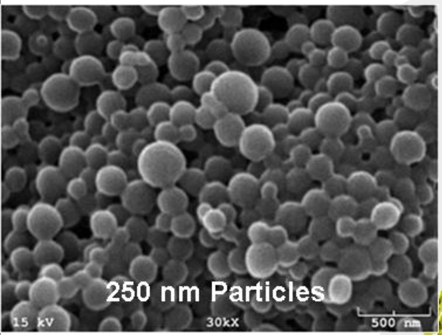
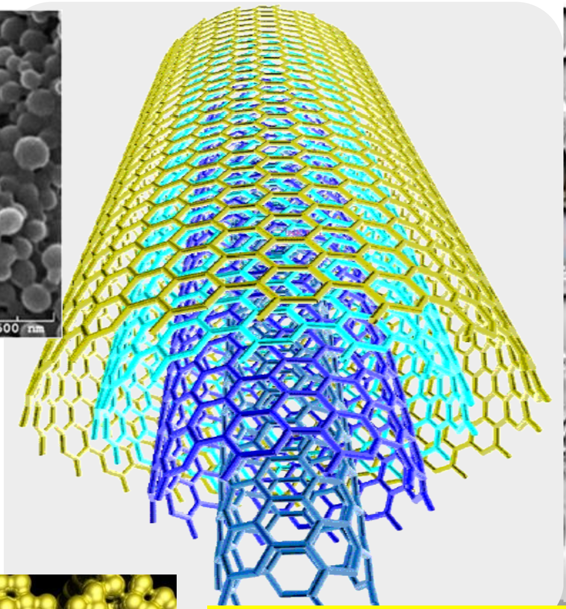
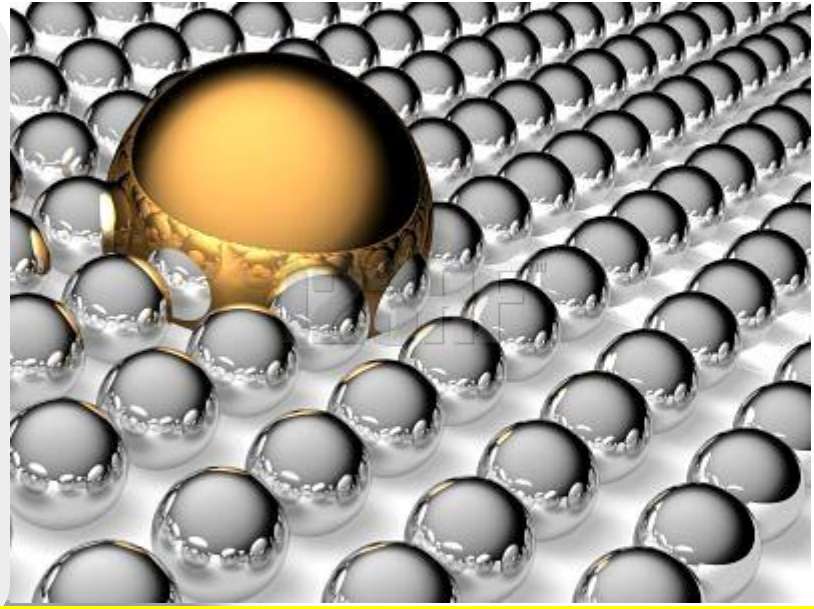
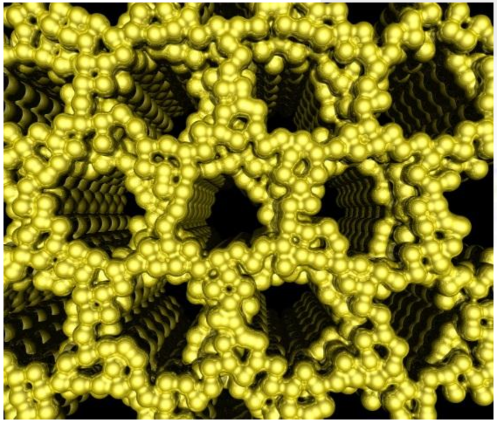
THE ROLE OF NANOPARTICLES IN ELECTROCHEMISTRY

Rubin Gulaboski, Goce Delcev University-Stip Macedonia



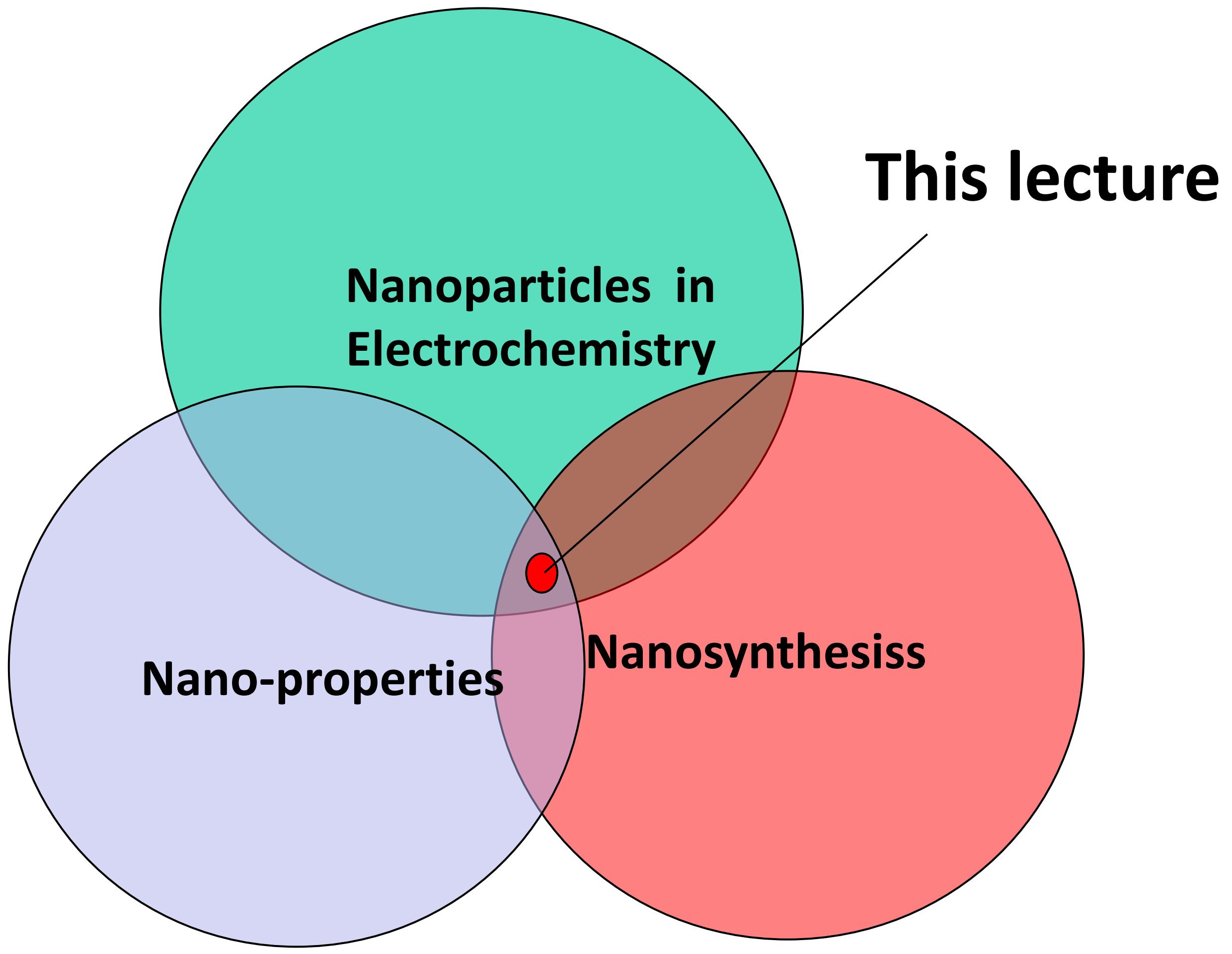




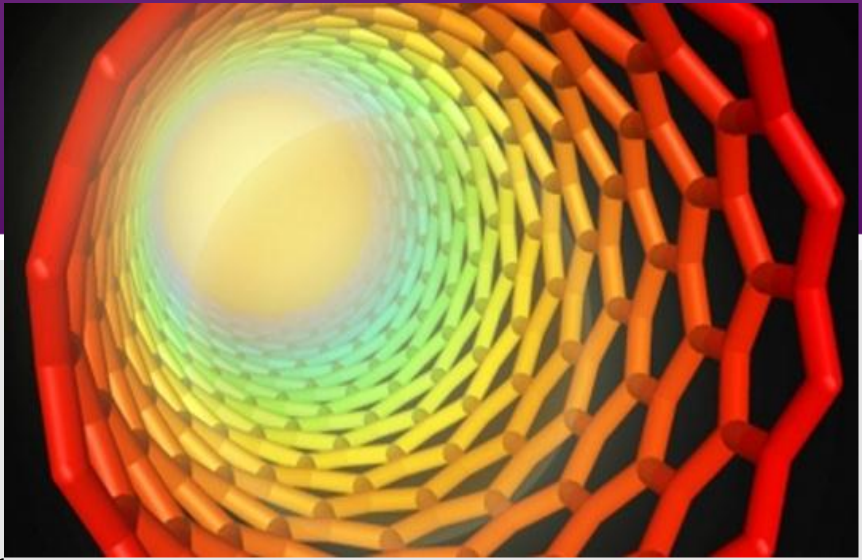


Objective of the lecture:

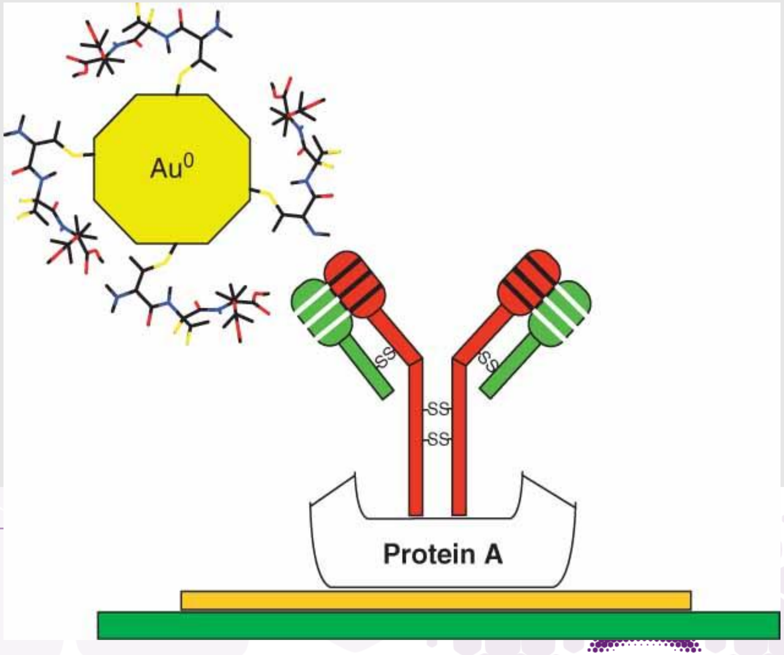
The aim of this lecture is introducing the methods of synthesis, the features and the application of some nanoparticles in electrochemistry


This lecture
Nanoparticles in
Electrochemistry
Nano-properties
Nanosynthesiss

Outlines



1.Application
2.Synthesis
3.Features
4.Metallic nanoparticles and carbon nanotubes (CNT)
5. Nanoparticles as biosensors
6.Conclusions

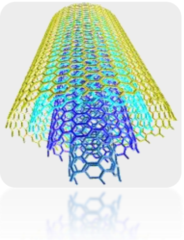


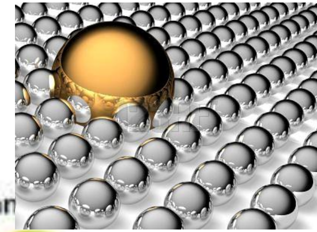
Nanotechnology is ancient history

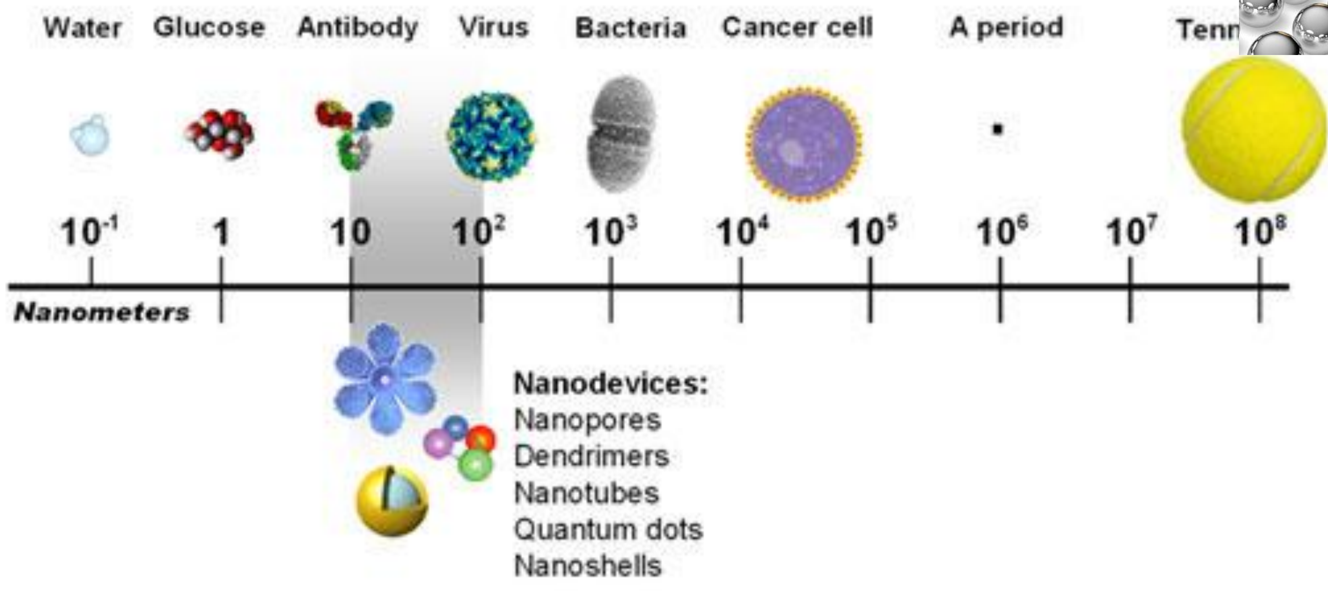
The stunning Lycurgus cup reveals a brilliant red when light passes through its sections of glass containing gold-silver alloyed nanoparticles.
Photograph: British Museum Images

In the antiquities, nanoparticles were used by Damascans to create swords with exceptionally sharp edges

Nanoscale = billionths (10^{-9})







