Carbon-based nanomaterials. Environmental applications

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Bucharest
Romania
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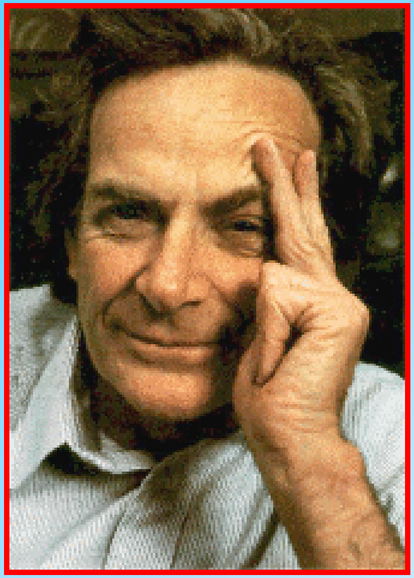
“There’s Plenty of Room at the Bottom”
Richard Feynman (Caltech,1959)



Now, the name of this talk is ``There is Plenty of Room at the Bottom''---not just ``There is Room at the Bottom.'' I now want to show that there is plenty of room. I will not now discuss how we are going to do it, but only what is possible in principle---in other words, what is possible according to the laws of physics. I am not inventing anti-gravity, which is possible someday only if the laws are not what we think. I am telling you what could be done if the laws <u>are</u> what we think; we are not doing it simply because we haven't yet gotten around to it.

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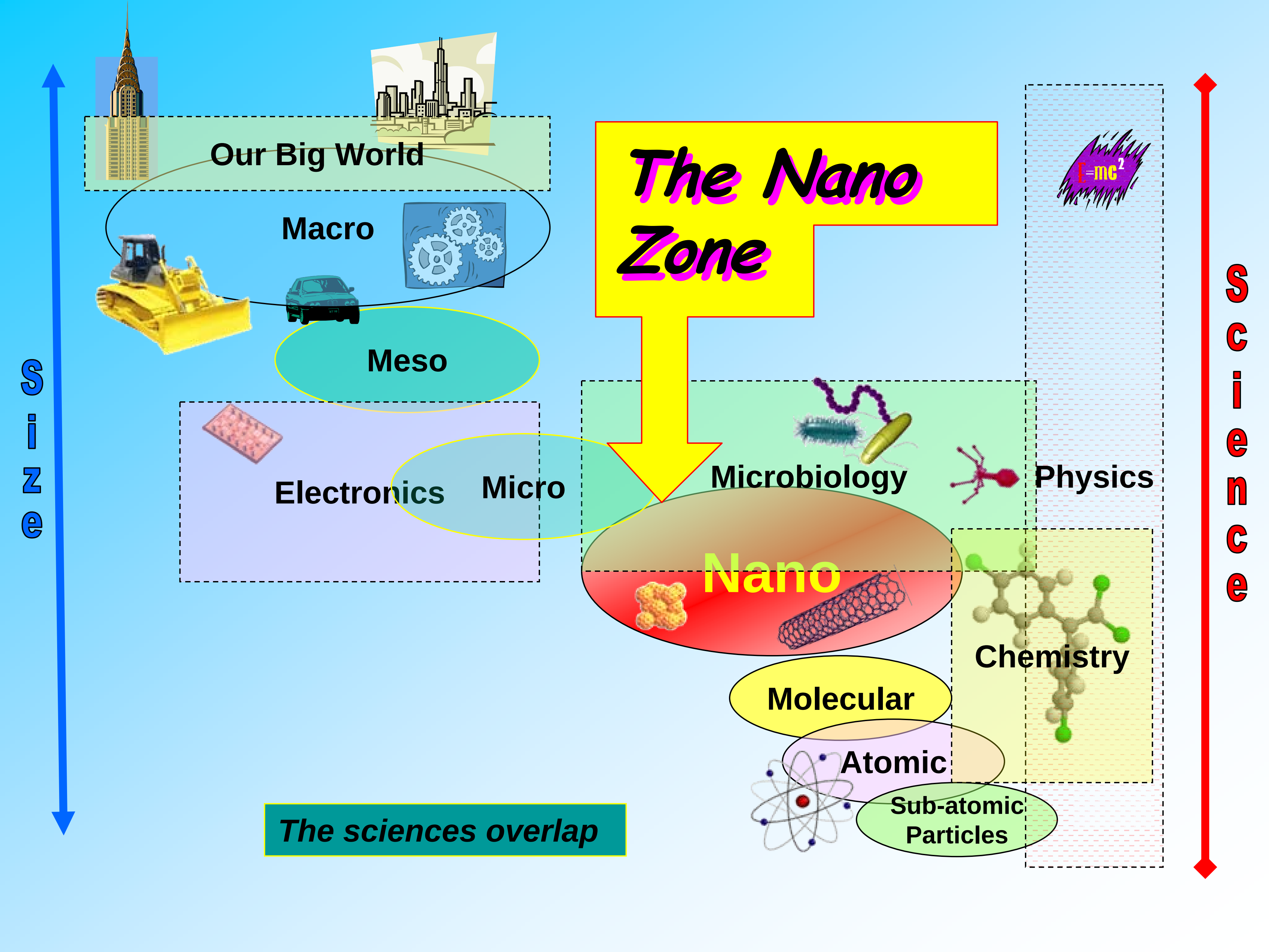
Size
Science
Our Big World
Macro
Meso
Electronics
Micro
The Nano Zone
Microbiology
Physics
E=mc²
Nano
Chemistry
Molecular
Atomic
Sub-atomic Particles
The sciences overlap

Classification of nanoparticles in the environment

- Natural nanoparticles: particles with one or more dimensions at the nanoscale originating from natural processes, e.g. soil colloids, volcanic ash, mineral composites…
- Incidental nanoparticles: nanoparticles formed as a by-product of man-made or natural processes, e.g. welding, milling, grinding or combustion
- Engineered nanoparticles: nanoparticles manufactured to have specific properties of a specific composition, e.g. nanotubes, quantum dots, graphenes…

Occurrence of nanoparticles

Air: contains large number of nano-sized particles, reaching concentrations of 10 000-500 000 particles/cm3

Water: extremely reach in natural nanoparticles as organic and inorganic colloids (humic substances, clays, silicate, iron oxides, humic-mineral complexes)

Sediments: colloidal part

Soil: the richest matrix in nanoparticles

Nanoparticles in Soil

- Clays, zeolites, imogolite, NOM
- Iron and manganese oxides
- Organic particles
- Coated and core-shell particles
- Issues of nutrient and pollutant transport, water retention, texture, bioavailability.
- **Soil is a *nano- micro- macro-composite***

