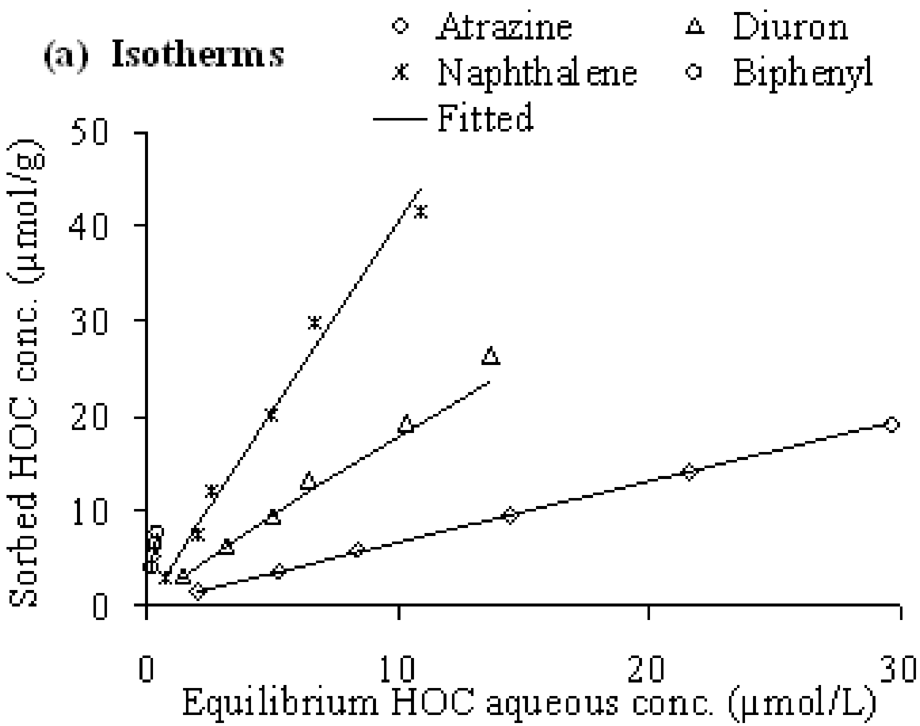
- Treatment at the source of a drinking water supply
  - to remove any known or potential organic contaminants
- Treatment of industrial process water contaminated with organic contaminants
  - for reuse within the process or for discharge to a municipal sewer
- Treatment of industrial materials which have been contaminated with hazardous organic chemicals
- Treatment of contaminated stormwater
- Treatment of soils and sediments contaminated with organic contaminants
  - difficult to desorb through traditional processes;
- Preparing samples for chemical analysis