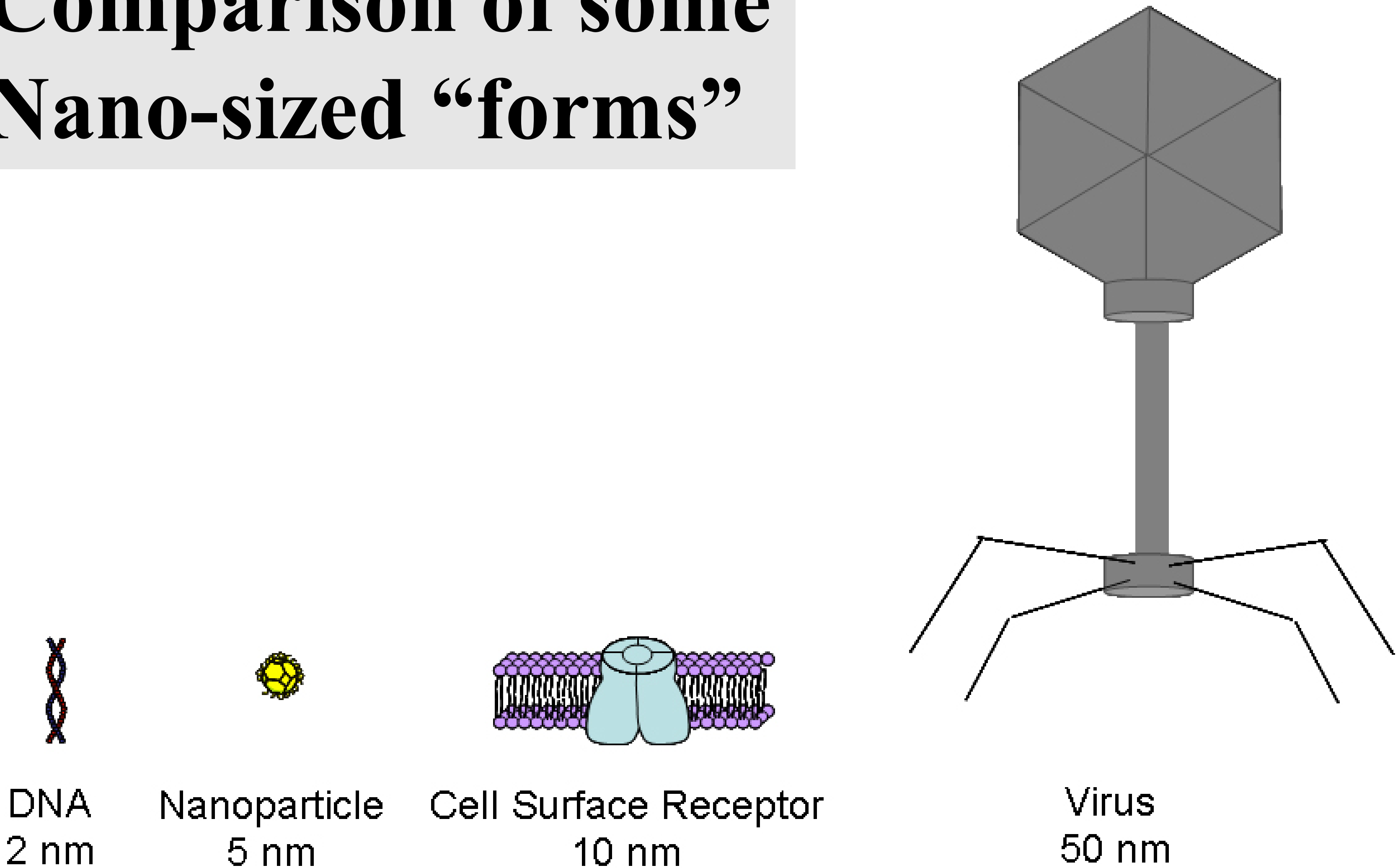
To understand how small one nm is let us see few comparisons

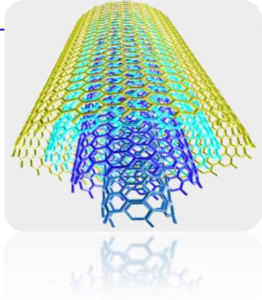
1. A **Red blood cell** is approximately **7000nm** wide.

2. **Water Molecule** is almost 0.3nm across.

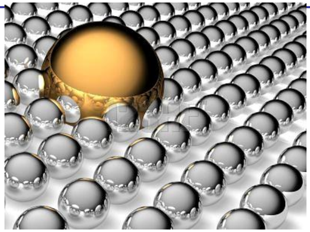
3. Human hair which is about **80,000nm** wide.

Comparison of some Nano-sized “forms”





Nano Materials



1. ***Nano Materials*** are defined as ***materials with at least one of its dimensions in the range*** *of a* ***Nano meter***.

3. Nanosystems i***n one dimension*** are **layers**, such as a **Thin films or Surface coatings**.

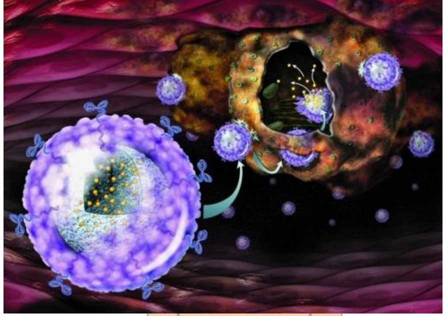
4. Nanosystems in ***two dimensions*** include **Nano wires and Nano tubes.**

5. Nanosystems in ***three dimensions*** are **particles for example precipitates, *colloids* and *quantum dots* (Small particles of Semiconductor Materials)**

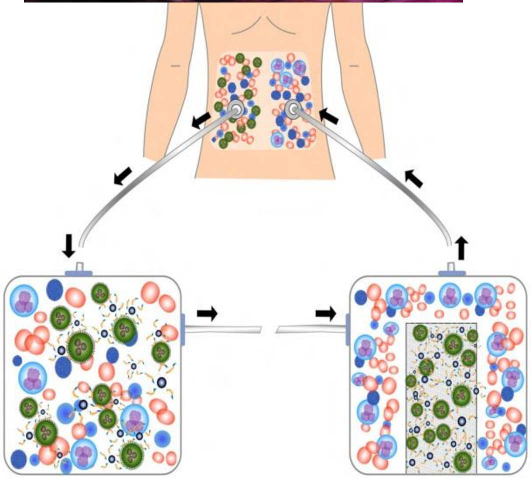
Important 'nano' Definitions

- ***Cluster***
  - A ***collection of units*** (atoms or reactive molecules) of up ***to about 50 units***
- ***Colloids***
  - A ***stable liquid phase*** containing particles in the ***1-1000 nm range***. A colloid particle is one such 1-1000 nm particle.
- ***Nanoparticle***
  - ***A solid particle in the 1-100 nm range*** that could be noncrystalline, an aggregate of crystallites or a single crystallite
- ***Nanocrystal*** - a solid particle that is a single crystal in the nanometer range

Nanoparticles
Some applications



NANOPARTICLES=Nanometer -sized particles that have optical, magnetic, chemical and structural properties that differ significantly from bulk solids



- <u>Potential applications</u>

DRUG DELIVERY

MEDICAL IMAGING

DIAGNOSIS & SENSING

THERAPY

High Tech

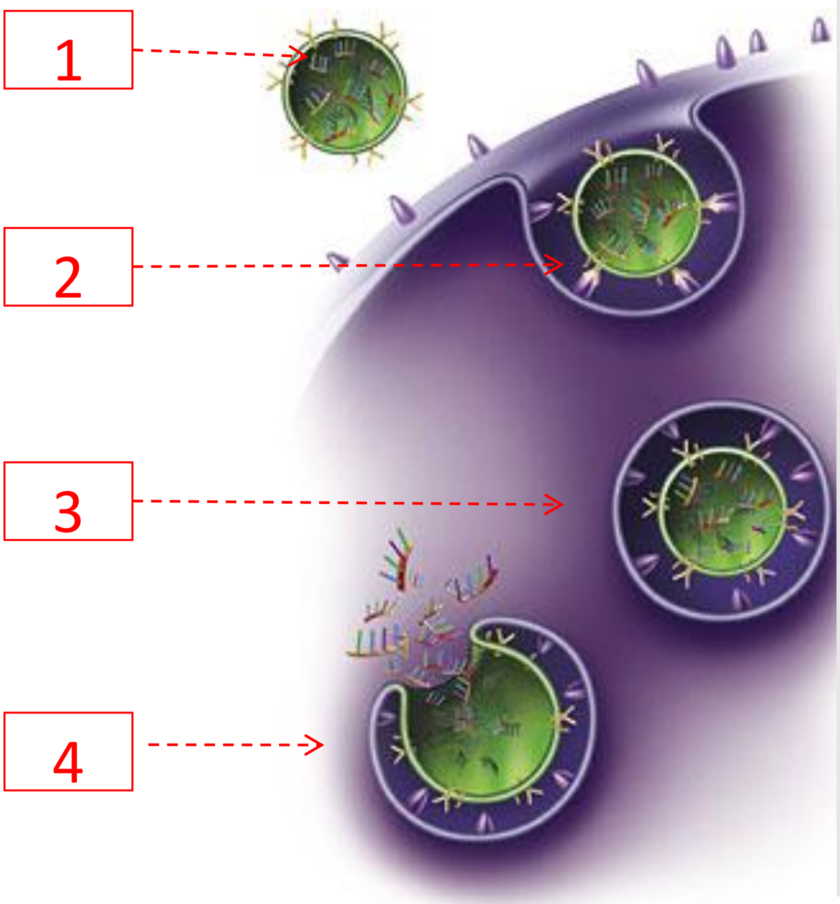
Electronics

Catalysis

....

Drug Delivery

A. Because of their small sizes, nanoparticles are taken by cells where large particles would be excluded or cleared from the body



1) A nanoparticle carries the pharmaceutical agent inside its core, while its shell is functionalized with a ‘binding’ agent

2) Through the ‘binding’ agent, the ‘targeted’ nanoparticle recognizes the target cell. The functionalized nanoparticle shell interacts with the cell membrane

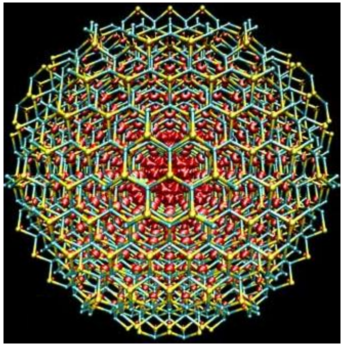
3) The nanoparticle is ingested inside the cell, and interacts with the biomolecules inside the cell

4) The nanoparticle particles breaks, and the pharmaceutical agent is released

Medical Imaging

A. Optical properties of nanoparticles depend greatly on its structure. **Particularly, the color (wavelength) emitted by a quantum dot (*a semiconductor nanoparticle*) depends on its diameter.**

B.

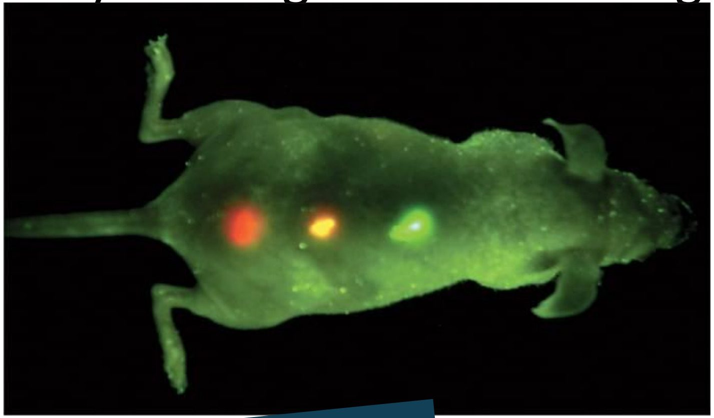


CdSe nanoparticle (QD) structure

Source: Laurence Livermore Laboratories

Solutions of CdSe QD's of different diameter

C. The quantum dots (QD) can be injected to a subject, and then be detected by exciting them to emit light



- ✓ Same material (compound)
- ✓ Different sized nanoparticles
- ✓ Different optical properties- different colours

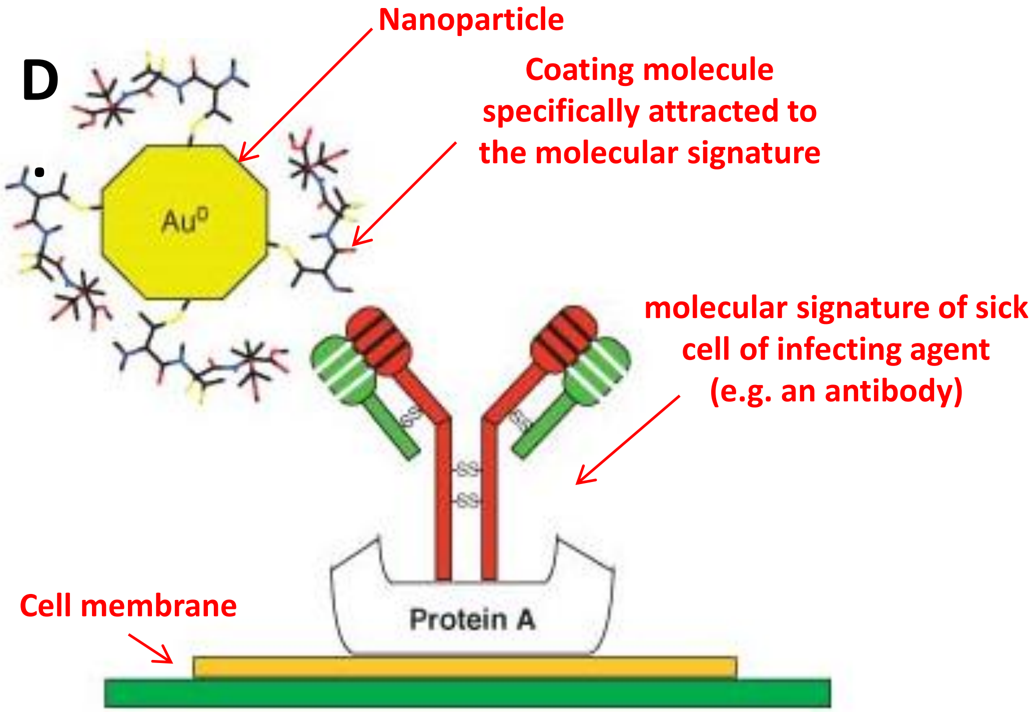
Diagnosis and Sensing

A. Diseases can be diagnosed through the (simultaneous) detection of a (set of) biomolecule(s) characteristic to a specific disease type and stage (biomarkers).

B. ***Each cell type has UNIQUE molecular signatures that differentiate healthy and sick tissues***. Similarly, an infection can be diagnosed by detecting the distinctive molecular signature of the infecting agent

C. A nanoparticle can be functionalized in such a way that specifically targets a biomarker. Thus, the detection of the nanoparticle is linked to the detection of the biomarker, and to the diagnosis of a disease

D.



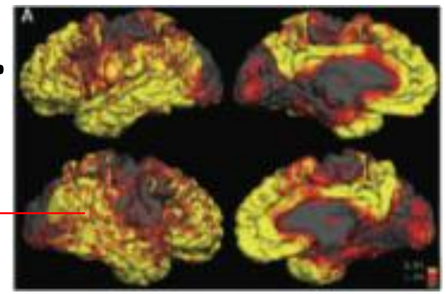
Huffman, Nanomedicine and Nanobiotechnology, Vol. 1, 1, 2009

Gold Nanoparticles vs. Alzheimer

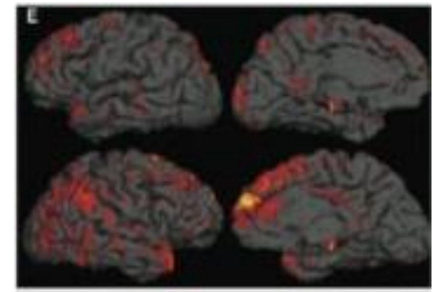
A. Alzheimer and other degenerative diseases are ***caused*** by the ***clustering of amyloidal beta (Aβ) protein***.

Source: Berkeley Lab

B.

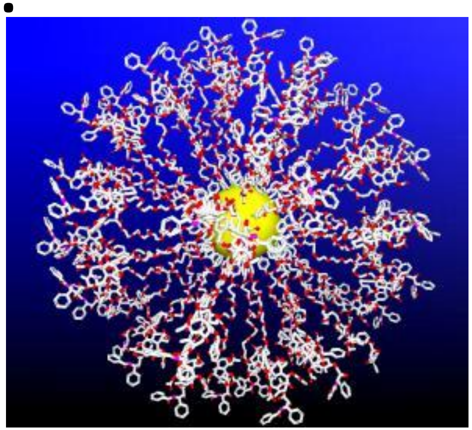


Alzheimer's brain



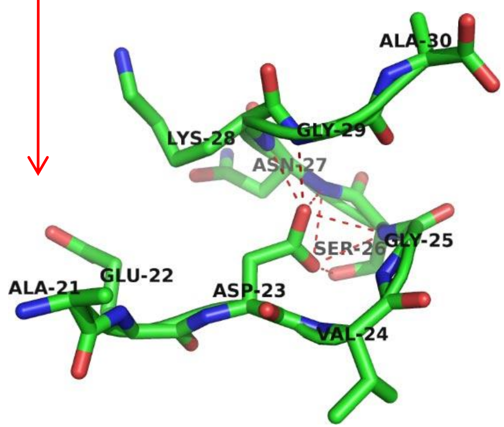
Healthy brain

C.