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Nanoparticles in Water

- Aluminum and iron oxides and other colloidal particles (carbon nanoparticles)
- Transport nutrients and pollutants, both organic and inorganic
- Markers of sources
- Modify (increase or decrease) concentrations and bioavailability calculated from simple equilibria of dissolved species

Nanoparticles in Air

- Natural sources plus agricultural dust, industrial and automotive pollution
- Trace sources by chemistry and mineralogy
- Contaminant and nutrient transport
- Health effects
- Global climate effects

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Overview of types of engineered nanoparticles (ENPs)

- Fullerenes (Buckminster fullerenes, CNTs, nanocones)
- Metal ENPs (e.g. elemental Ag, Au, Fe)
- Oxides or binary compounds (e.g. TiO_2, FeO, Fe_2O_3)
- Complex compounds (alloys, composites, nanofluids, consisting of two or more elements)
- Quantum dots (binary or complex compounds coated with a polymer), e.g. CdSe
- Organic polymers (dendrimers, polystyrene)

Quantitative methods for measurement in environmental samples (I)

- Chemical analysis: in samples where their background levels are very low; these analyses do not distinguish between particles and dissolved ions;
- Auto-fluorescence: for q-dots and aromatic structures with intrinsic fluorescence properties
- Gas – chromatography and HPLC
- UV-VIS spectroscopy

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Quantitative methods for measurement in environmental samples (II)

- Raman spectroscopy
- Isotopic labeling
- Chromatographic methods

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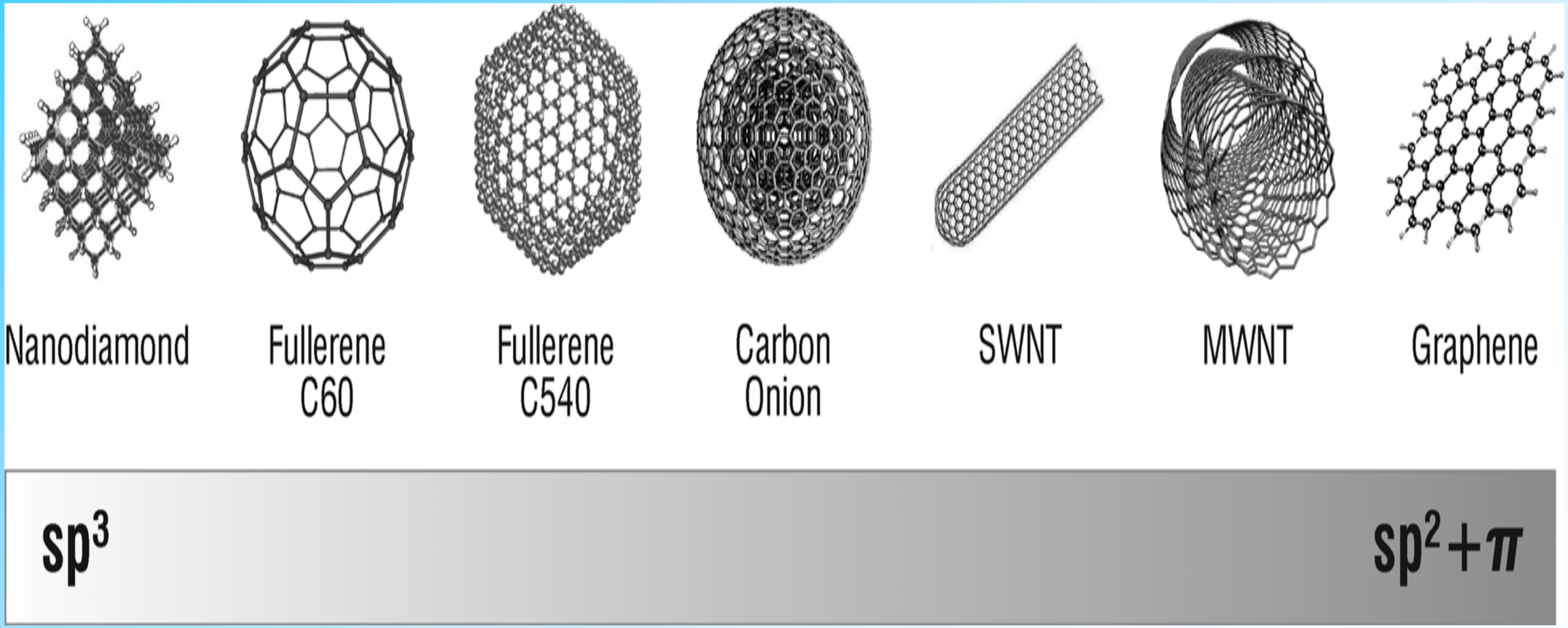
Carbon-based nanomaterials



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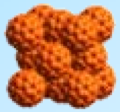
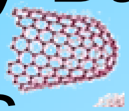
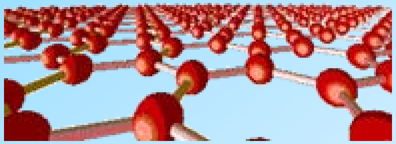
Nano Building Blocks

- Powders & thin films/coatings – old nano
- Small 3D molecules
  - Bucky Balls (fullerenes)

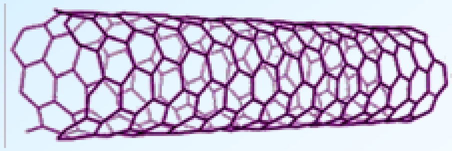


  - Horns





  - Graphene
  - Carbon Nanotubes (CNT)



- Wires & ropes
- Self-assembling entities
- Complex shapes (in future)

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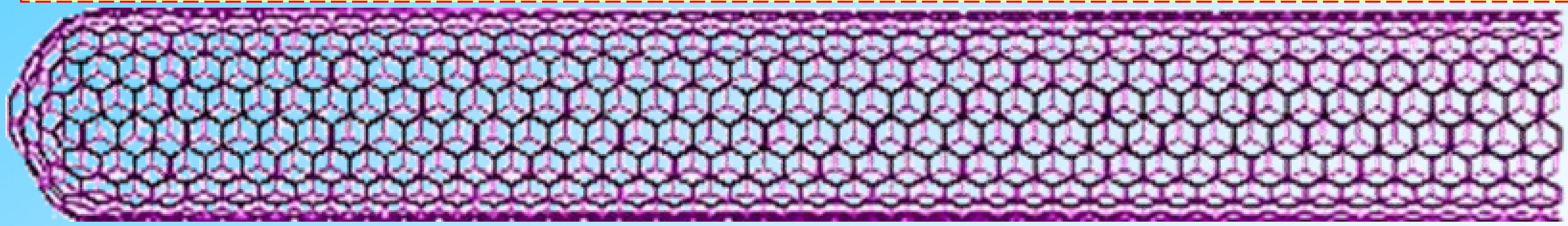
Carbon Nanotubes (CNT)