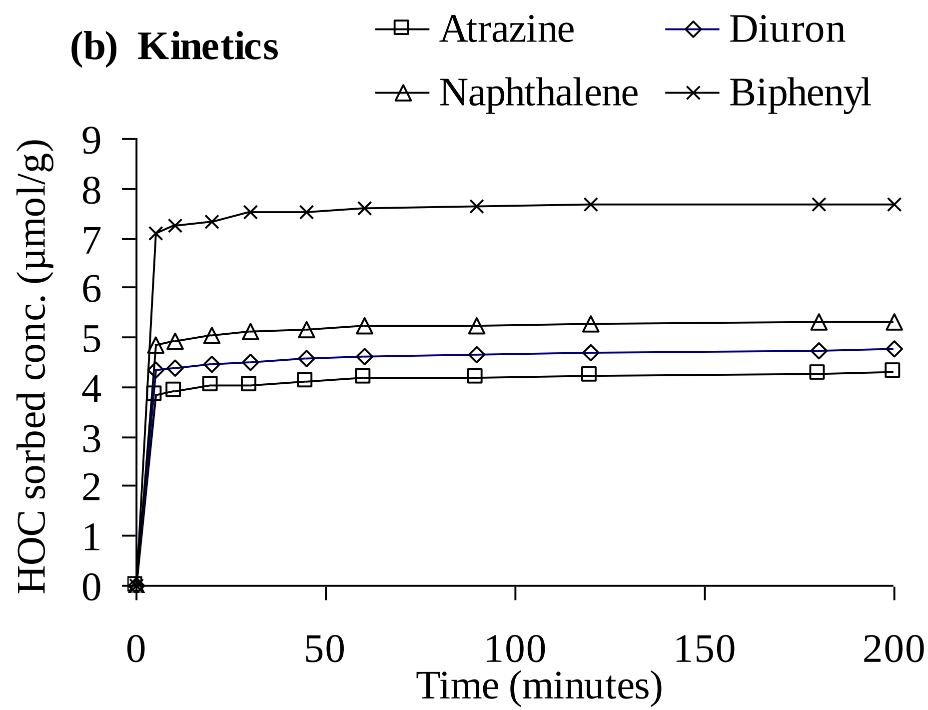


Possible applications of technology



Pesticide and PAH removal from water using Mag-PCMAs