Functionalized nanoparticle

Source: www.internetchemistry.com



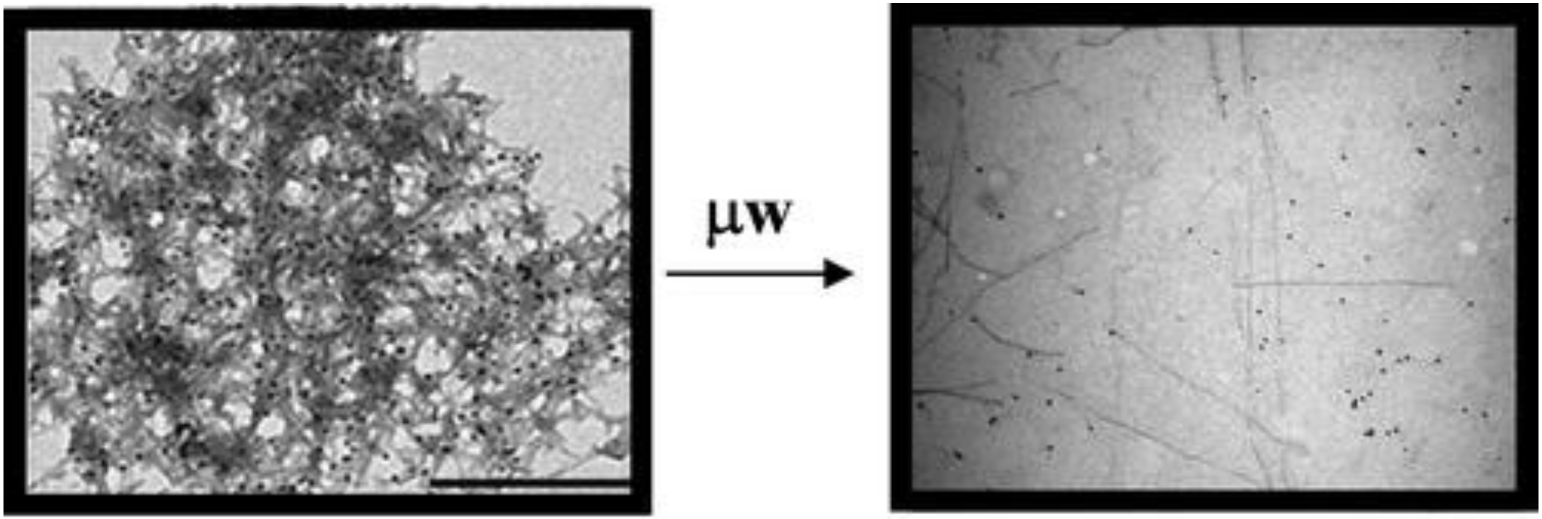
Chemical structure of Aβ-protein

Source: wwwthefutureofthings.com

D. Gold nanoparticles can be functionalized to specifically attach to aggregates of this protein (amyloidosis)

Gold Nanoparticles vs. Alzheimer

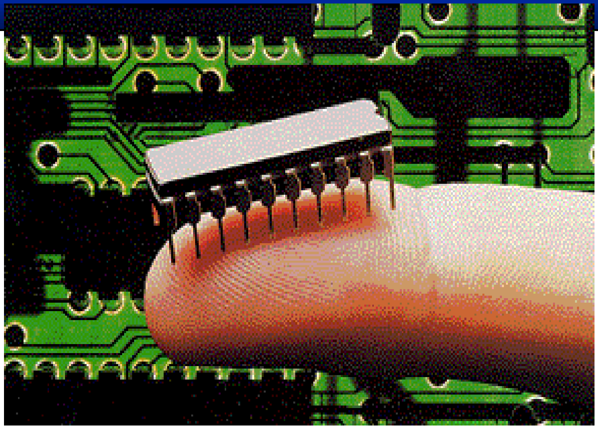
A. The functionalized gold nanoparticles selectively attach to the aggregate of amyloidal protein. The microwaves of certain frequency are irradiated on the sample. Resonance with the gold nanoparticles increases the local temperature and destroy the aggregate

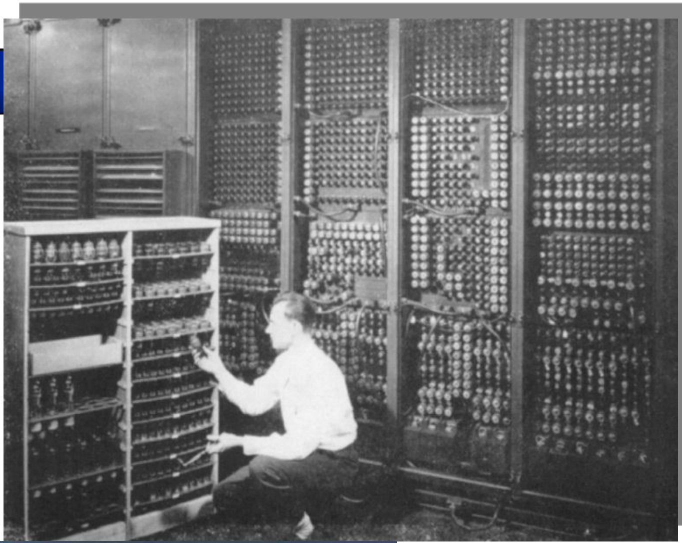


Before irradiation *After irradiation*

Nanoletters 2006, Vol. 6, pp.110-115

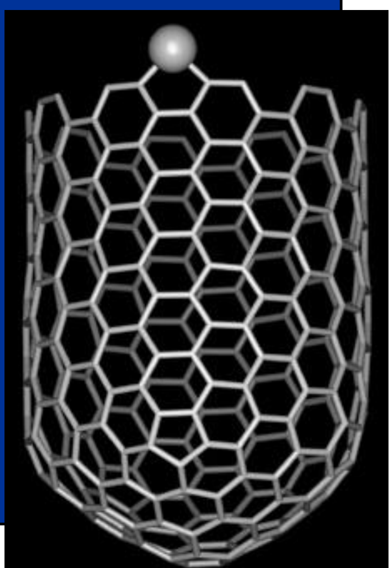
Nanoparticles are inevitable part of Computing

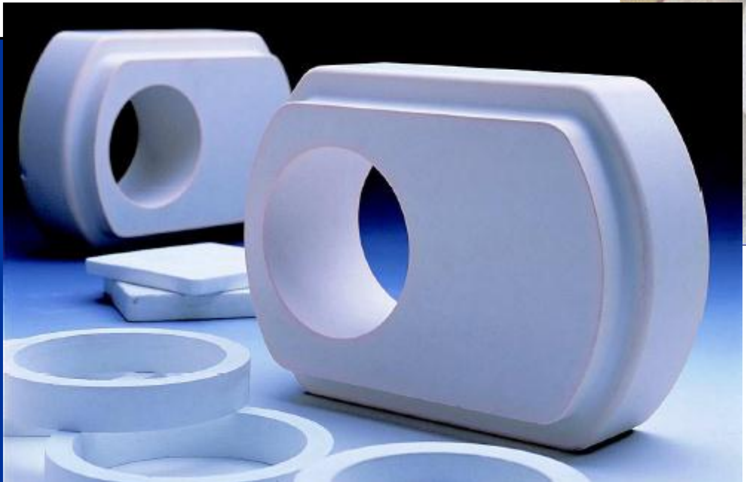




Materials and Manufacturing
Some Recent Advances

- Carbon Nanotubes
- Nanostructured Polymers
- Optical fiber preforms through sol-gel processing of nanoparticles
- Nanoparticles in imaging systems
- Nanostructured coatings
- Ceramic Nanoparticles for netshapes





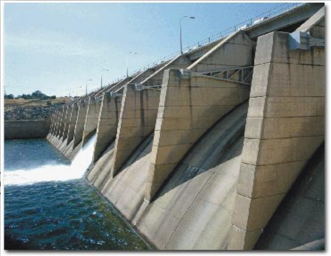
Nanoparticles Applications as Building Materials

Carbon Nanotubes (*CNT*) 1D, Iijima in 1991 .

***Fantastic* MECHANICAL PROPERTIES**

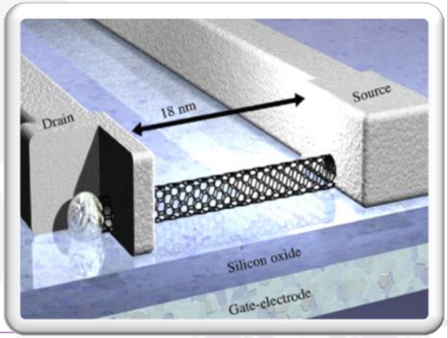
•stiffness &strength due to Sp2 bond

- ***Much stronger structure than diamond***
  - •May replace steel in the future
    - •Construction purposes like using nanocomposites -bridges



Light- Low mass

Aerospace industry to build aircrafts and satellites.



Thermal and **Electrical** conductivity

Nanoparticles in the service of Medicine

- DNA microchip

- ‘***Gene gun***’ that ***uses nanoparticles to deliver genetic material to target cells***

IMPORTANT TO UNDERSTAND:
Properties of Nanoparticles are SIZE DEPENDENT!!!
THE SIZE MATTERS!!!

- **The physical and chemical properties of a given material STRONGLY DEPEND on its size**

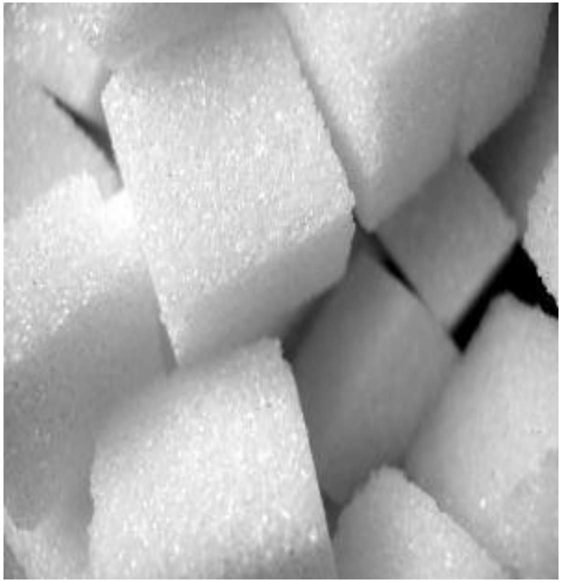
Mainly affected are:

- **Optical properties!!!**
- Melting point
- **Specific heat**
- ***Surface reactivity!!!***
- ***Conductivity***

- Even if nanoparticles are aggregated into macroscale solids, new properties of bulk materials are possible.
  - Example: ***enhanced plasticity***

PROPERTIES CHANGE AT THE NANOSCALE

How does the surface area affect the rate of change?



Why properties of Nano Materials are different *than those of the bulk material*?

The *properties of Nano Materials* are very much ***different from those at a larger scale***.

TWO PRINCIPAL FACTORS cause ***the properties*** of Nano Materials to differ significantly from bulk materials:

1. ***INCREASED relative surface area.***

2. *Quantum confinement effect*

THESE FACTORS can change or enhance ***properties such as reactivity , strength and electrical characteristics.***

Increase in a Surface Area to Volume ratio

Nano Materials **HAVE A RELATIVELY LARGER SURFACE AREA** when compared to the same volume or mass of its bulk material produced in a larger form.

Let us consider a Sphere of radius "r".

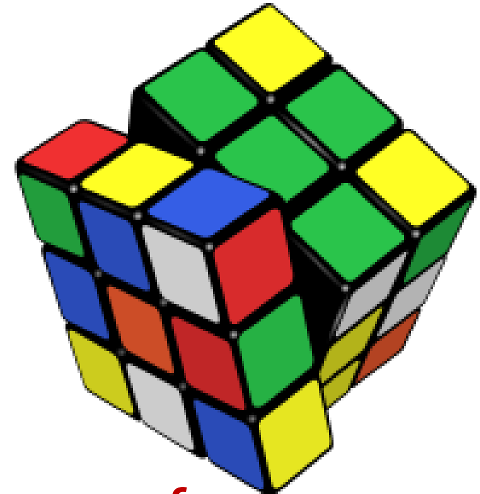
Its Surface Area $=4\pi r^2$.

Its volume= $4/3\pi r^3$

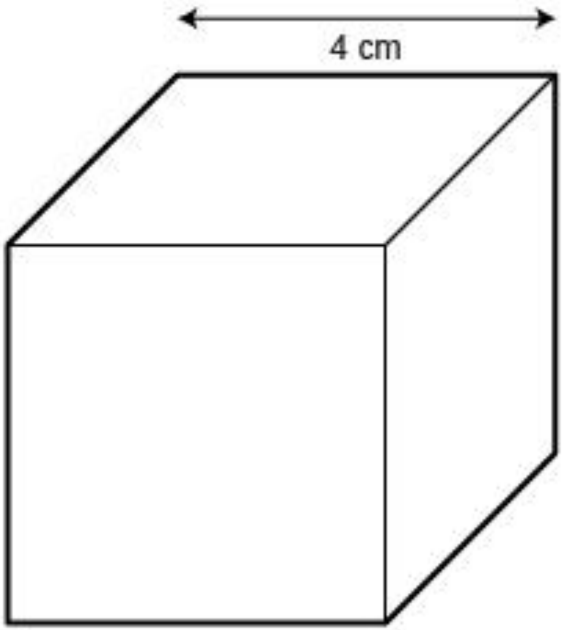
Surface Area to Volume Ratio= 3/r.

THUS WHEN *THE RADIUS OF THE SPHERE DECREASES*, ITS *SURFACE TO VOLUME RATIO* INCREASES!!!

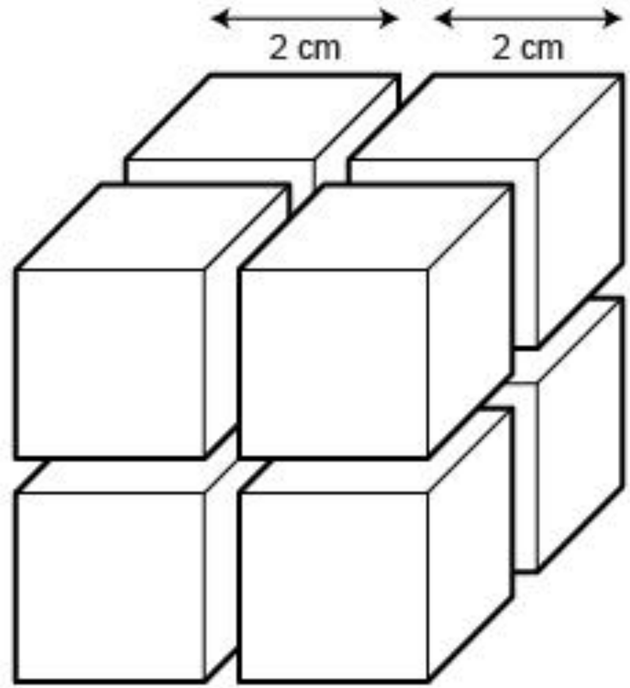
PROPERTIES CHANGE AT THE NANOSCALE



- ***If the cube is continually cut****, the surface area will increase* but **the volume does not change**
- This is significant in nanoscience - ***nanoparticles acquire new chemical or physical properties!***
- Two **different sized nanoparticles** of the same material may have **different properties.**



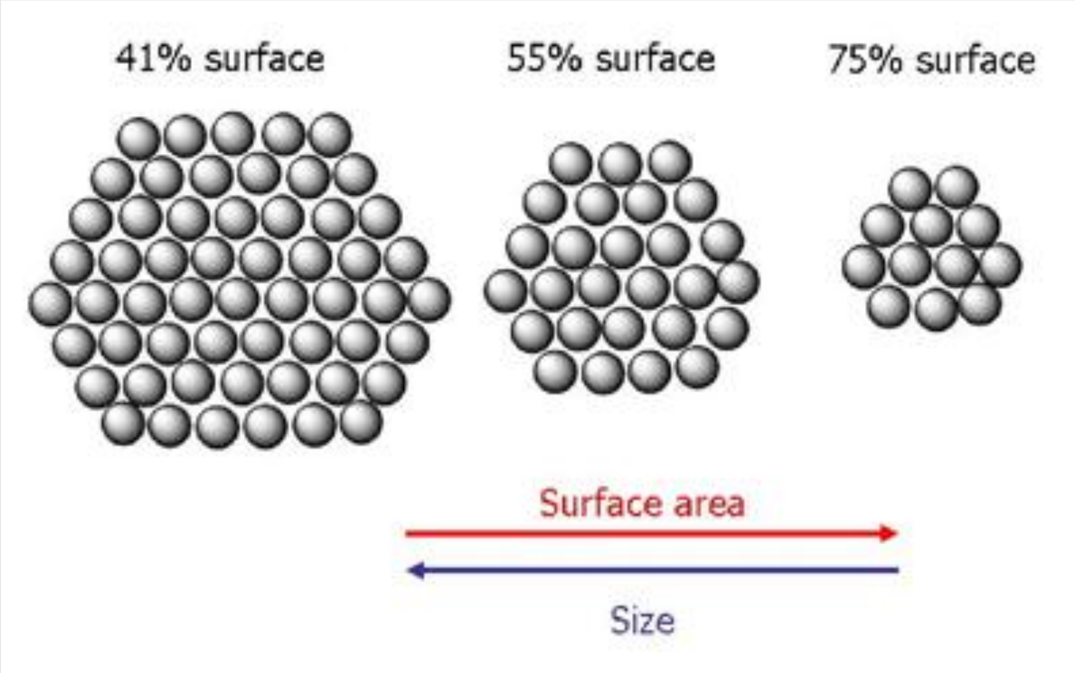
Surface area
= (4 cm x 4 cm x 6 faces) = 96 cm^2



Surface area of one cube
= (2 cm x 2 cm) x 6 faces = 24 cm^2

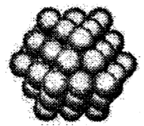
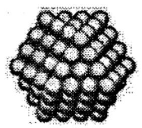
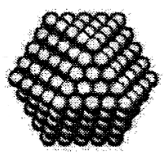
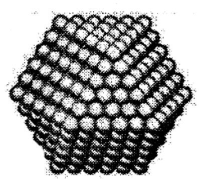
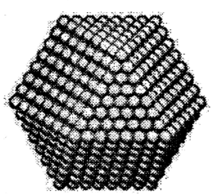
Total surface area
= 24 cm^2 x 8 cubes = 192 cm^2

- When the given volumeis divided into smaller pieces the Surface Area increases.
- Hence *as particle size decreases* a *greater proportion of atoms are found at the surface* compared to those inside.