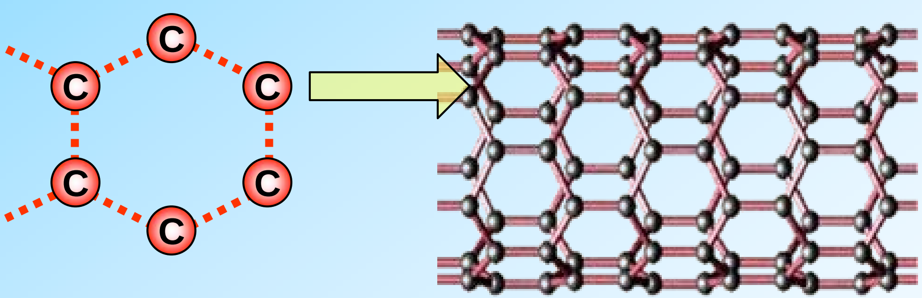
Carbon Nanotubes: graphene cylinders closed at either end; new elemental form of carbon (C).

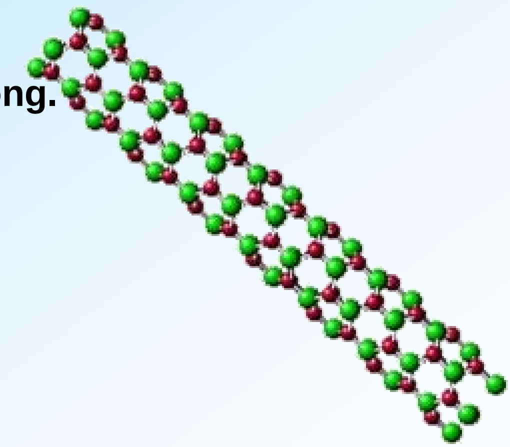
Uses: semiconductors, electrically conductive non-metals, high thermal conductors and reinforcement - strongest known fibers.

New uses are being discovered every monthly.



CNTs are usually 1-50 nanometers in diameter and typically a few microns long.





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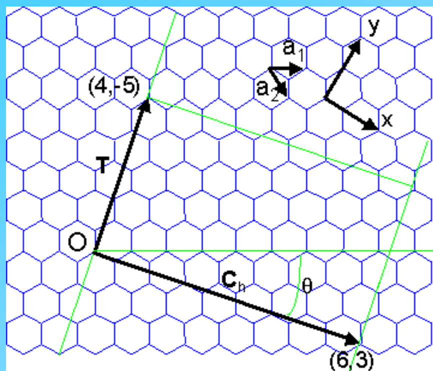
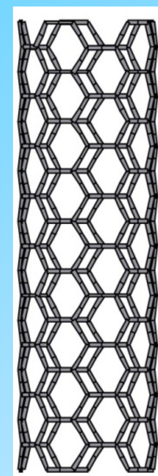
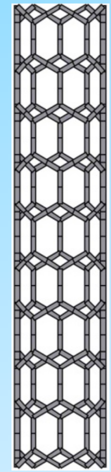
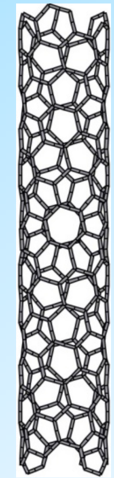
Rolling-up a graphene sheet