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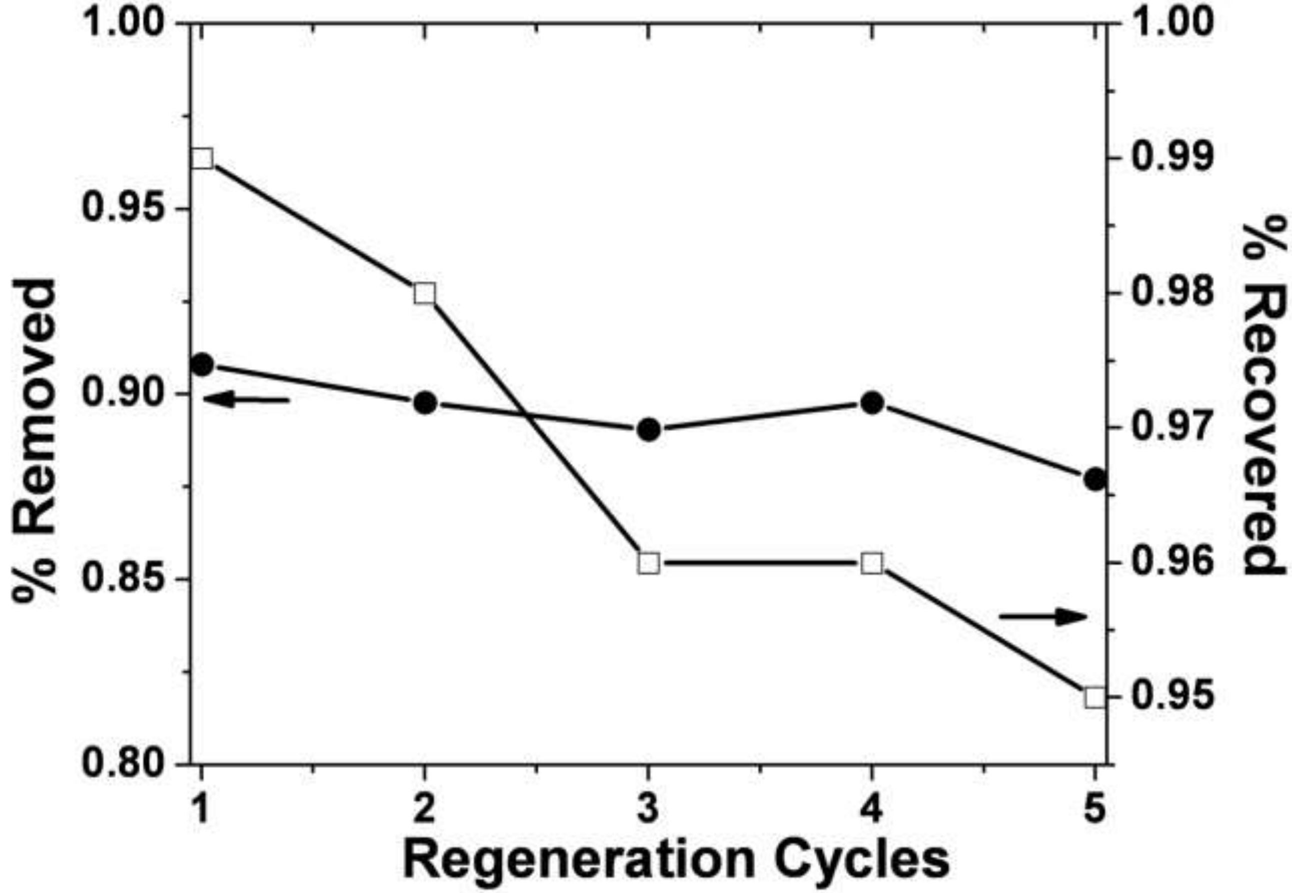
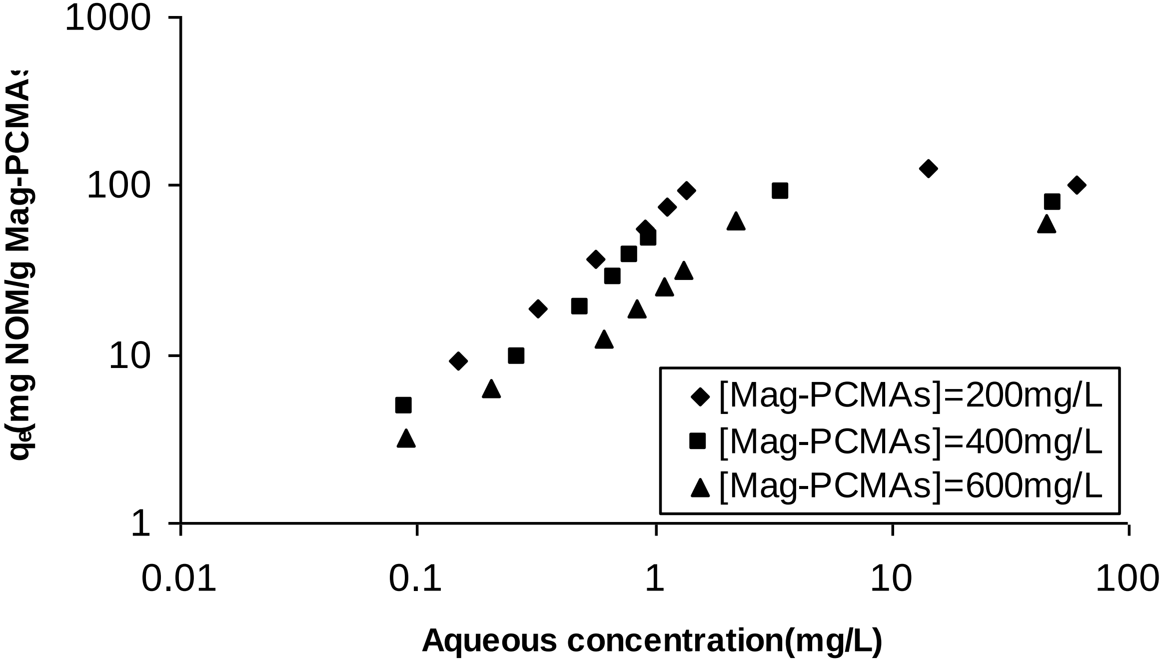
Regeneration of Mag-PCMAs