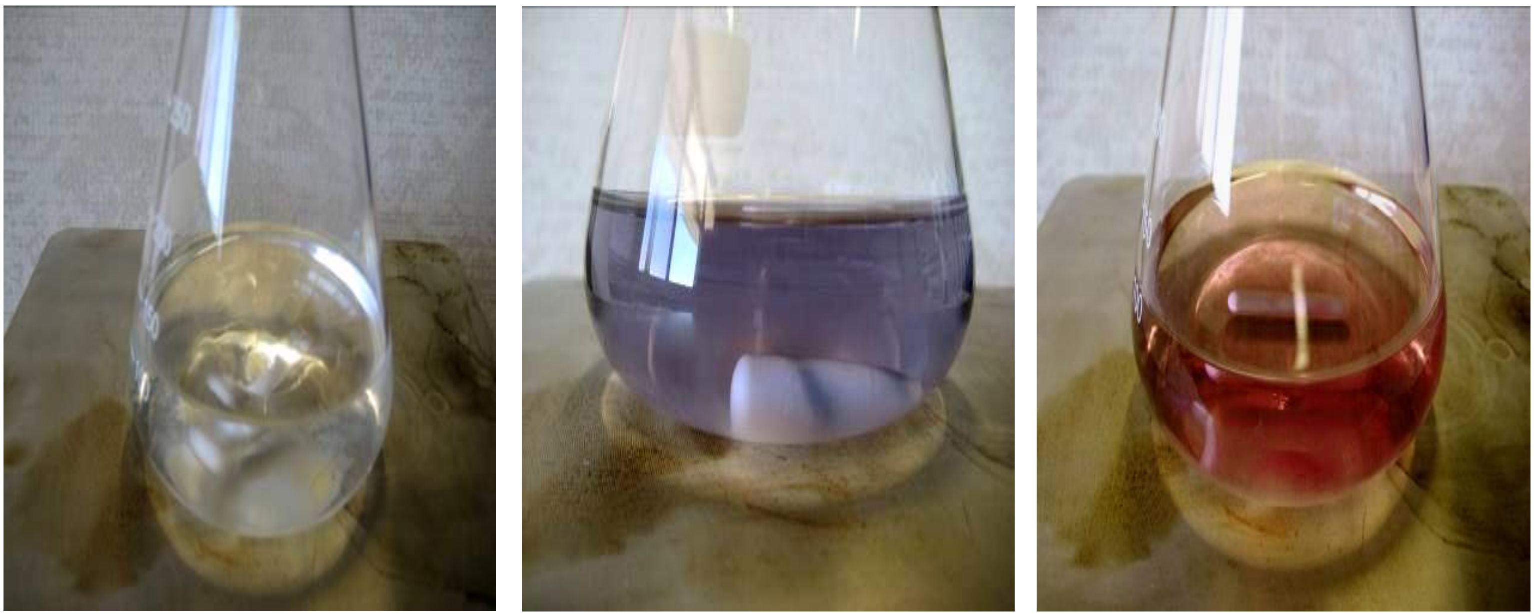
- *Nano particles have a <u>much greater surface area per given volume</u> compared with larger particles. It makes materials more <u>Chemically reactive.</u>*

Percentage of Surface Atoms in nano-Clusters

Full-shell Clusters		Total Number of Atoms	Surface Atoms (%)
1 Shell		13	92
2 Shells		55	76
3 Shells		147	63
4 Shells		309	52
5 Shells		561	45
7 Shells		1415	35

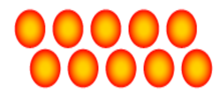
Source: Nanoscale Materials in Chemistry, Wiley, 2001

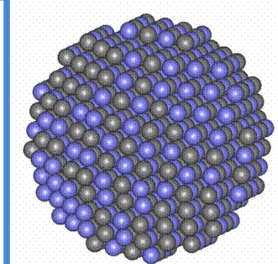
PROPERTIES at NANOSCALE



WHAT HAPPENS TO BULK PROPERTIES AT THE NANOSCALE?

Gold acquires new properties at the nanoscale.

Bulk Gold 	Gold as nanoparticles 
•Shiny •Always gold in colour •Inert •Conducts electricity	•Varies in appearance depending on size and shape of cluster •Never gold in colour, found in a range of colour •A very good catalyst •Not a metal but a semiconductor



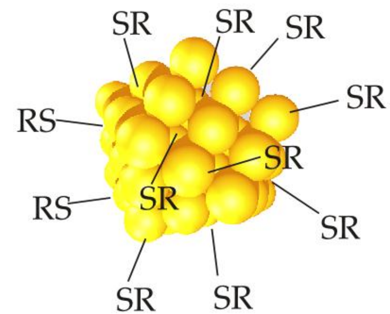
Metallic Bonding

Nanoscale gold has different properties than bulk gold, including:
appearance, solubility, and melting point.

Gold Soccer World Cup

melting point: 1337 °K

Gold nanoparticles



thiol stabilized gold nanoparticle

gold nanoparticles (2 nm) in solution

melting point: 650 °K

Jim Hutchison, U. Oregon
http://darkwing.uoregon.edu/~hutchlab

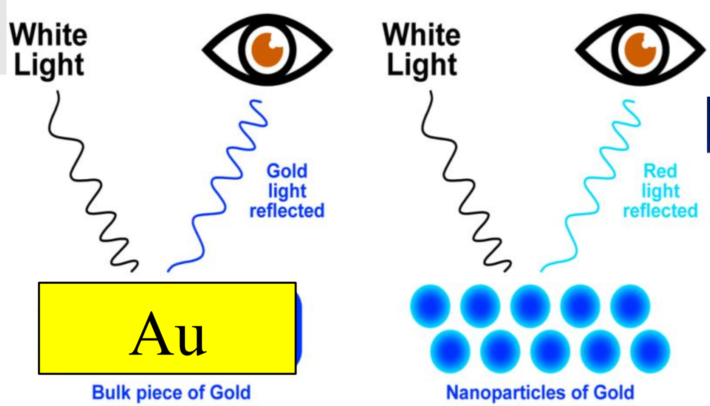
Color

- In a classical sense, ***color is caused by the partial absorption of light by electrons in matter***, resulting in the visibility of the complementary part of the light

- ***On a smooth metal surface***, *light is totally reflected by the high density of electrons* → no color, just a mirror-like appearance.

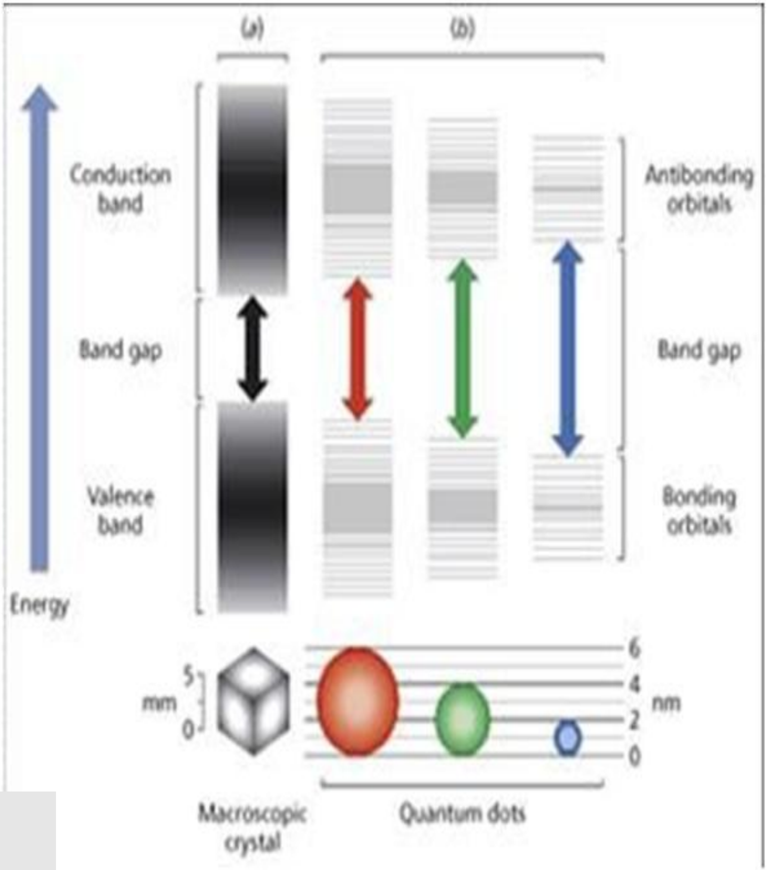
- **Small particles absorb light**, giving as a consequence some color. This is a size dependent property.

BULK & NANO GOLD



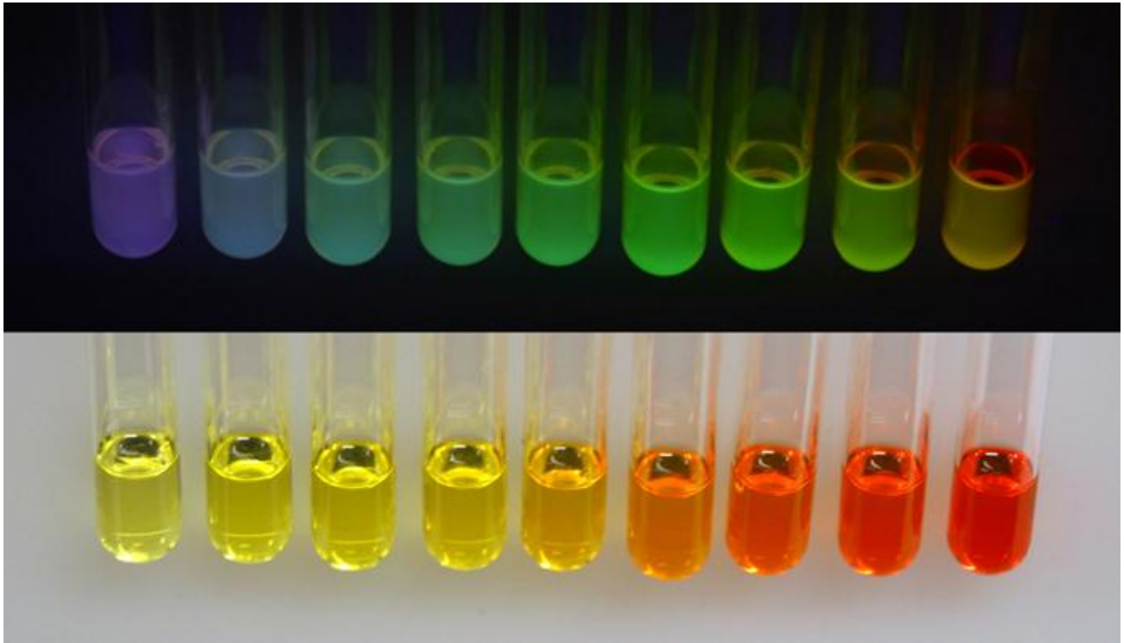
QUANTUM EFFECTS-BAND gap depends on particle size (number of atoms in the particle)

Fluorescence of CdSe nanoparticles having different size



Quantum effects of nano-particles-Quantum Dots

Quantum dots are **very, very tiny particles** in nanometer size. **They are composed of a hundred to a thousand atoms.** These semiconductor materials can be made from an element, such as silicon or germanium, or a compound, such as CdS or CdSe. ***These tiny particles can differ in color depending on their size***. Below is a collection of CdSe quantum dot nanoparticles that different in size as a result of how long they were allowed to form in the synthesis reaction



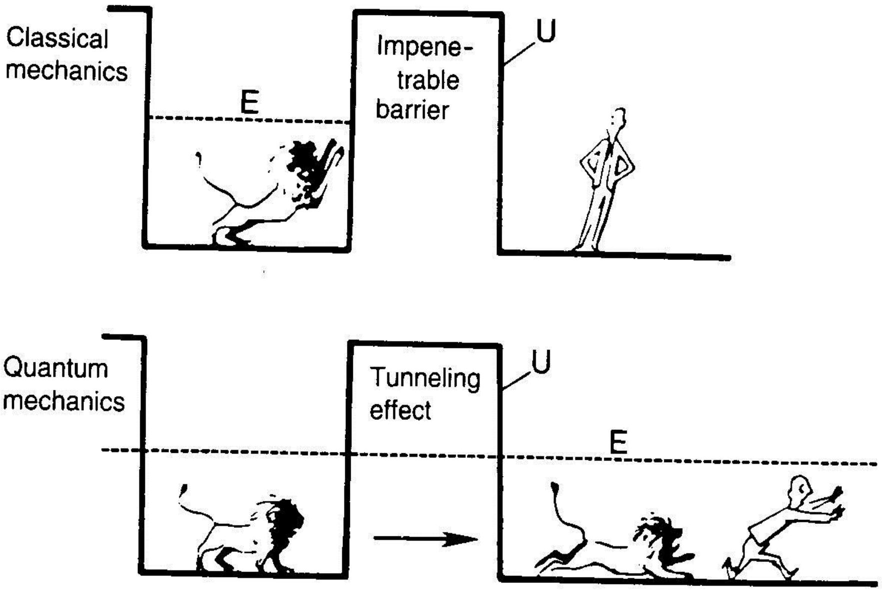
Chemical Properties of the nano-particles

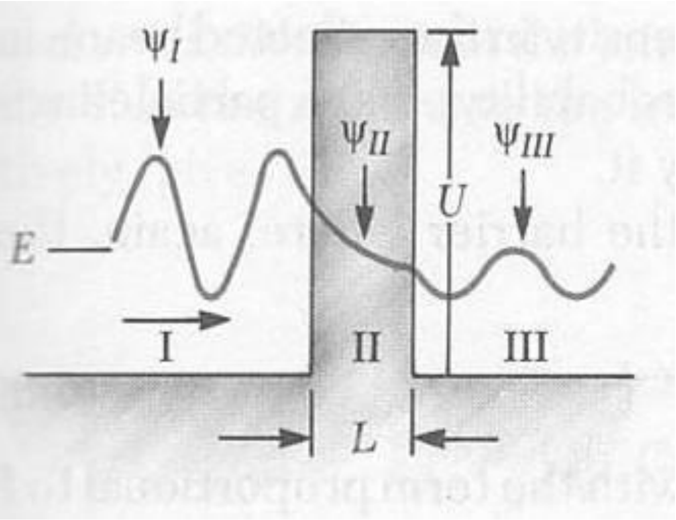
- The ***Electronic structure of Nanoparticles is dependent on its size*** and the ability of Nano cluster to react, depends on cluster size.