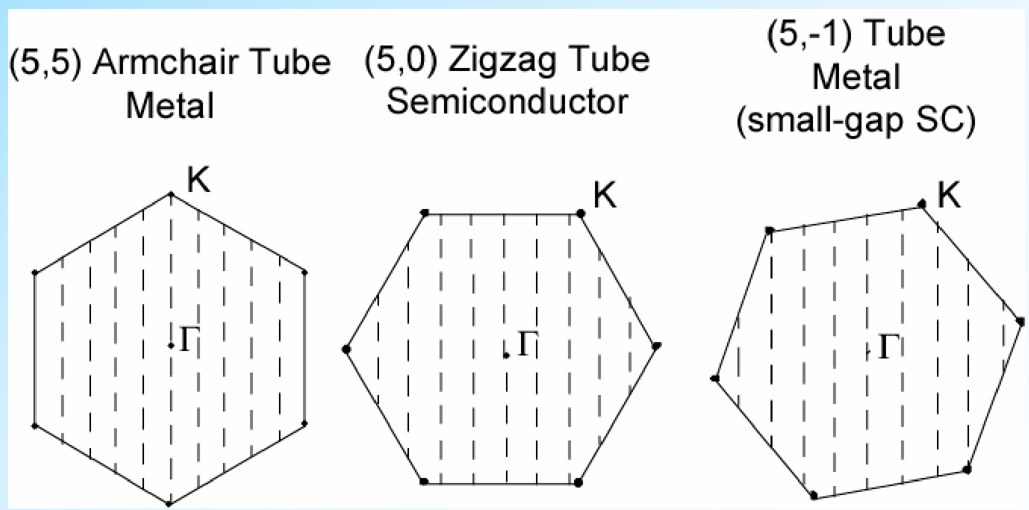






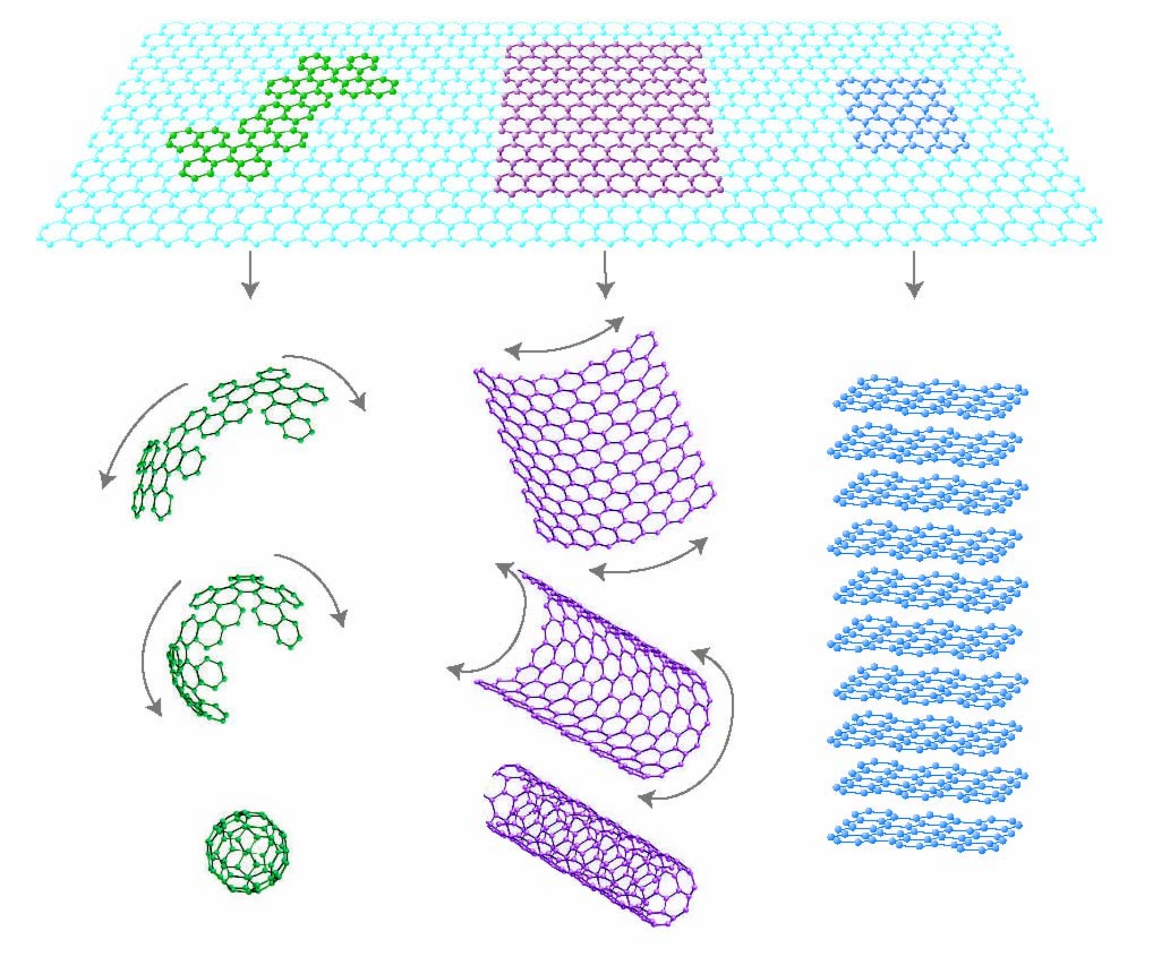


The wrapping has to match the period of the graphene lattice (m,n)



m=n **mod(m-n,3) = ±1** **mod(m-n,3) = 0, m≠n**

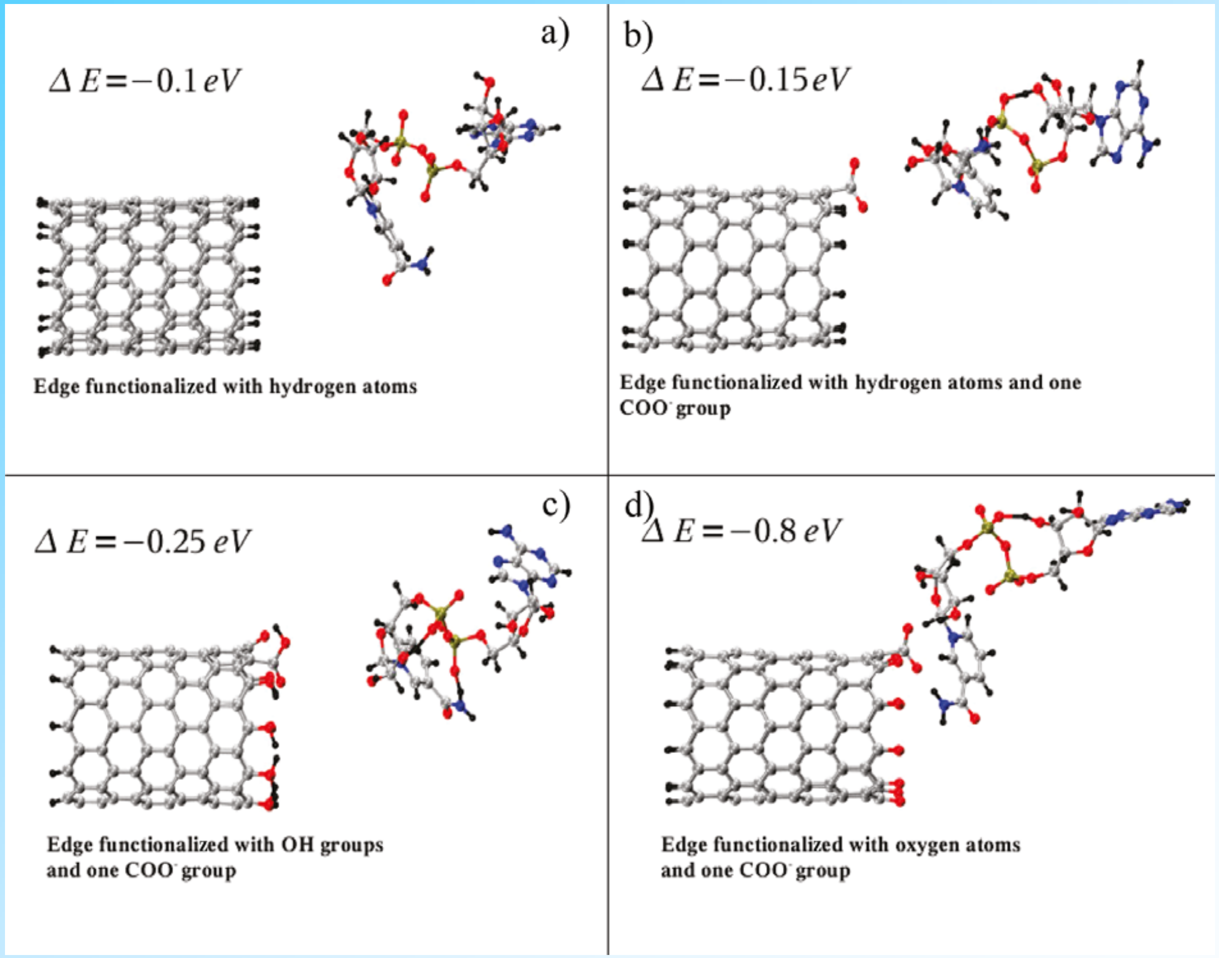
What is graphene?