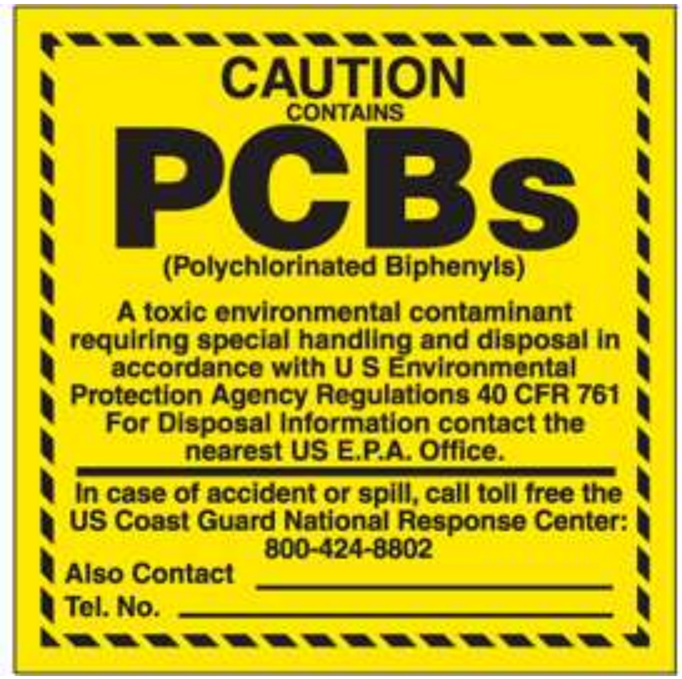


Removal of NOM with Mag-PCMAs



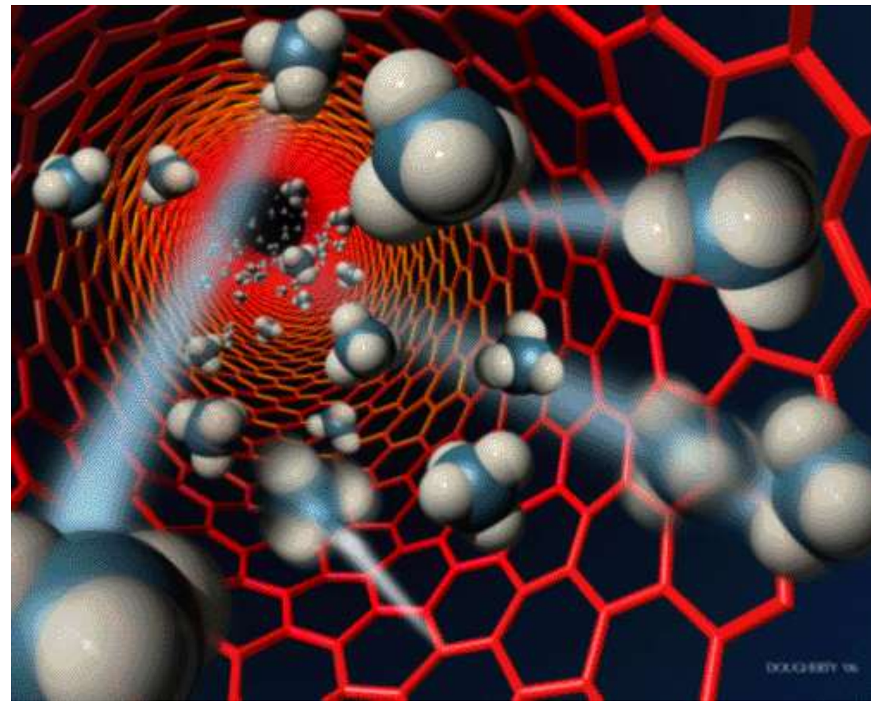
Compounds that can be removed

- Pesticides
- PAHs
- PCBs
- Dissolved organic matter
- Trace Pharmaceuticals & hormones
- Oil & grease (at low levels)
- Possibly viruses



Quiz

- What are is the major challenge for using CNTs as adsorbents today?
  – A: Size
  – B: Availability
  – C: Cost
  – D: Effectiveness
  – E: pH of the water



Nanoparticles as Environmental Sensors



CNTs for sensors

- **Palladium Nanoparticles Decorated Single-Walled Carbon Nanotube Hydrogen Sensor**