- ***The large Surface area to volume ratio*** the variations in geometry and the electronic structure of Nano particles have a ***strong effect on catalytic properties.***

- ***Commonly they show a tunneling effect by CATALYZING the chemical reactions***

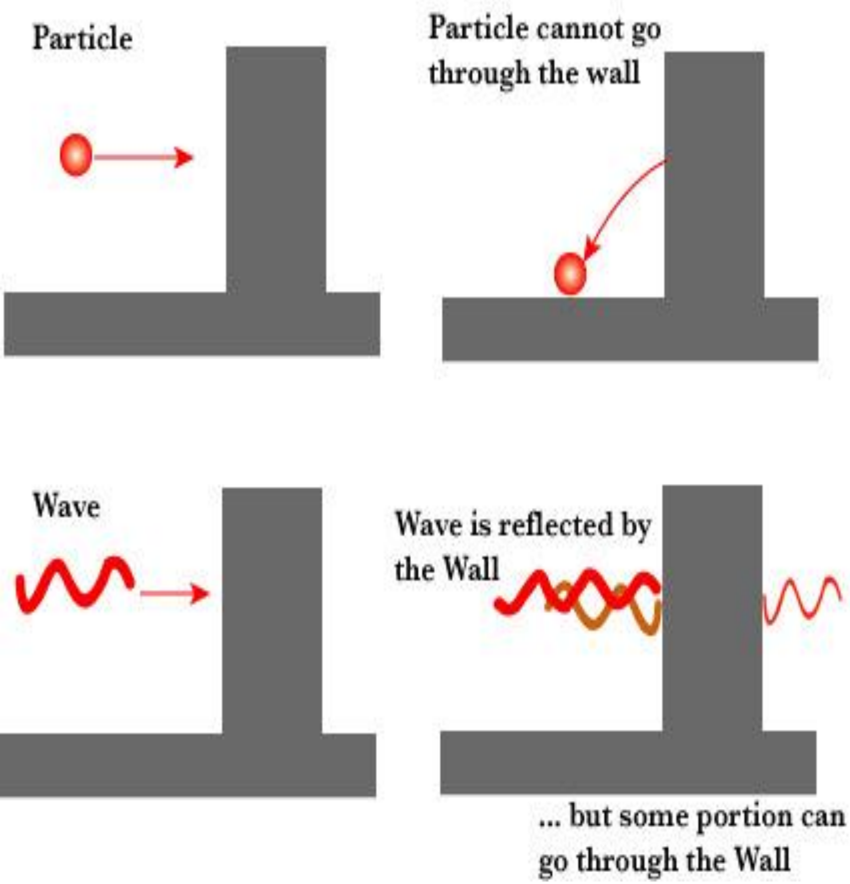
What is Tunneling?



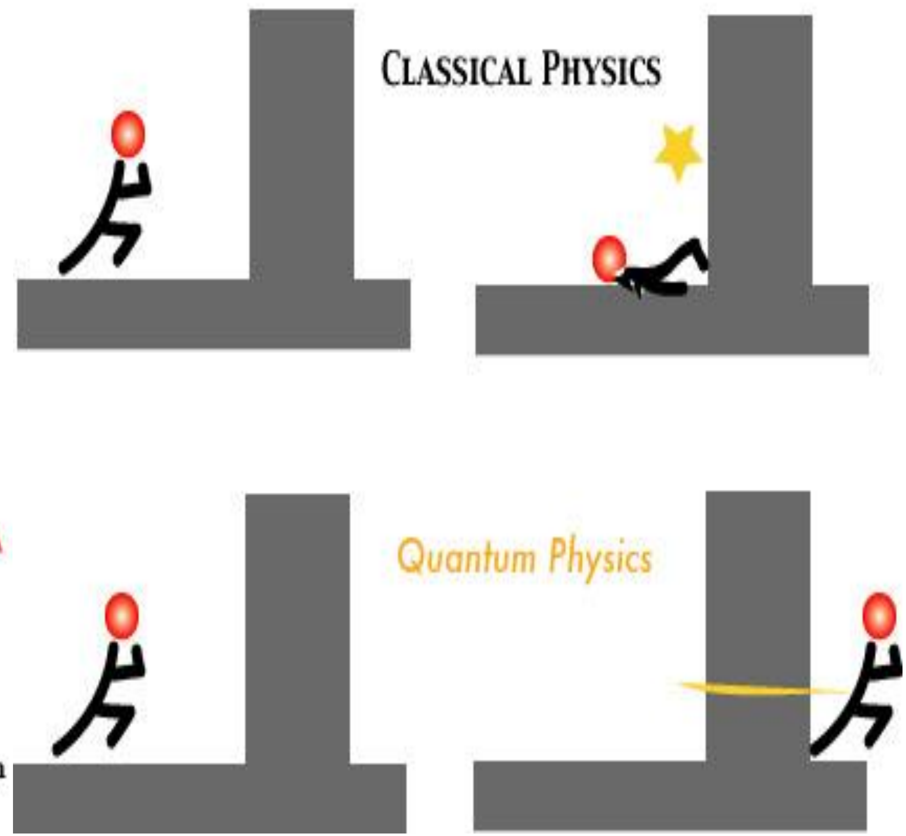


$$T \sim e^{-\beta L} \qquad \beta = 2\frac{\sqrt{2m(U-E)}}{\hbar}$$

Tunnel Effect



Tunnel Effect 2



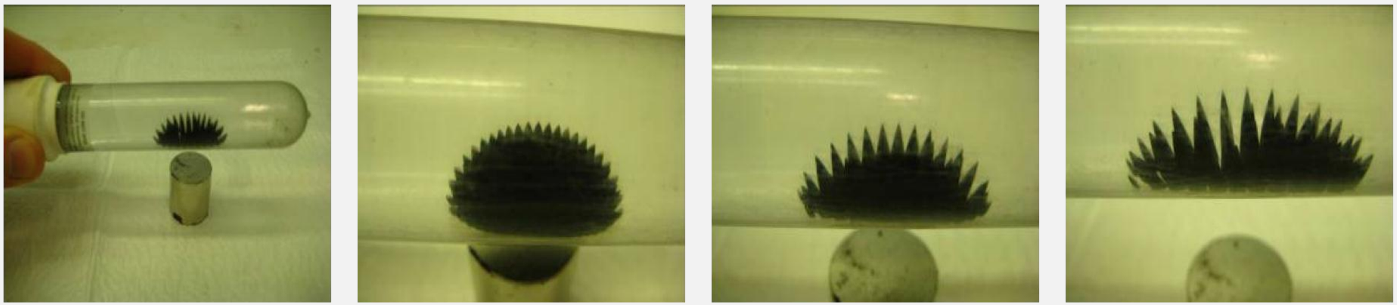
Electrical properties

- Nano clusters of different sizes will have different electronic structures and different energy level separations.

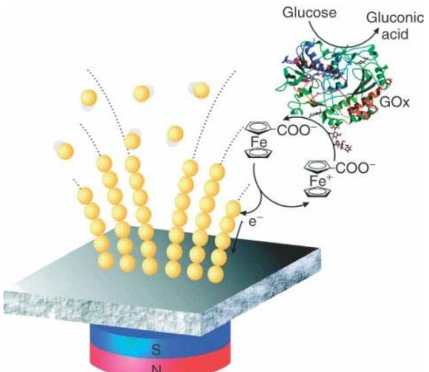
- The Ionization potential at Nano sizes are higher than that for the bulk materials

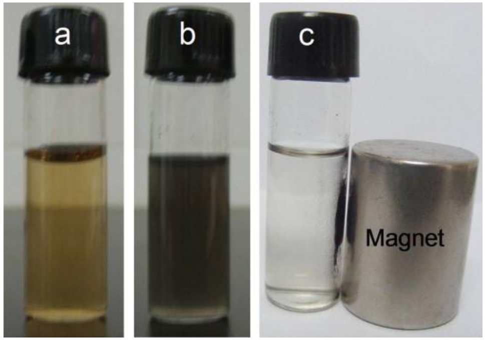
Magnetic Properties

- The Magnetic Moment of Nano particles is found to be very less when compared them with its bulk size. Much better magnetic properties in liquid rather than in solid

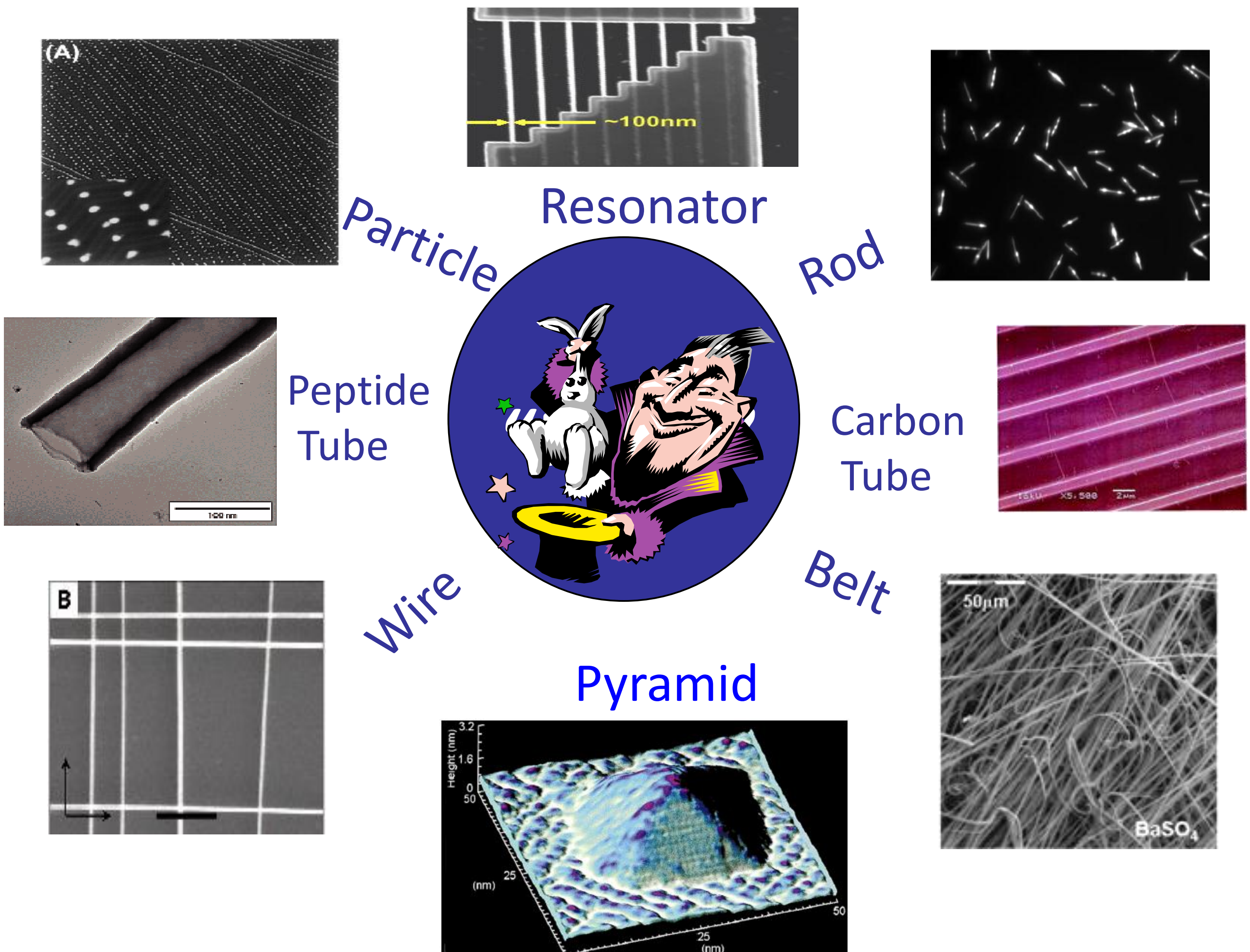


- Nanoparticles made of semiconducting materials Germanium , Silicon and Cadmium are not Semiconductors.

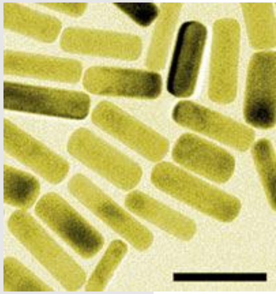




NANO-FEATURING Forms

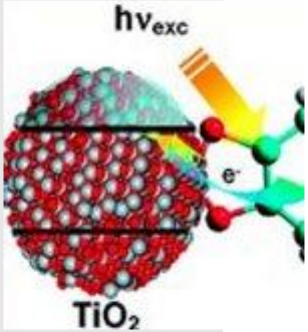


TYPES OF NANOPARTICLES:



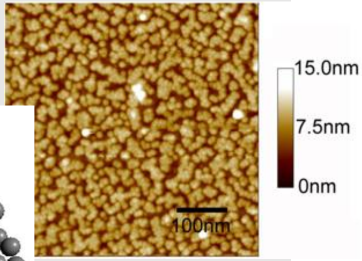
-Metalic nanoparticles (mainly from Noble metals Au, Ag, Pt, Pd…) (usually they are stabilized)

-Bimetalic nanoparticles Au-Ag; Pt-Pd…



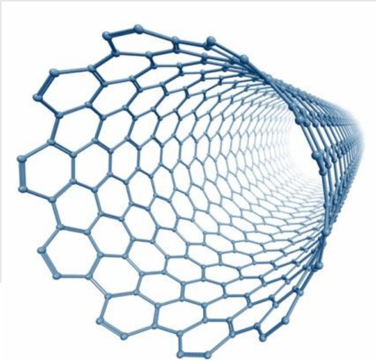
-Oxide nanoparticles..Fe_2O_3, TiO_2…

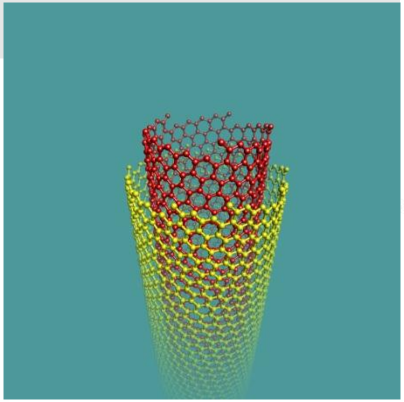
-Sulfide, Selenide nanoparticles CdSe, CdS…

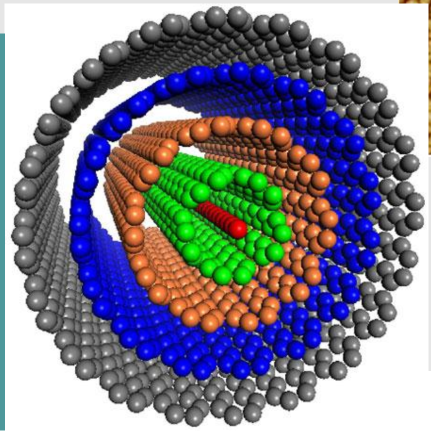


-Carbon nanoparticles

….