- 2-dimensional hexagonal lattice of carbon
- sp^2 hybridized carbon atoms
- Basis for C-60 (bucky balls), nanotubes, and graphite
- Among strongest bonds in nature

A. K. Geim & K. S. Novoselov. The rise of graphene. ***Nature Materials Vol 6*** 183-191 (March 2007)

Mechanism of adsorption of organic molecules on carbon nanotubes



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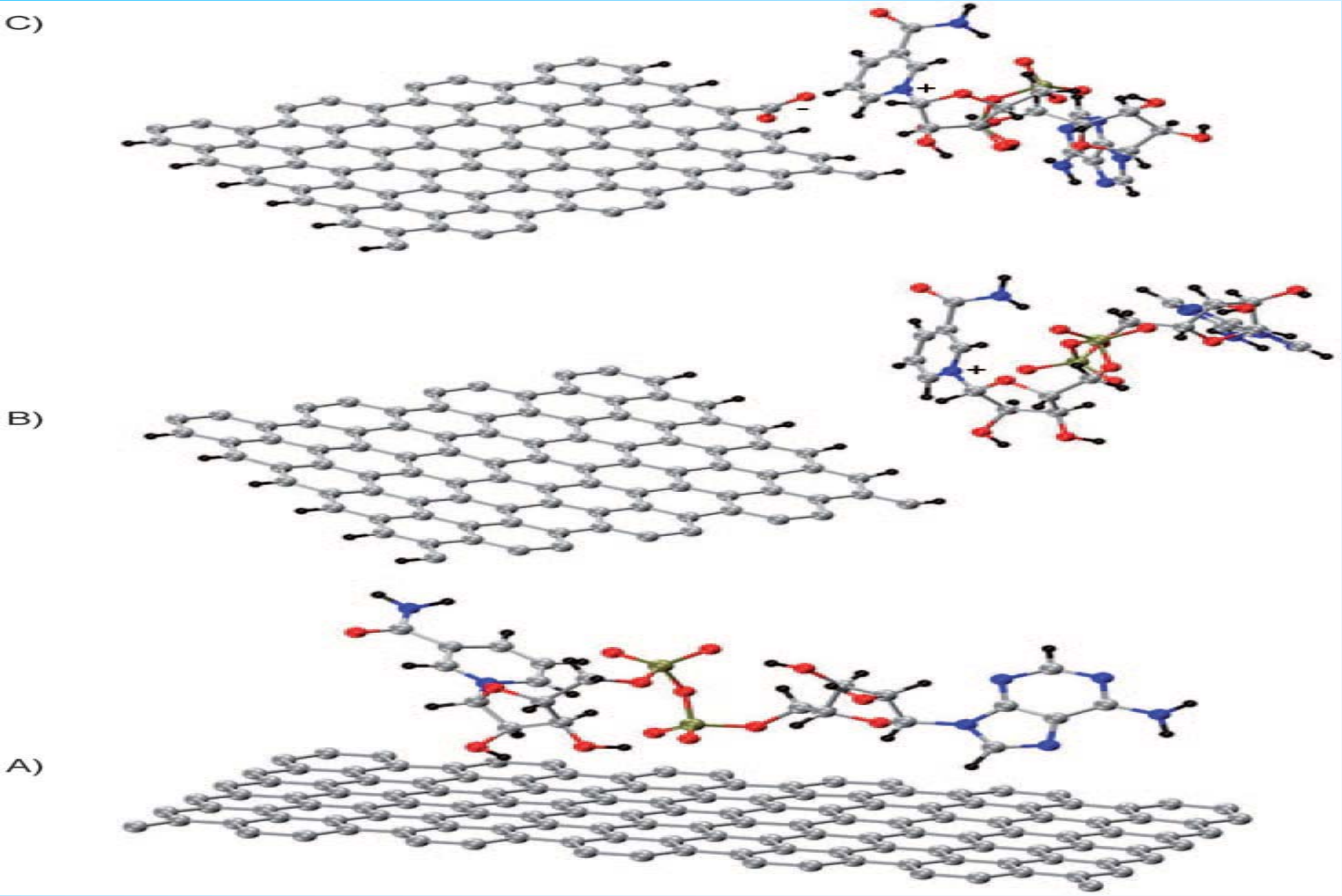
Mechanism of adsorption of organic molecules on graphene



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Environmental nanotechnology

- Which are the most effective nanotechnologies for prevention or cleanup of pollution?
- How dependable and close to the market are the remediation techniques based on nanotechnologies?
- What additional research is needed to exploit the full potential of nanotechnology for remediation?
- What are the potential risks of using nanotechnologies in remediation applications?

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Nanotechnology and the Environment

The bad…

- Nature of nanoparticles themselves.
- Characteristics of the products made.
- Manufacturing processes involved.
  - As nano-xyz is manufactured, what materials are used?
- What waste is produced?
- Are toxic substances used in the manufacturing of nano-xyz?
- What happens when nano-xyz gets into the air, soil, water, or biota?

"The emerging fields of nanoscience and nanoengineering are leading to unprecedented understanding and control over the fundamental building blocks of all physical things. This is likely to change the way almost everything - from vaccines to computers to automobile tires to objects not yet imagined - is designed and made."

- Interagency Working Group on Nanoscience, Engineering, and Technology Report (1999)

“As EPA looks to the future, it will need to employ innovative approaches and sound science to investigate complex, interdisciplinary problems in environmental protection.”

- EPA FY 2001 Annual Report

Nanotechnology and the Environment

The good…

Nanotechnology has the potential to substantially benefit environmental quality and sustainability through

- **Pollution prevention**
- **Treatment**
- **Remediation**
- **Information**

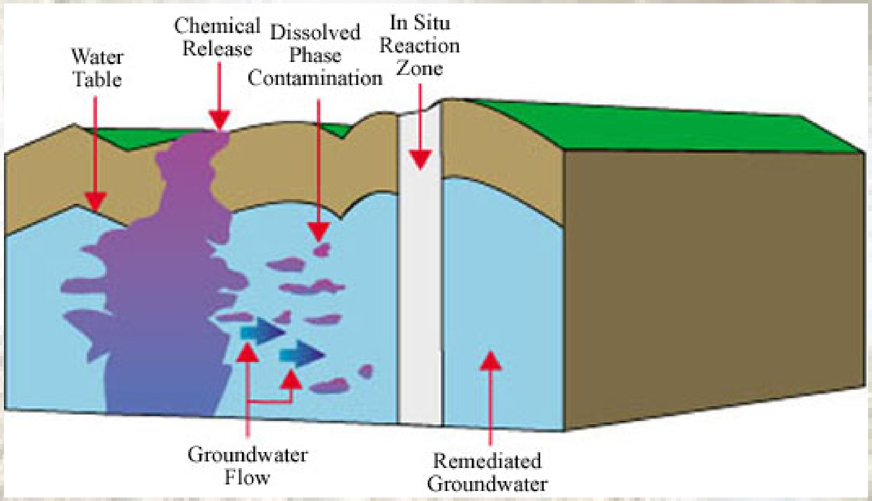
Nanotechnology for pollution prevention

- Synthetic or manufacturing processes which can occur at ambient temperature and pressure.
- Use of non-toxic catalysts with minimal production of resultant pollutants.
- Use of aqueous-based reactions.
- Build molecules as needed --“just in time.”
- Nanoscale information technologies for product identification and tracking to manage recycling, remanufacture, and end of life disposal of solvents.