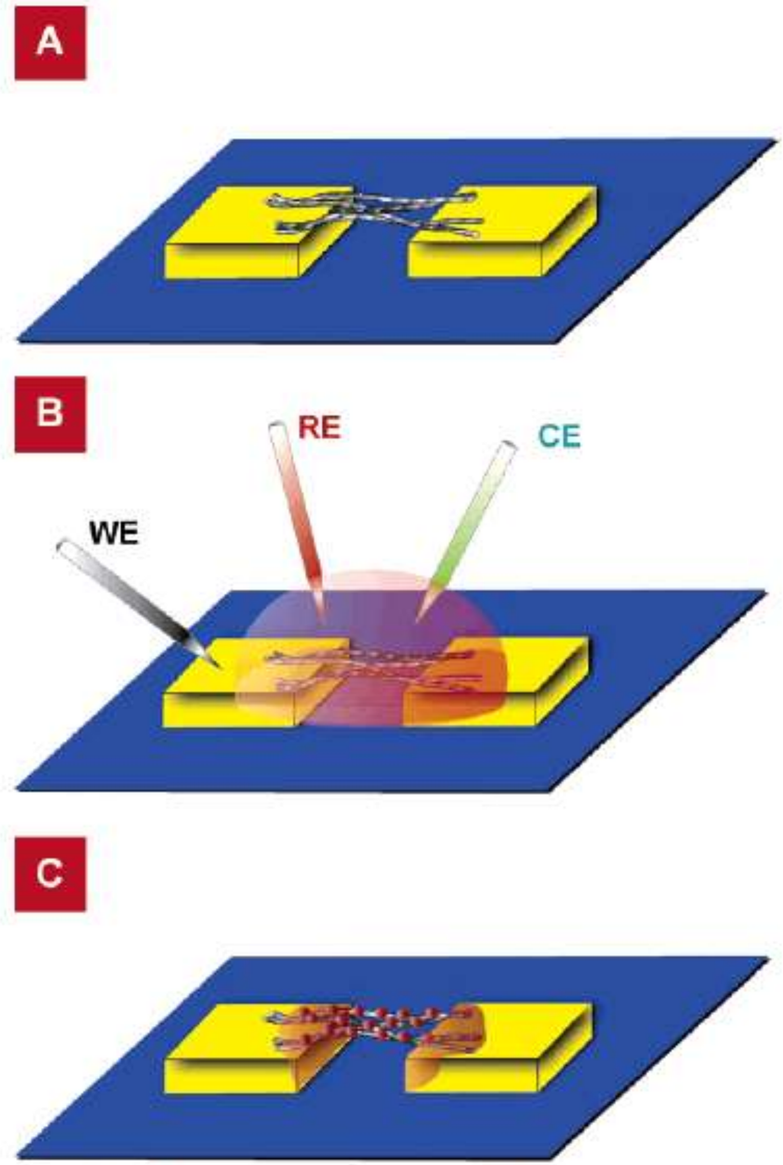


Figure 2. Schematic of the electrochemical synthesis method. (A) Nanotubes are deposited across the electrodes. (B) Electrochemical functionalization of the SWNTs: WE = working electrode; CE = counter electrode; RE = reference electrode. (C) Pd nanoparticles formed on SWNTs.

Mubeen et al. *J. Phys. Chem. C* ***200***

CNTs for sensors

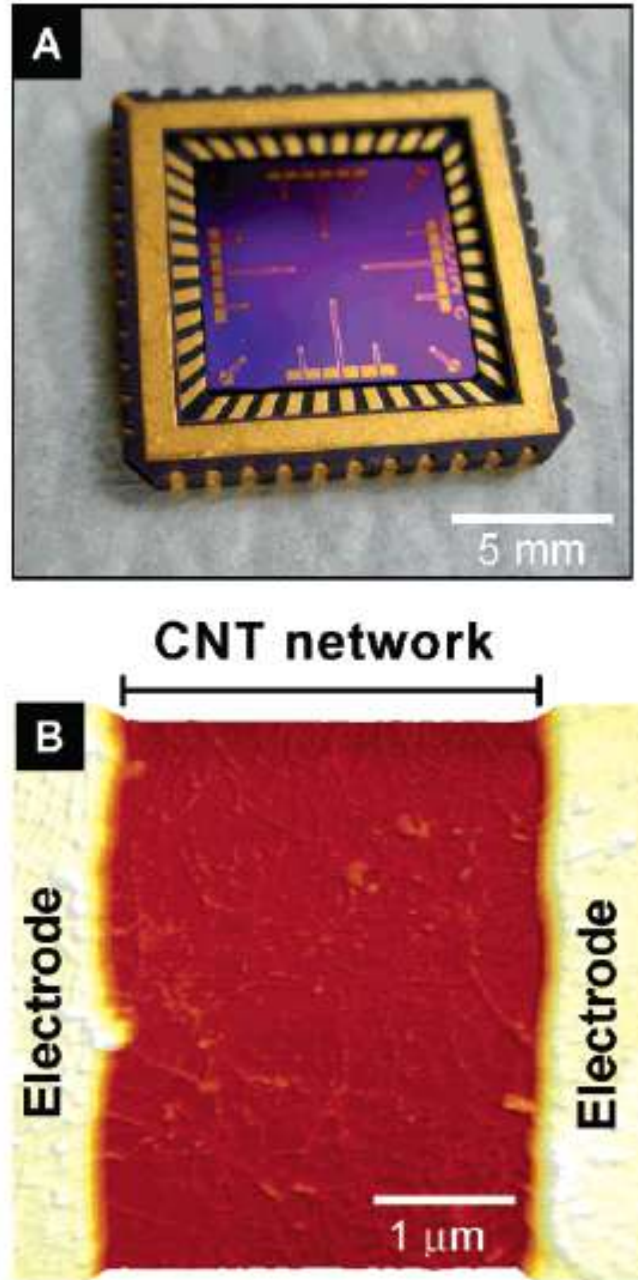


Figure 1. Optical image of 16 sensors array on chip carrier (A) and AFM image of SWNT network across microfabricated gold electrodes (B).