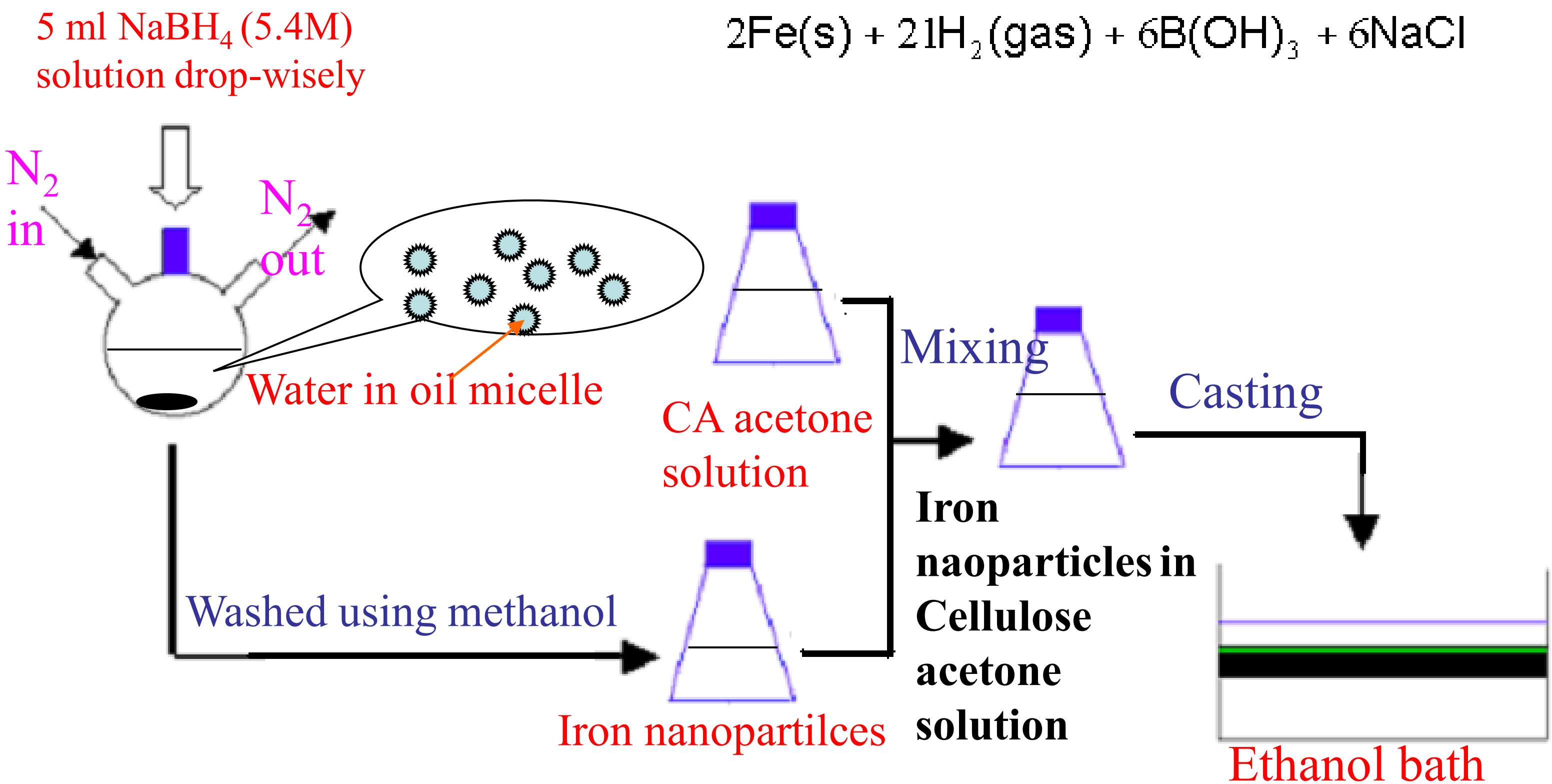




Preparation of some nanoparticles

❖**Synthesis reaction:** $2FeCl_3 + 6NaBH_4 + 18H_2O \rightarrow$

$$2Fe(s) + 21H_2(gas) + 6B(OH)_3 + 6NaCl$$

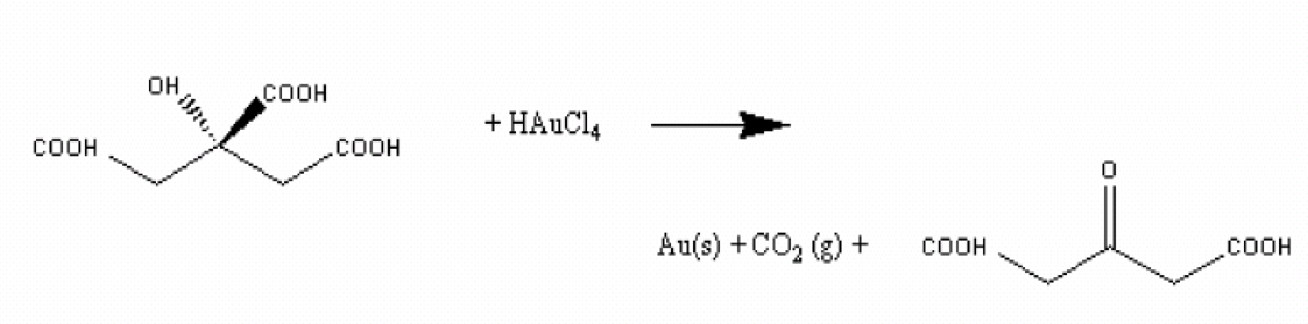


❖ **The weight content of iron is 6.6% by AA (Atomic Absorption).**

Synthesis of Gold Colloids

Modified method by Turkevich *et al.* (Reduction by citrate) in 1951 is mainly used until today

A STUDY OF THE NUCLEATION AND GROWTH PROCESSES IN THE SYNTHESIS OF COLLOIDAL GOLD by J. Turkevich, P. C. Stevenson, J. Hillier
DISC



Gold chloride is dissolved in water while heating and stirring
Trisodium citrate dihydrate is dissolved in a small amount of water then added
Reflux for one hour, as citrate reduces Gold(III).

Citrate as reducing and stabilizing agent

Synthesis of Gold Colloids

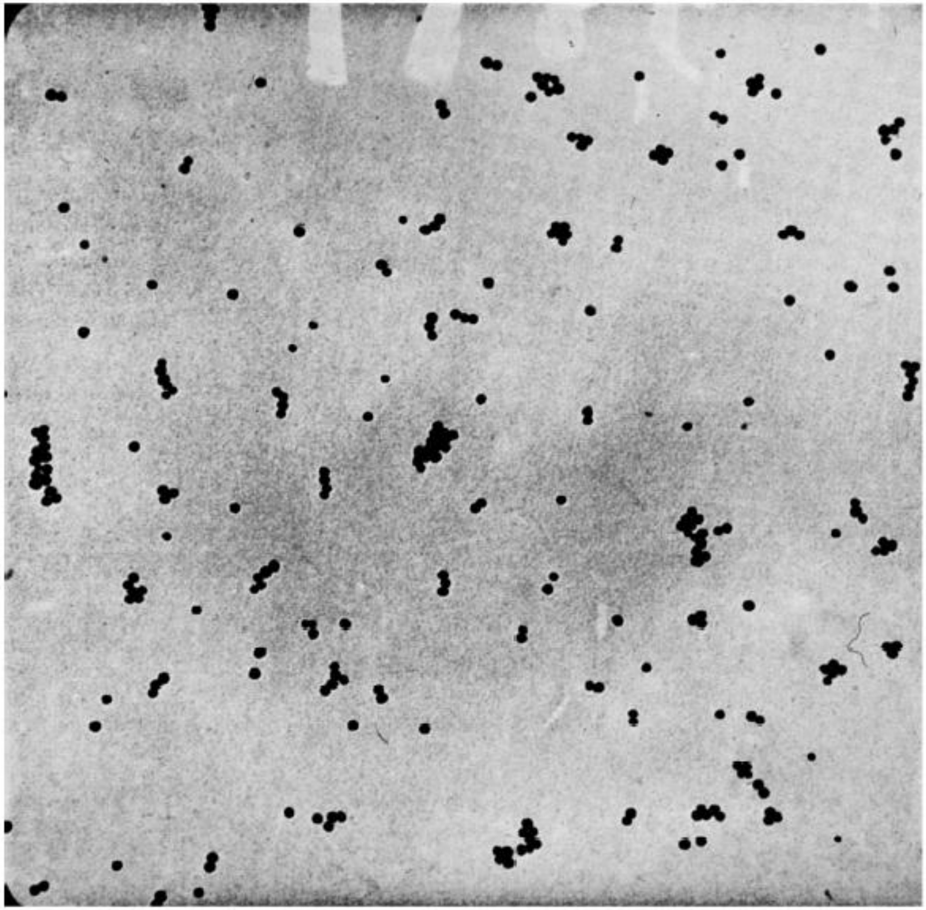


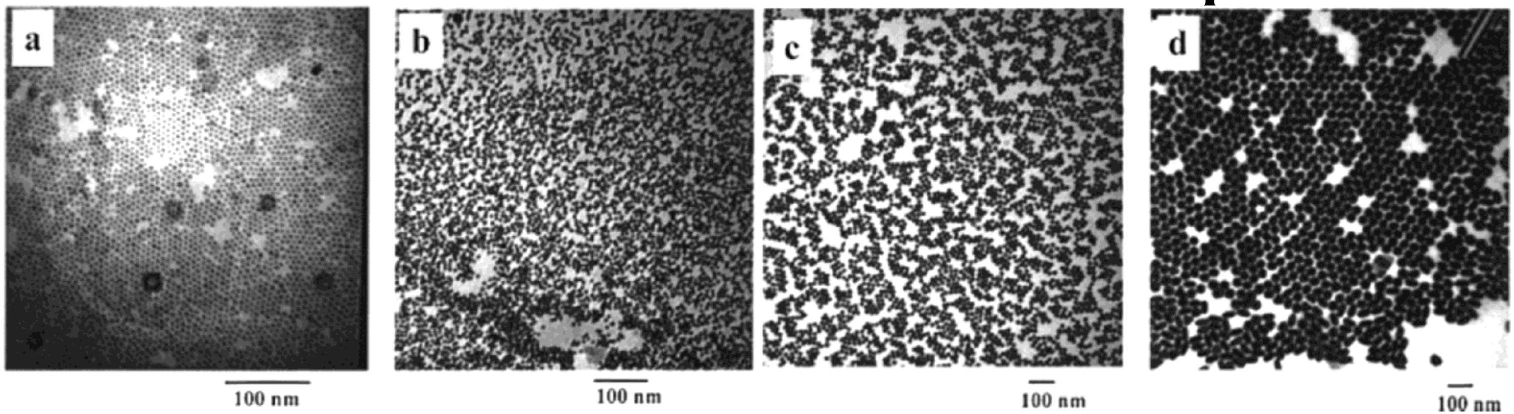
FIG. 3.—Electron micrograph of a gold sol reduced with sodium citrate (standard citrate sol) magnification 50,000 diameters.

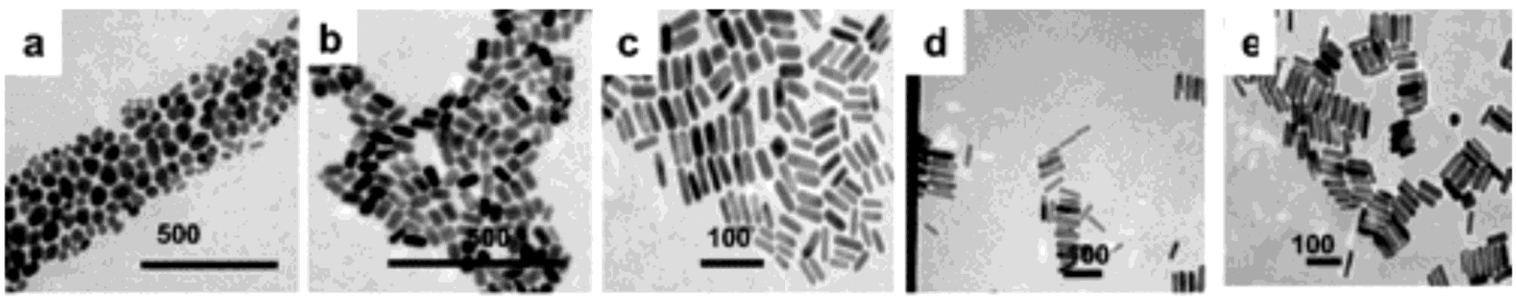
Gold colloids with uniform diameters of about 20 nm