- Involved in making a manufacturing process environmentally benign.
- An environmentally benign material or manufactured product that replaces toxic substances or minimizes raw materials.

Treatment & Remediation

End-of-pipe management and cleanup of pollution

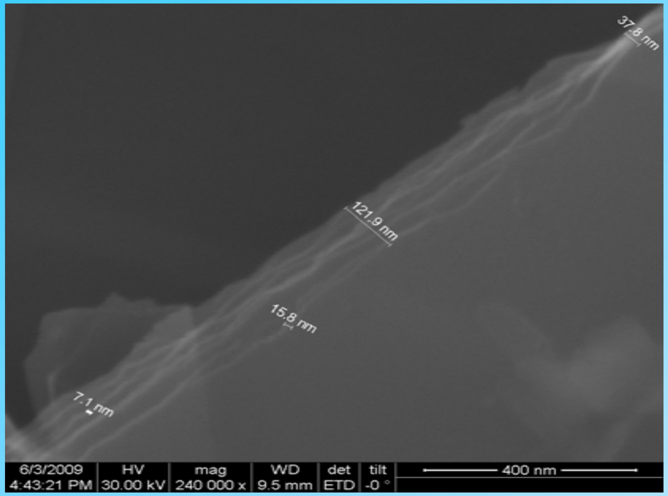


Carbonaceous nanomaterials as sorbents

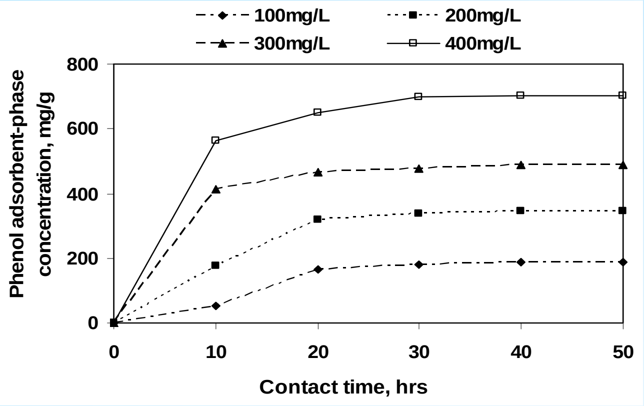
- Possible uses in groundwater treatment.
- Direct sorption of organic environmental contaminants.
- Removal of specific hazardous contaminants: trihalomethanes, PAHs, naphtalene
- Selective functionalization for targeting specific micropollutants.
- High surface area scaffold for oxides or macromolecules with intrinsic sorbent capacity
- Nanoscaffolds tailored to adsorb or complex ions and metals in solution.
- Current applications focused on metal preconcentration, removal or oxidation.

* Elliot and Zhang *ES&T* **2001**, *35*, 4922-4926

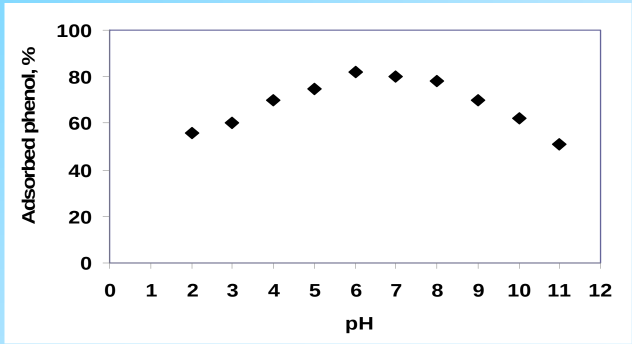
Phenol sorption on exfoliated graphitic nanoplatelets



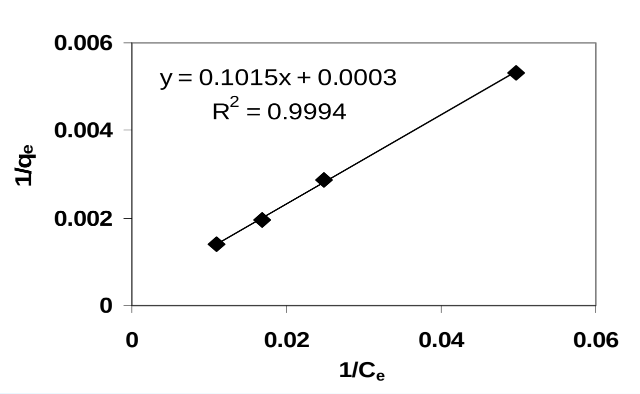
SEM images of xGnPs surface: a – image taken at 240 000X magnification, b- image taken at 16 000X magnification.



Effect of contact time on phenol adsorption to 400 mg/L xGnPs at different initial phenol concentrations.



pH effect on the phenol adsorption by xGnPs. Initial conditions: xGnP loading is 400 mg/L; initial phenol concentration is 300 mg/L.

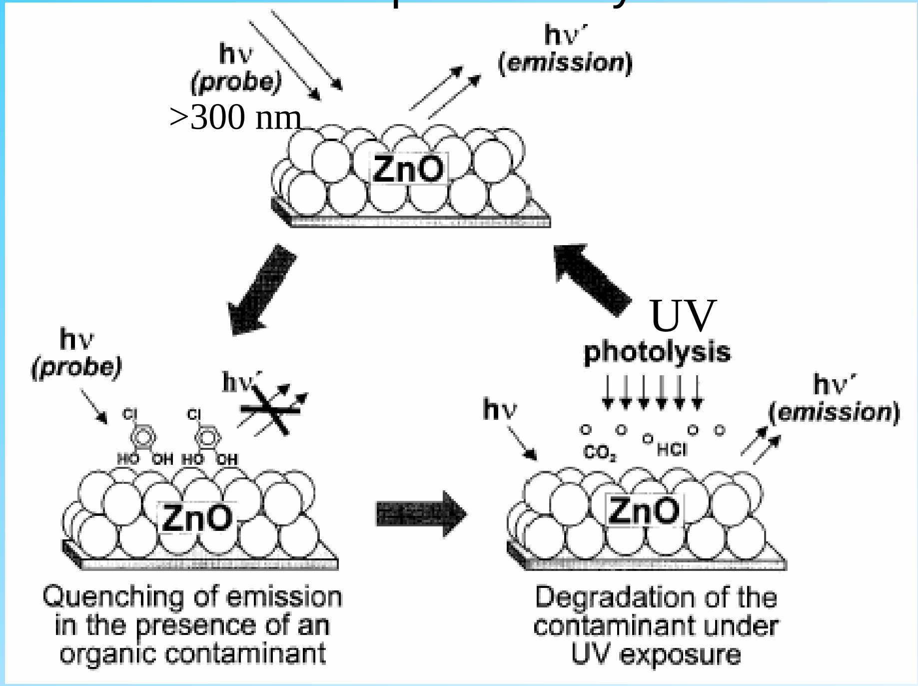


Langmuir fitting for the phenol adsorption by xGnPs. Initial conditions: xGnPs loading 400 mg/L; initial phenol concentration range (100-400) mg/L.