CNTs for sensors

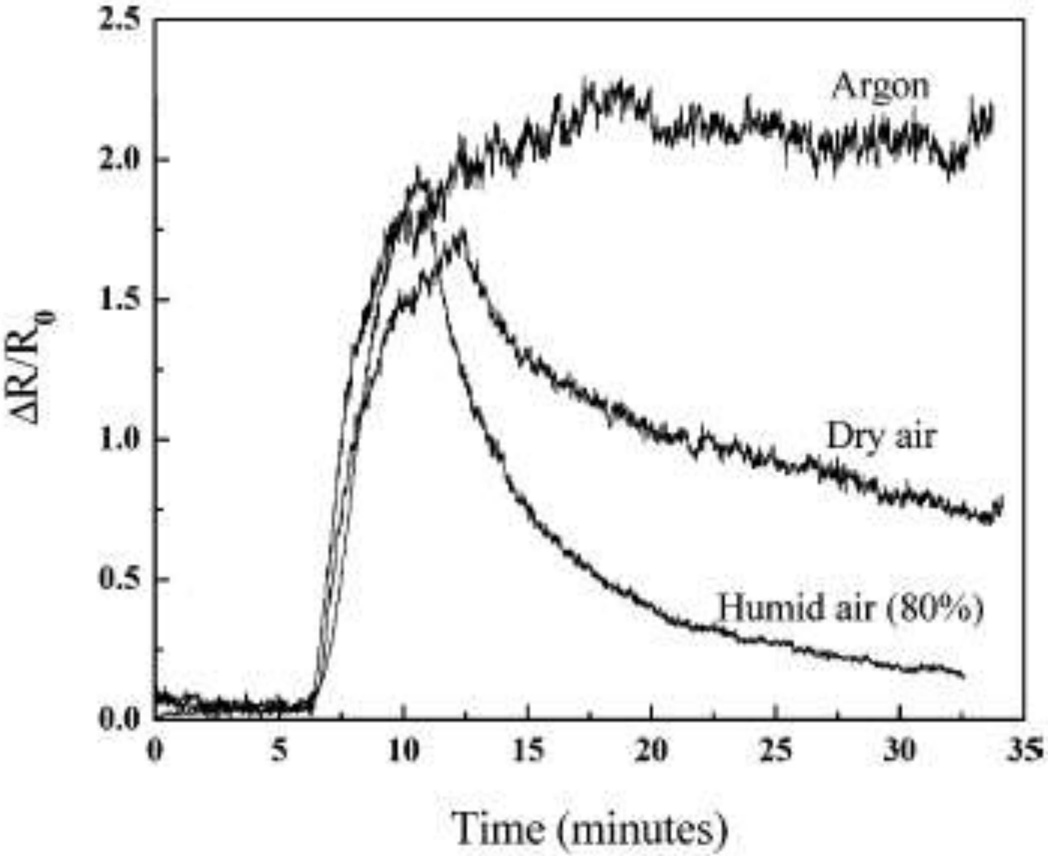


Figure 7. Sensor response to 400 ppm hydrogen for three different carrier gases.

CNTs for sensors

- Carbon Nanotube Sensors for Gas and Organic Vapor Detection

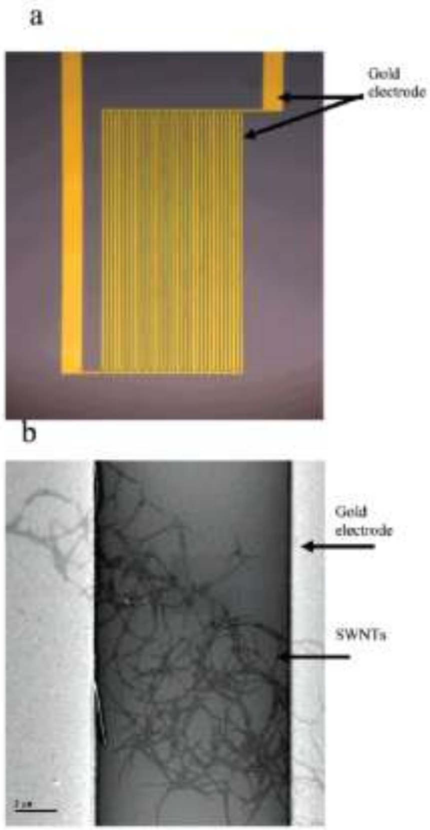


Figure 1. (a) Interdigitated electrodes. (b) SEM image of SWNTs across two gold electrodes.