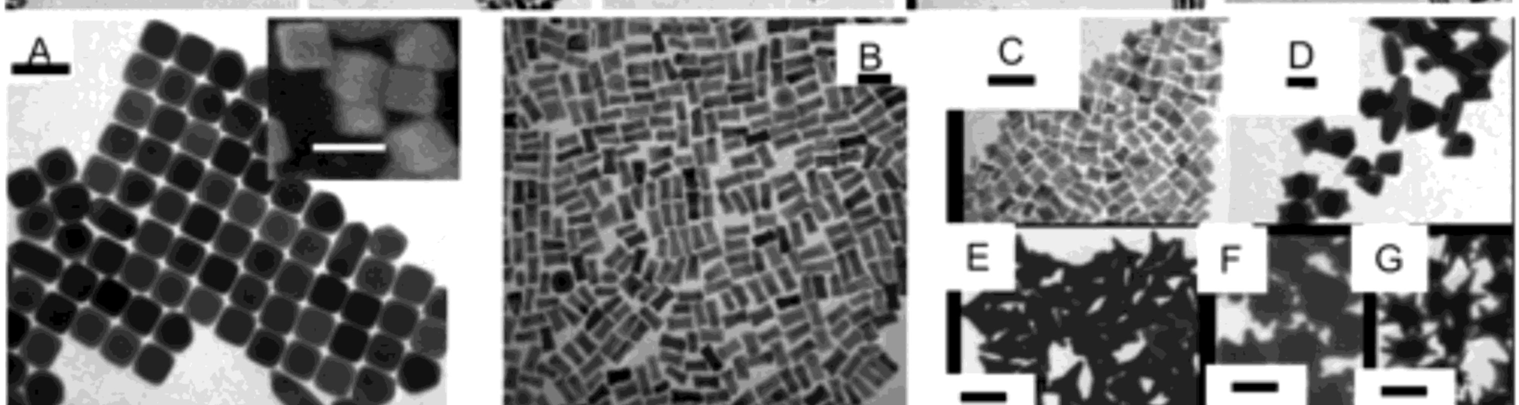
Size dependent on citrate concentration

Synthesis of Gold Colloids

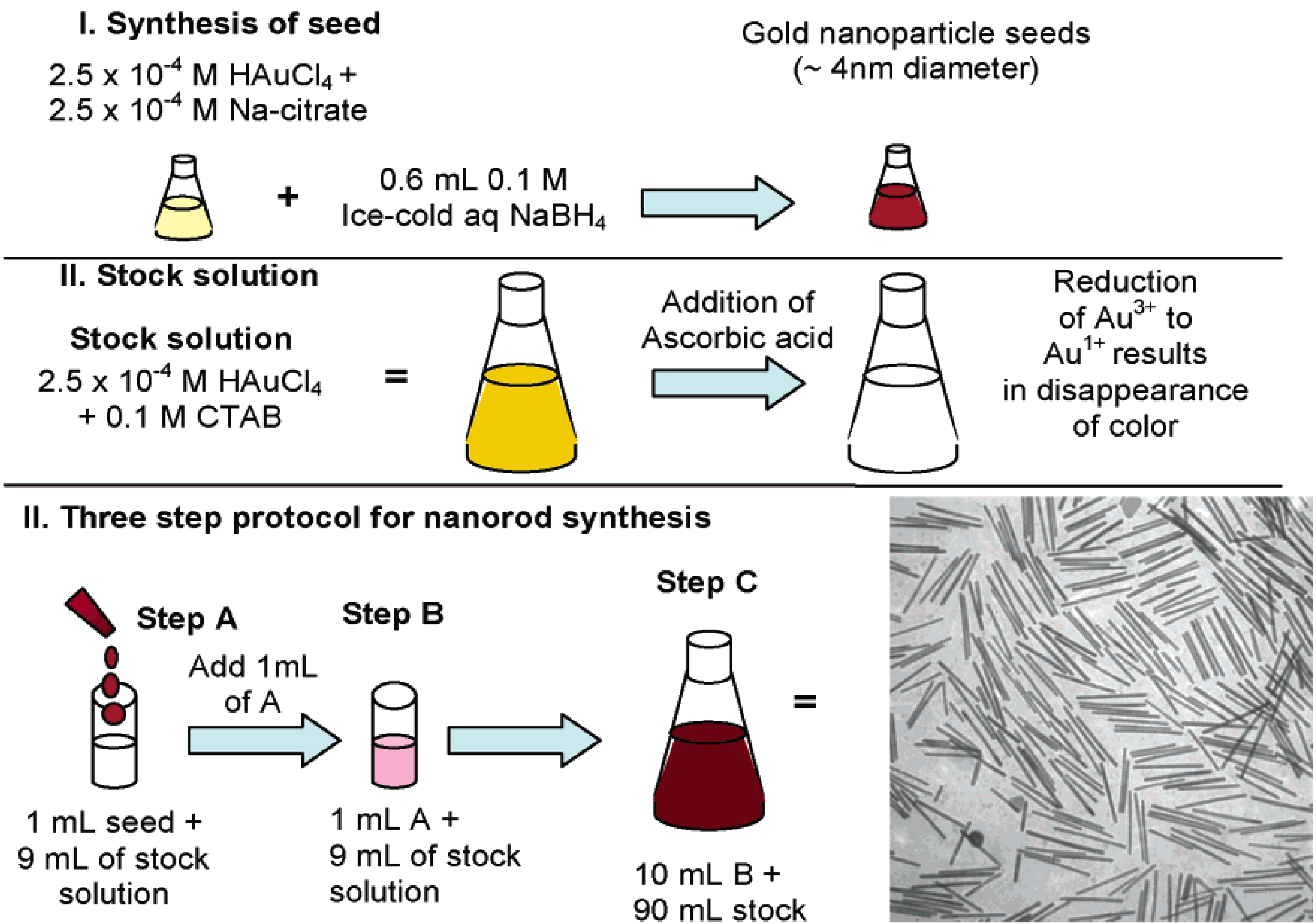
Excellent control over size and shape





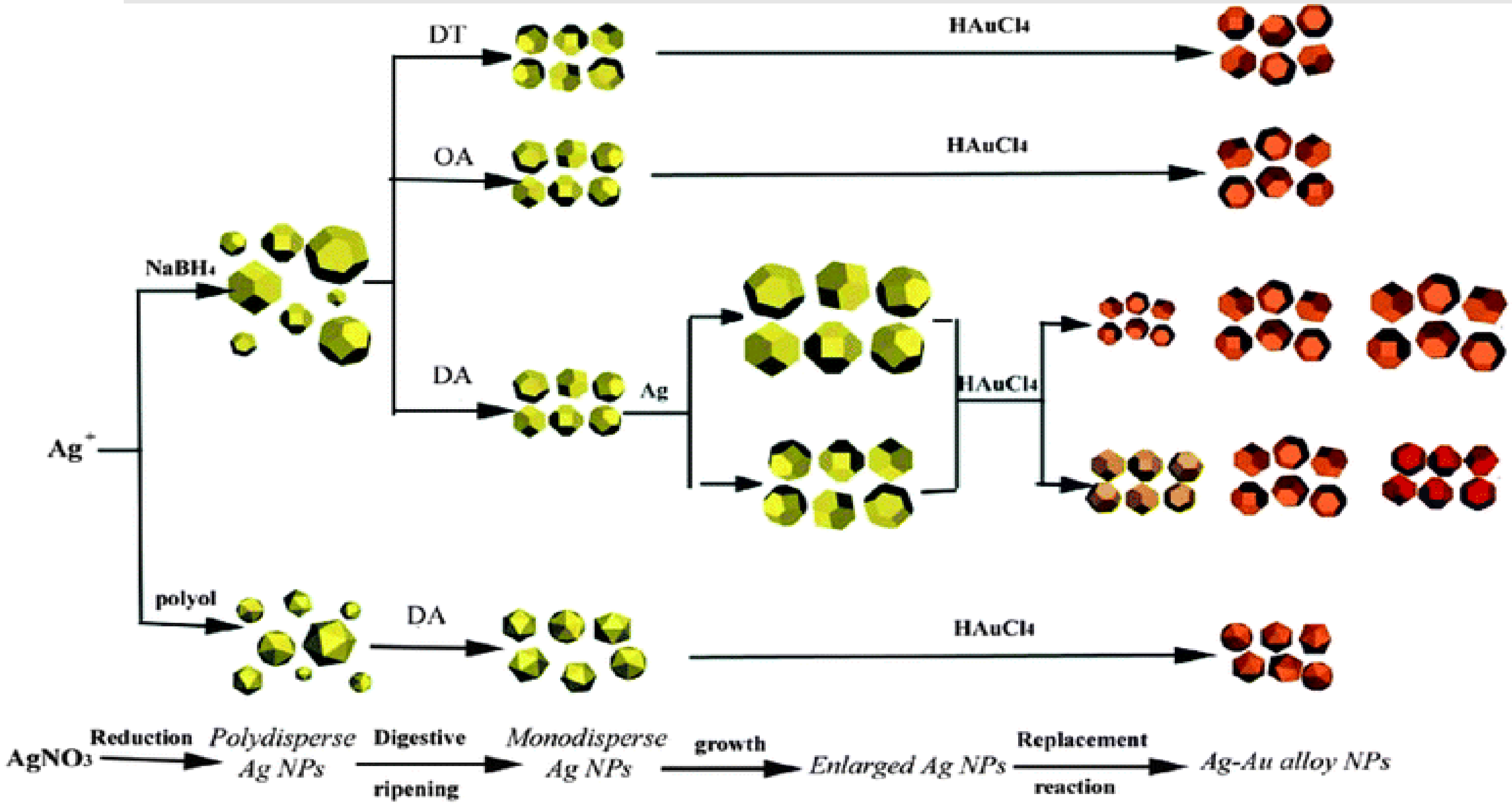


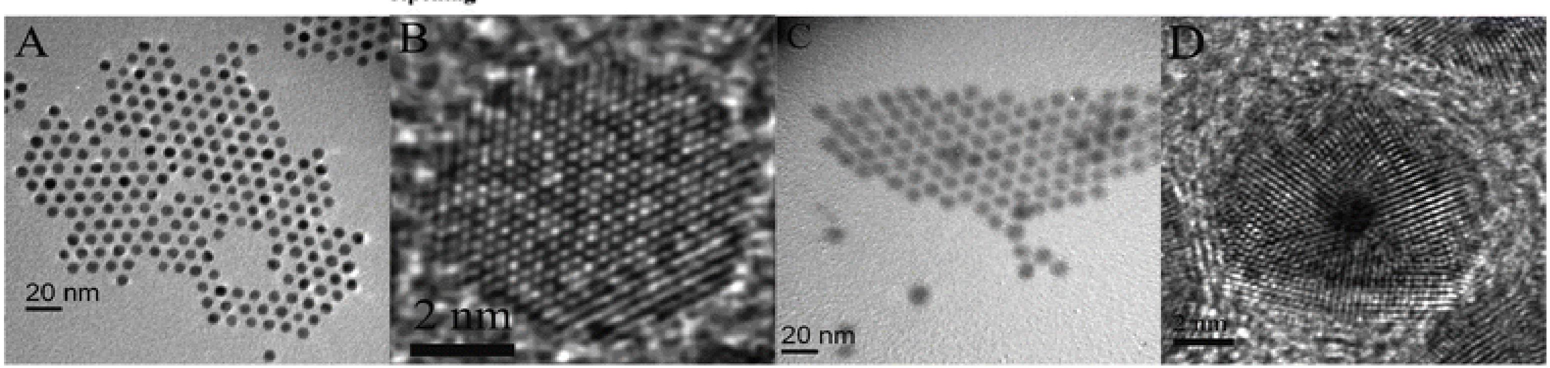
Synthesis of gold nanorods



CTAB = cetyltrimethylammonium bromide

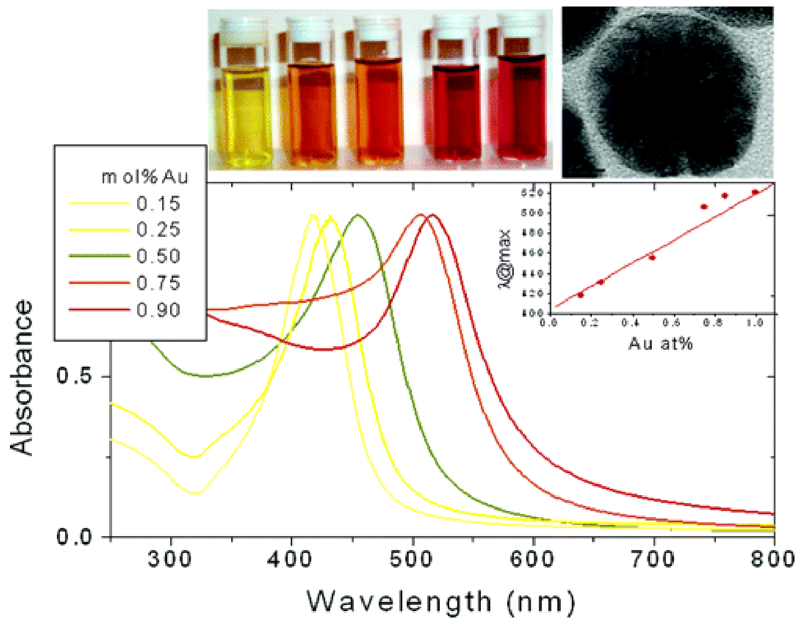
Synthesis of bimetallic Ag-Au nanoparticles



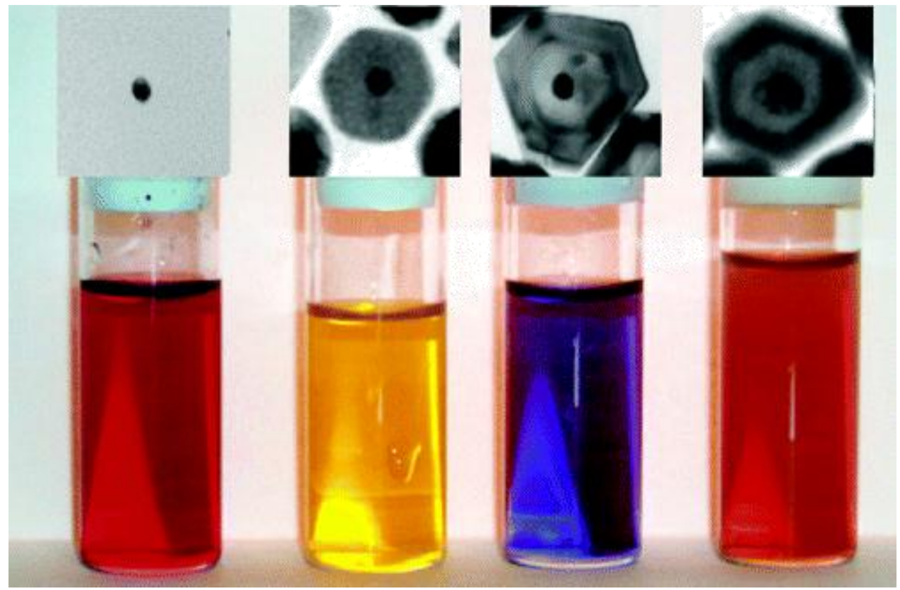


Tailoring of the Optical Properties of Gold Colloids

AuAg Bimetallic Nanoparticles: Alloys vs. Core-Shells



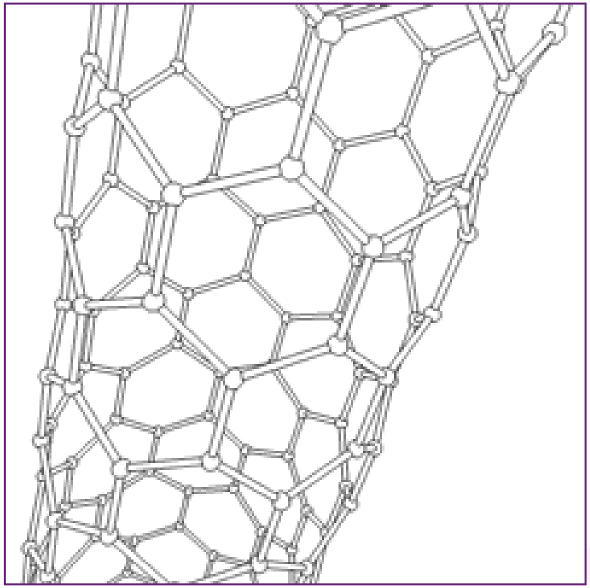
Variation in optical properties (UV-vis spectra and color) for AuAg alloy nanoparticle colloids with varying compositions.

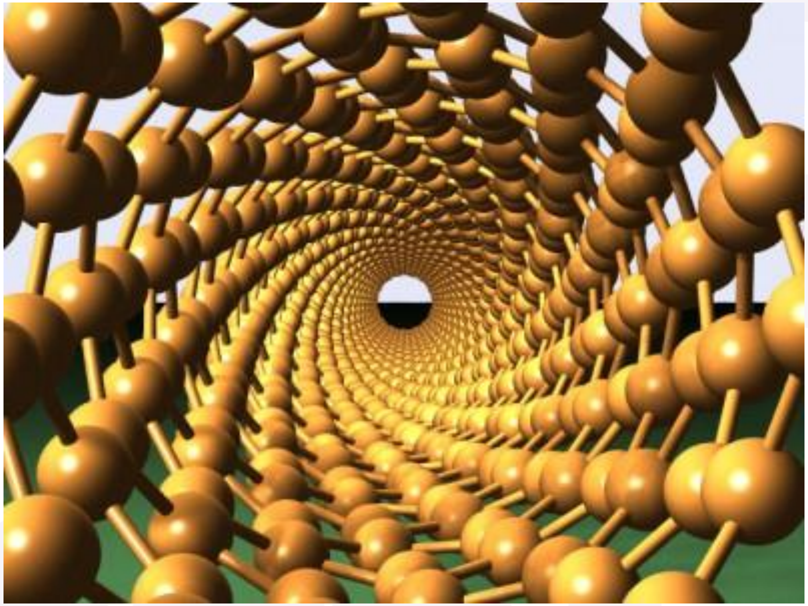


Photographs of aqueous dispersions of (from left to right) Au, Au@Ag, Au@Ag@Au, and Au@Ag@Au@Ag nanoparticles, and the corresponding TEM images. Au core size: 16 nm.

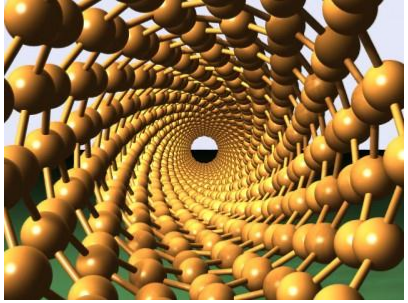
Carbon Nanotubes-the most exploited and most important nanoparticles

Given their unique properties, what can carbon nanotubes be used for?