A.C. Ion et al., Environ. Sci. Technol., 2010, in press

"Sense and Shoot" Approach to Pollution Treatment

ZnO semiconductor film on CNTs conductive scaffold as a sensor and photocatalyst



Kamat, P.V, et al. *J.Phys.Chem. B* **2002**, *106*,788-794.

- Nanosized zinc oxide (ZnO) "senses" organic pollutants indicated by change in visible emission signal.
- The ZnO "shoots" the pollutants via photocatalytic oxidation to form more environmentally benign compounds.
- Sensing capability means that the energy-consuming oxidation stage only occurs when the pollutants present.
- Multifunctionality and "smartness" is highly desirable for environmental applications.

Sensors

Used for

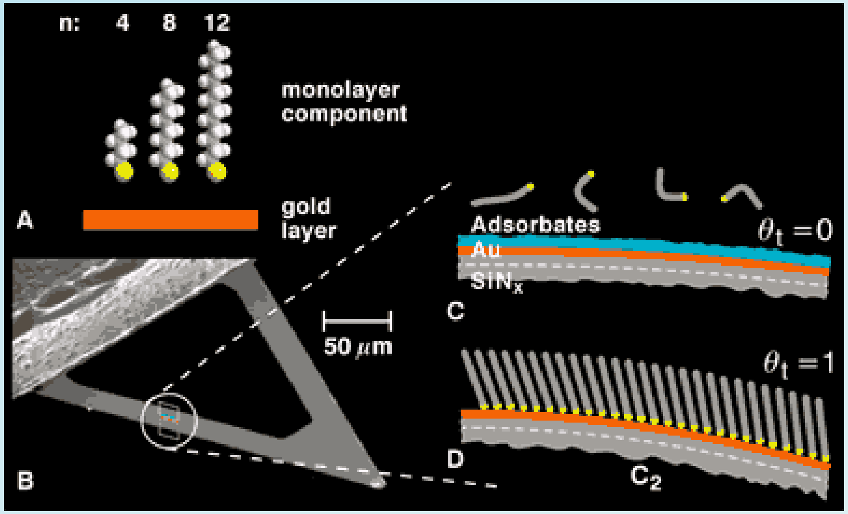
- Process control, compliance and ecosystem monitoring, and data/information interfaces.

Need to be

- Low cost, rapid, precise, and ultra sensitive.
- Operated remotely and continuously, *in situ*, and in real time.

Single Molecule Detection

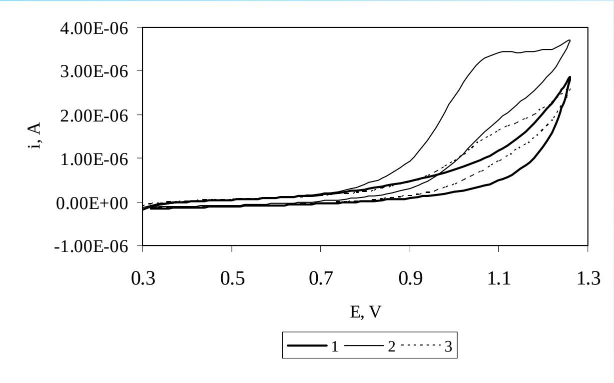
- Molecules adsorb on surface of micro cantilever, causes a change in surface stress, cantilever bends.
- Used to detect chemicals using either a specific reaction between analyte and sensor layer or chem/physisorption processes.
- Applications to bio-toxins as well.



IBM--Berger et al., Science 1997 June 27; 276: 2021-2024

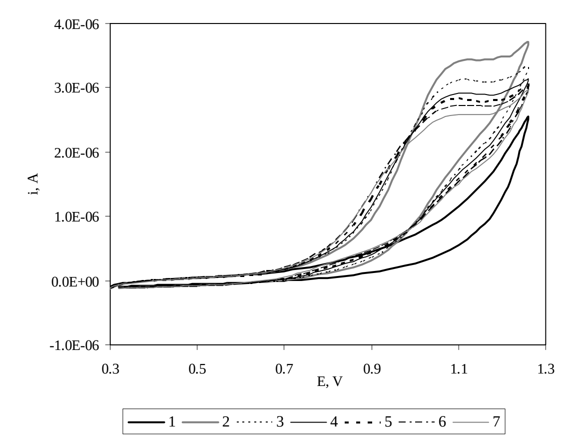
Acetylcholinesterase voltammetric biosensors based on carbon nanostructure-chitosan composite material for organophosphate pesticides

Inhibition	Enzyme	Technique	Sample	LOD	Ref.
CPF	AChE	Voltammetric	Wine	< 300 ng mL^{-1}	[i]
CPF	BChE	Voltammetric	Grape juice	$2x10^{-8}$ M	[ii]
CPF	AChE	Voltammetric	Aqueous samples	$3x10^{-8}$ M	[iii]
CPF	AChE	Voltammetric	Aqueous samples	$2x10^{-10}$ M	This work

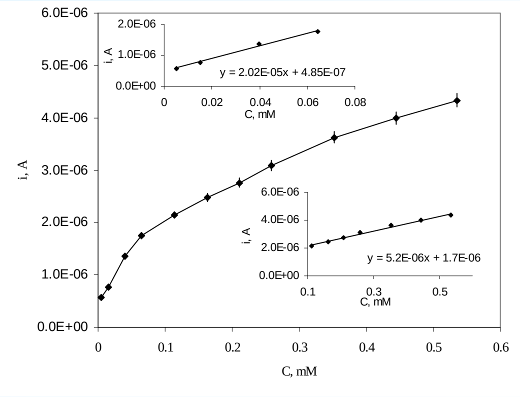


Cyclic voltammograms: AChE – chitosan modified-GCE in pH 7.4 phosphate buffer; scan rate 100 mVs-1 (1) chitosan-GCE in 0.01 M phosphate buffer pH 7.4;(2) AChE-xGnP-chitosan modified-GCE+ 0.250 mM ATCI; (3) AChE-chitosan modified-GCE without xGNP + 0.250 mM ATCI