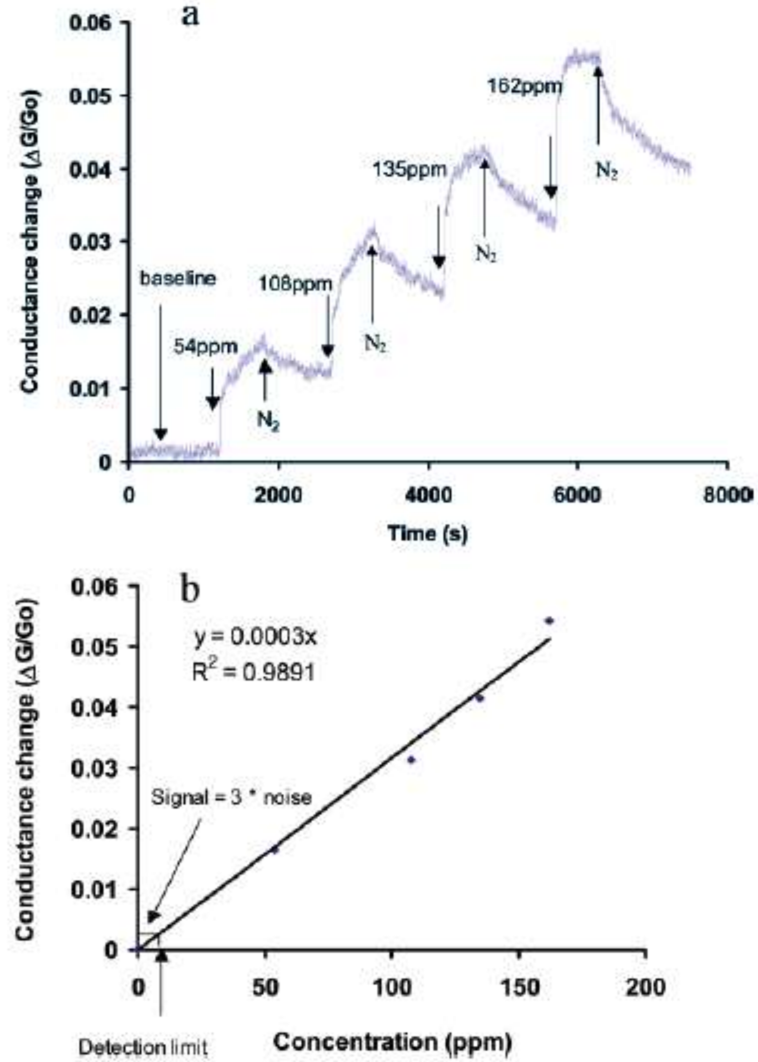


Figure 4. Representative sensor response from group 3 for nitrotoluene. (a) Sensor response is a step function of concentration. (b) Calibration curve from a. The nitrotoluene vapor was evaporated

Li et al, Nanoletters 2003

Gold NP-CNT sensor

- For electrochemical determination of organophosphate pesticides

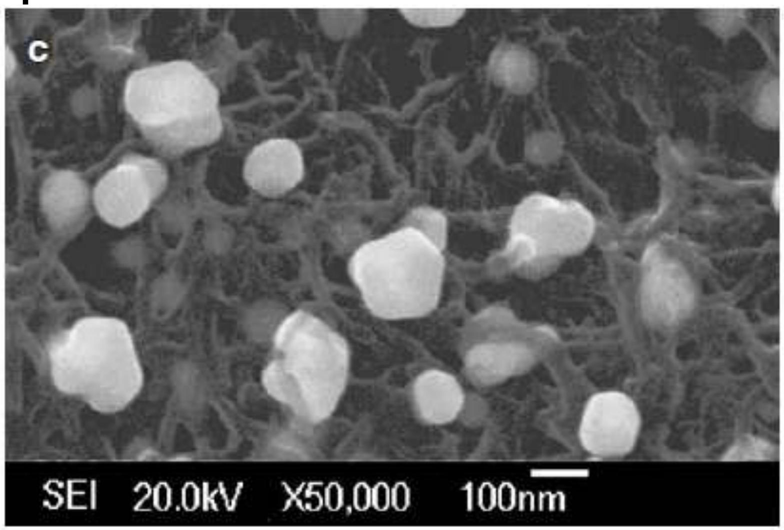


Fig. 1 FE-SEM of the CNTs (a); Au nanoparticles (b) on GCE; Au nanoparticles combined with CNTs on GCE (c)

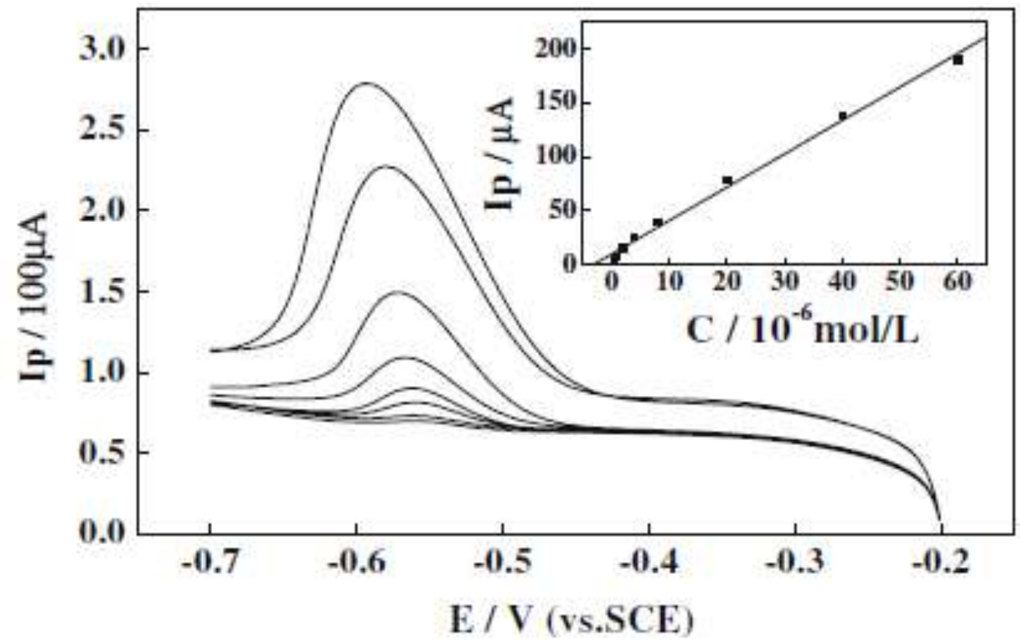
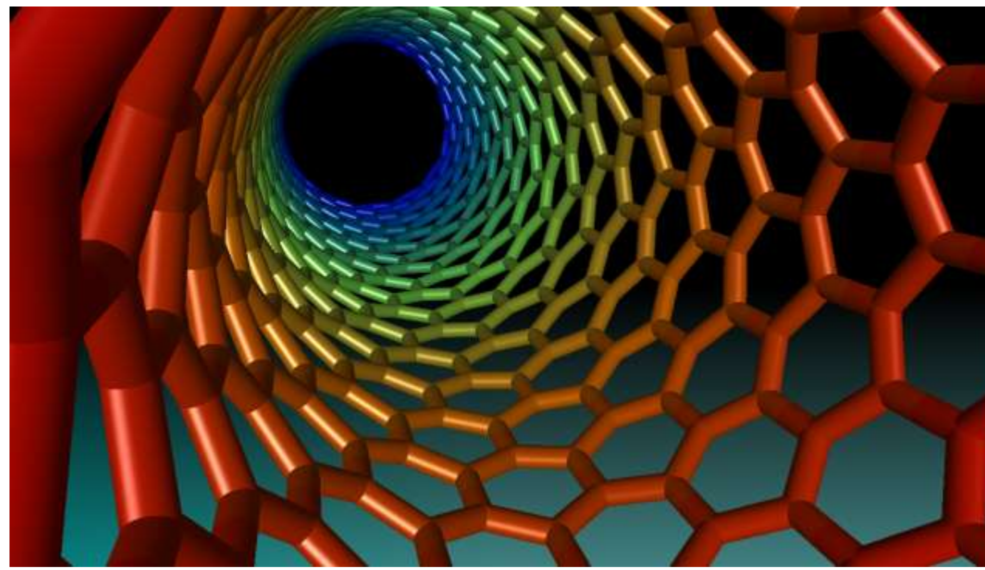


Fig. 4 Linear scan voltammograms of parathion in PBS at Au/CNTs/GCE, from bottom to top, 0.5, 0.8, 2, 4, 8, 20, 40, 60 μM parathion, respectively. Scan potential range: from -0.2 to -0.7 V. Inset: plot of i_p vs. *c*. other conditions as in Fig. 3

Zhang et al., Microchim Acta 2009

Poll

- What environmental application of nanomaterials do you find most interesting?
  - A: as reactants
  - B: as catalysts
  - C: as adsorbents
  - D: as sensors
  - E: all of the above



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Aug 8-12 Workshop B (covering last 3 NACK Courses)

A = Safety, Technology, Processing, & Materials (STPM)

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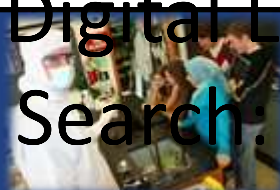

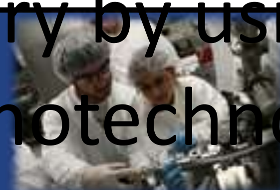

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