[i] M. Del Carlo, M. Mascini, A. Pepe, D. Compagnone, J. Agric. Food Chem., 2002, 50, 7206-7210
[ii] A. Ivanov, G. Evtugyn, H. C. Budnikov, F. Ricci, D. Moscone, G. Palleschi, Anal. Bioanal. Chem., 2003, 377, 624-631
[iii] E. V. Suprun, H. C. Budnikov, G. A. Evtugyn, Kh. Z. Brainina, Bioelectrochemistry, 2004, 63(1-2), 281-284



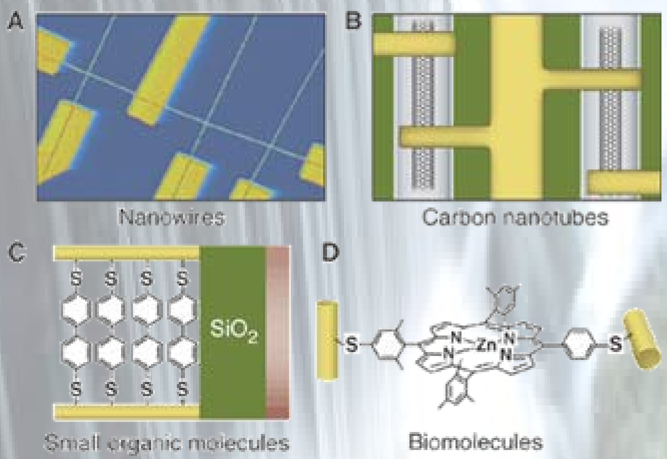
Cyclic voltammograms obtained from the AChE – chitosan modified-GCE with xGnPs in 0.01 M phosphate buffer pH 7.4 (1) containing 0.250 mM ATCI (2) added with 10-10 M CPF (3); 10-9 M CPF (4); 10-8.5 M CPF (5); 10-8 M CPF (6); 10-7 M CPF (7); scan rate 100 mVs-1



Calibration plot of the voltammetric response of AChE – chitosan modified-GCE electrode towards ATCI

A.C. Ion et al., Mat. Sci. Eng. C, 2010, in press

Conclusions

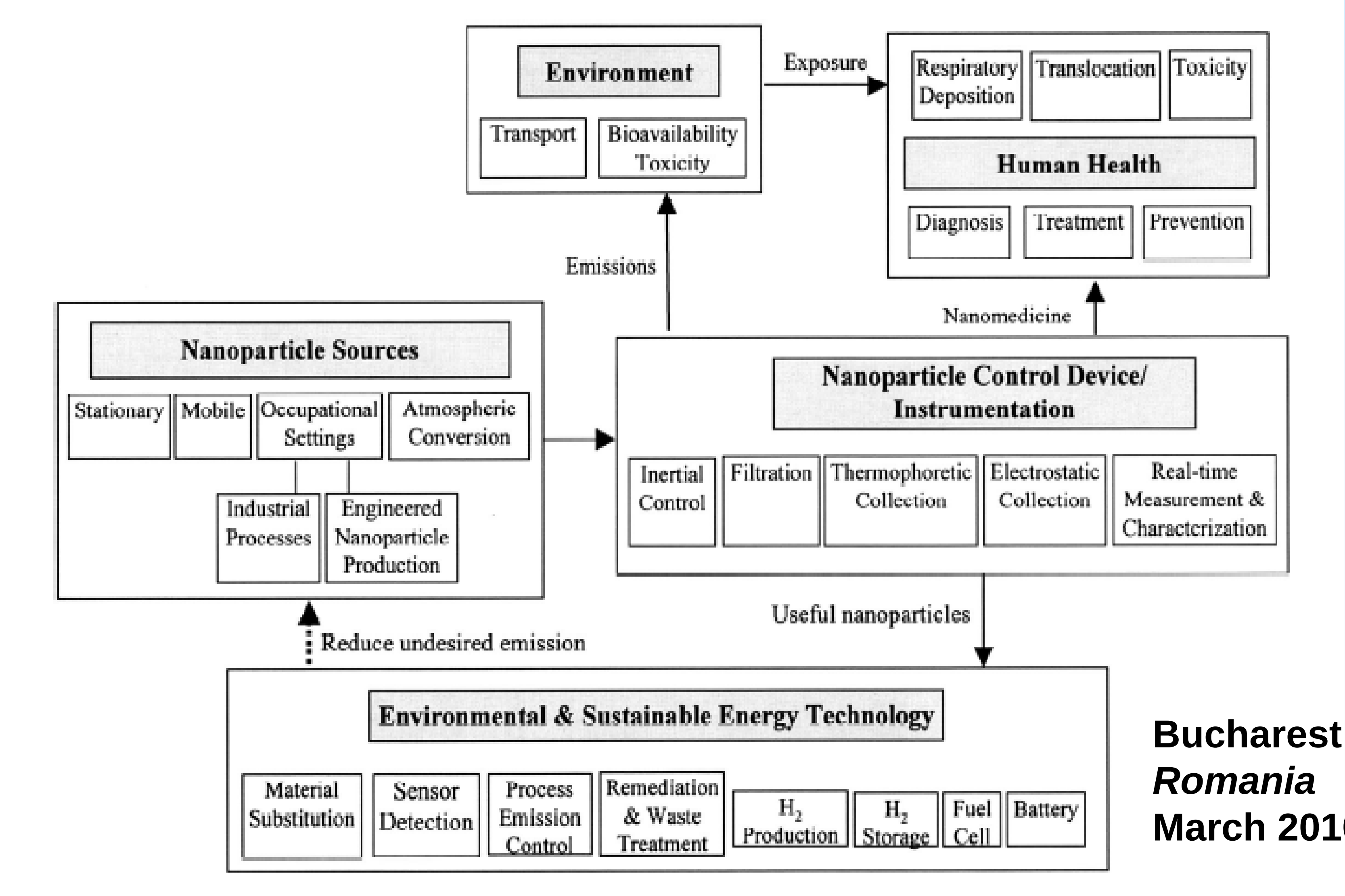


Science and Engineering approaches are needed that offer new capabilities to prevent or treat highly toxic or persistent pollutants, and that result in the more effective monitoring of pollutants or their impact in ways not currently possible.

Nanoscience, engineering, and technology holds great potential for the continued improvement of technologies for environmental protection. The recent breakthroughs in creating nanocircuitry, give further evidence and support the predictions that nanoscale science and engineering "will most likely produce the breakthroughs of tomorrow."

BUT the environmental implications (nano <u>in</u> the environment) need to be considered as we consider nano <u>for</u> the environment.

PERHAPS AN HOLISTIC APPROACH COULD BE USED TO HELP US UNDERSTAND THE POTENTIAL HEALTH IMPLICATIONS



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Understanding Nanoparticles and Nanoscale Phenomena

- can make agriculture more efficient and
- help mitigate environmental problems

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