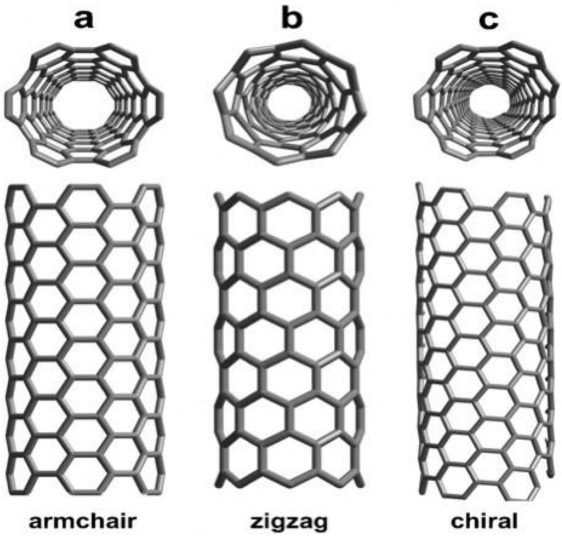


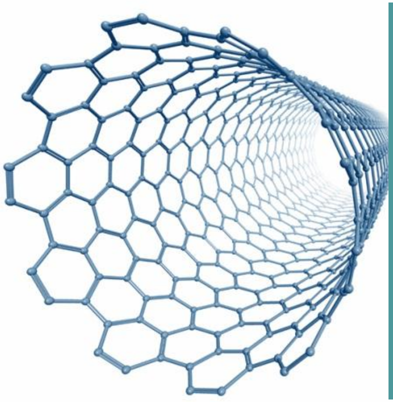


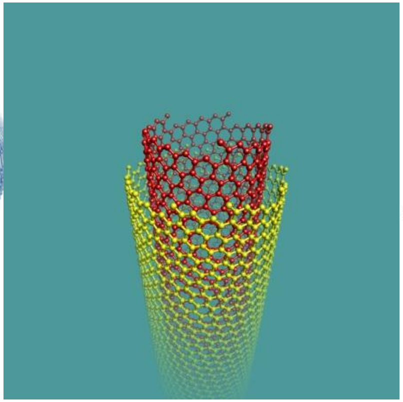
Carbon Nanotubes

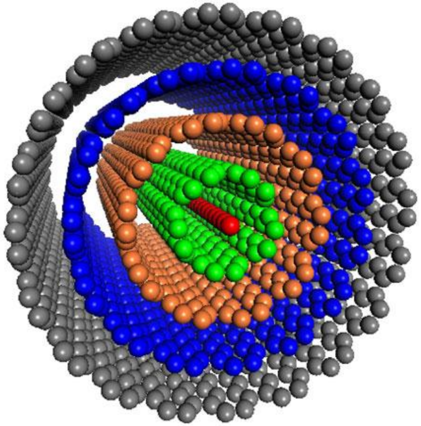


- What are they?
  - Graphite sheets rolled into a cylinder to form nanometer tubes
- Preparation
  - Arc evaporation (non-catalytic)
  - Chemical Vapor Deposition (CVD)
- Multi-wall and single-wall

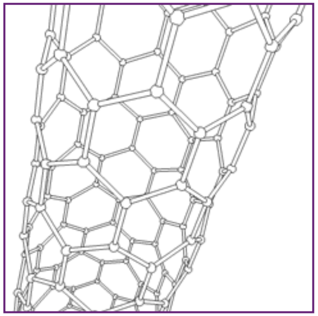
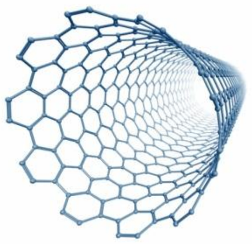
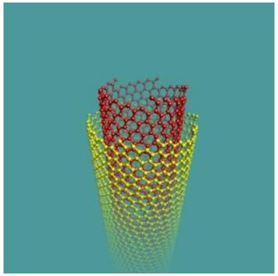
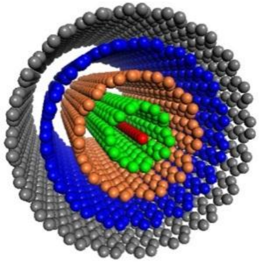








WHY CARBON NANOTUBES (CNT)?

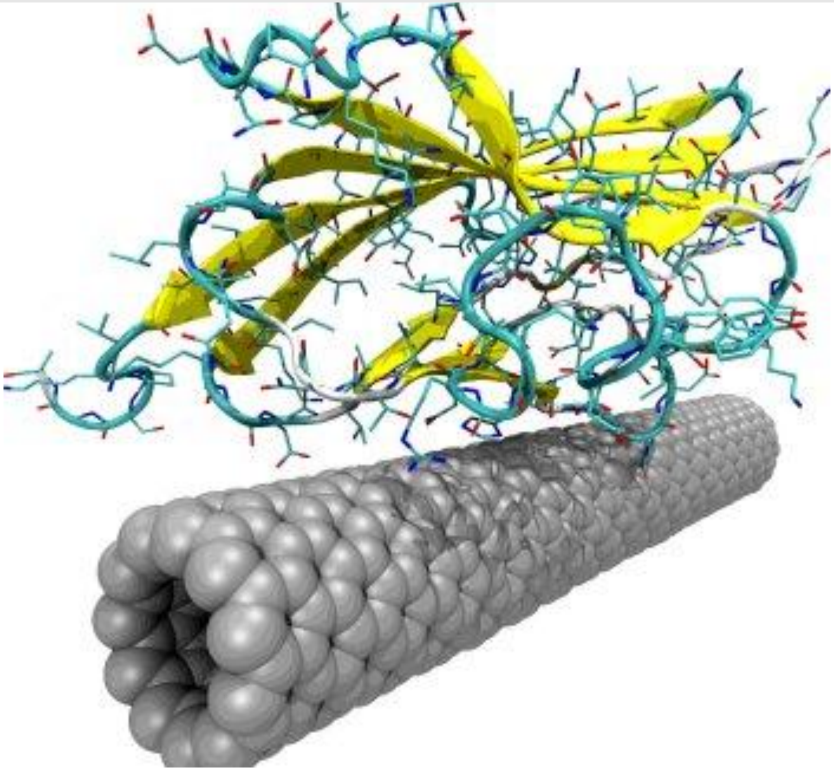
   

CARBON NANOTUBES POSSESS REMARKABLE *ELECTRONIC, MECHANICAL AND CHEMICAL PROPERTIES WHICH MAKES THEM EXTREMELY ATTRACTIVE FOR VARIOUS SENSING DEVICES*.

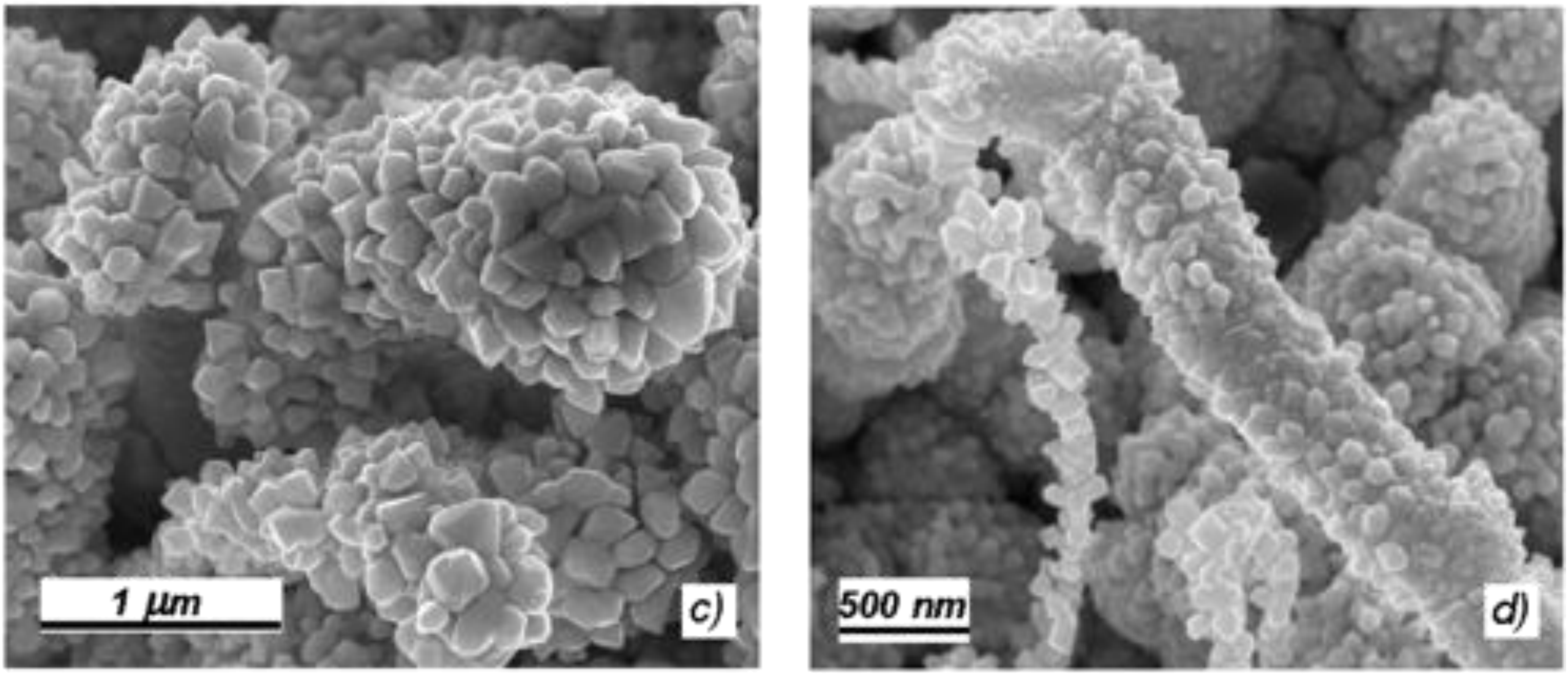
CARBON NANOTUBES WERE SHOWN *USEFUL TO PROMOTE ELECTRON-TRANSFER REACTIONS* AND IMPARTS HIGHER RESISTANCE TO SURFACE FOULING

Nanotubes-functionalization

Chemical properties of nanotubes are quite interesting-it is quite easy to functionalized the carbon nanotubes with various functional groups! Consequently, they can be used for various purposes depending on the functionalized groups attached on them



Covalent Bonding - Carbon



Carbon nanotubes coated with diamond nanocrystals

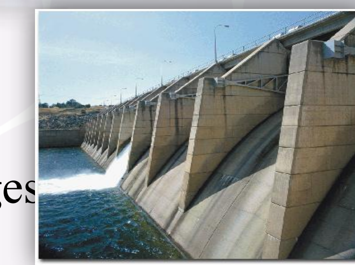
M. L. Terranova, et al., *Chem. Mater.*, *17*(12) pp 3214 - 3220

Carbon Nanotubes applications

Carbon Nanotubes (***CNT***) 1D, Iijima in 1991 .

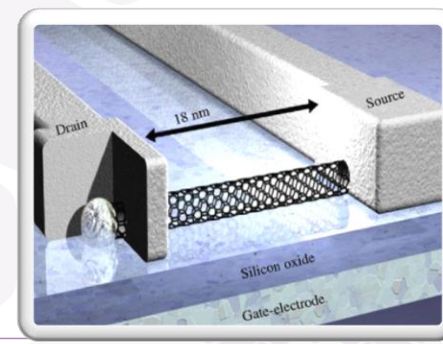
Fantastic MECHANICAL PROPERTIES

- stiffness &strength due to Sp2 bond
  - ***Much stronger structure than diamond***
    - May replace steel in the future
      - Construction purposes like using nanocomposites -bridges



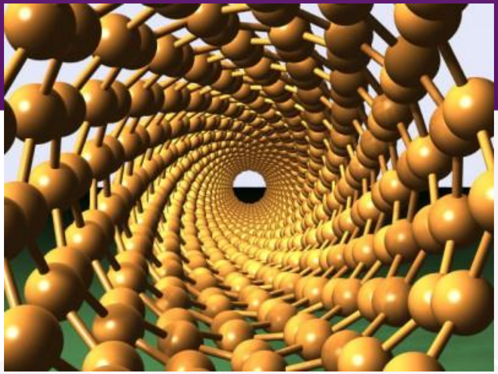
Light- Low mass

Aerospace industry to build aircrafts and satellites.



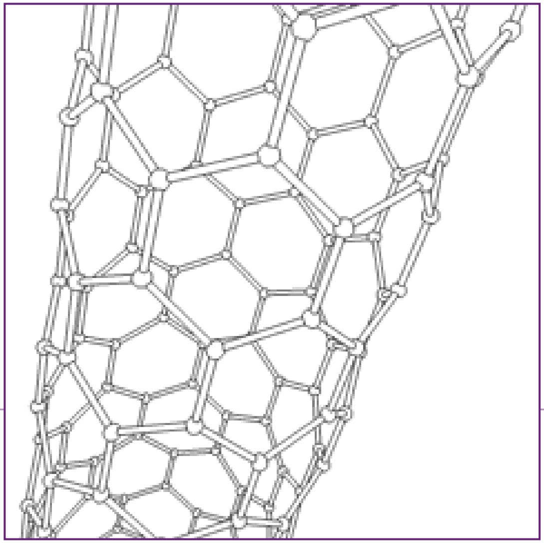
Thermal and **Electrical** conductivity

Drawbacks



Few drawbacks:

- Difficulty of production.
- Low solubility of CNTs in the water



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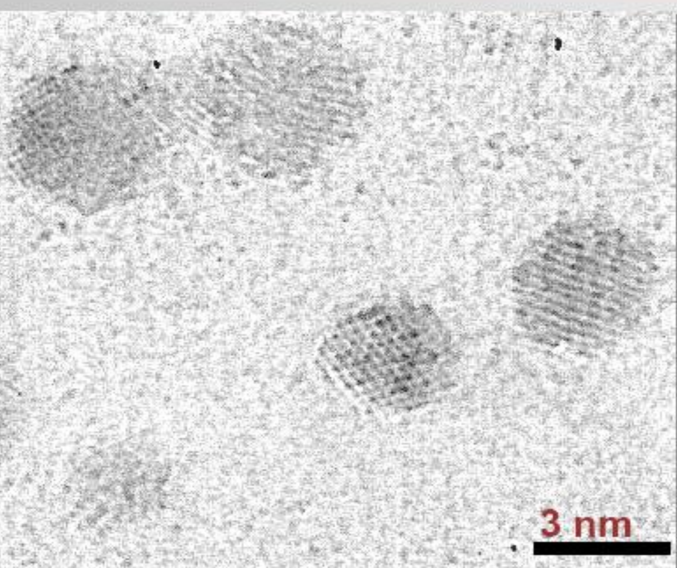
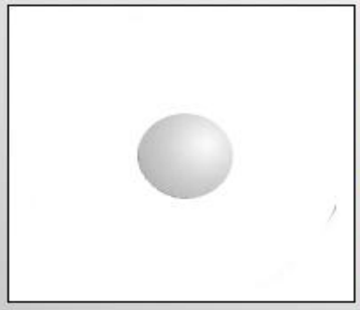
Techniques for characterization of nanoparticles

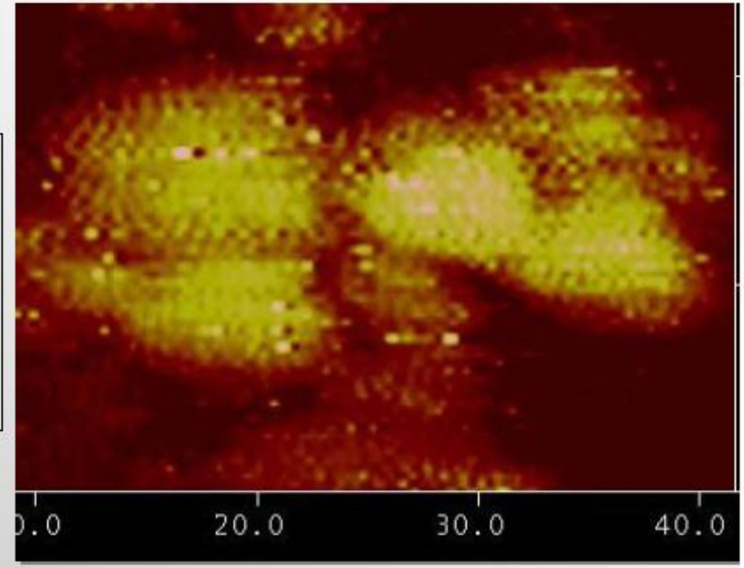
- Image analysis
  - FE-SEM
  - AFM
  - TEM
- Microbeam technologies
  - FTIR
- Particle size / sorting
  - Flow cytometry
  - Air separation
  - Size exclusion
  - Dynamic light scattering

Characterizing Metal Nanoparticles

S u N M a G



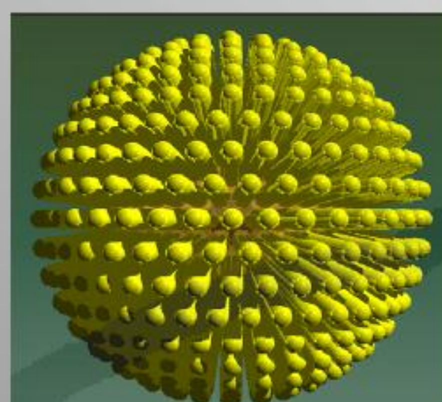


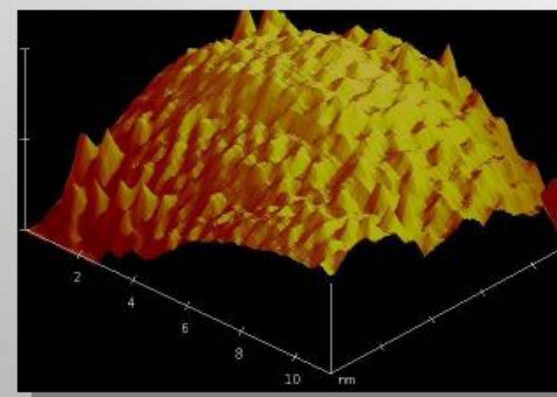


TEM shows atoms in the core

STM shows ligands in the shell

2.7 nm

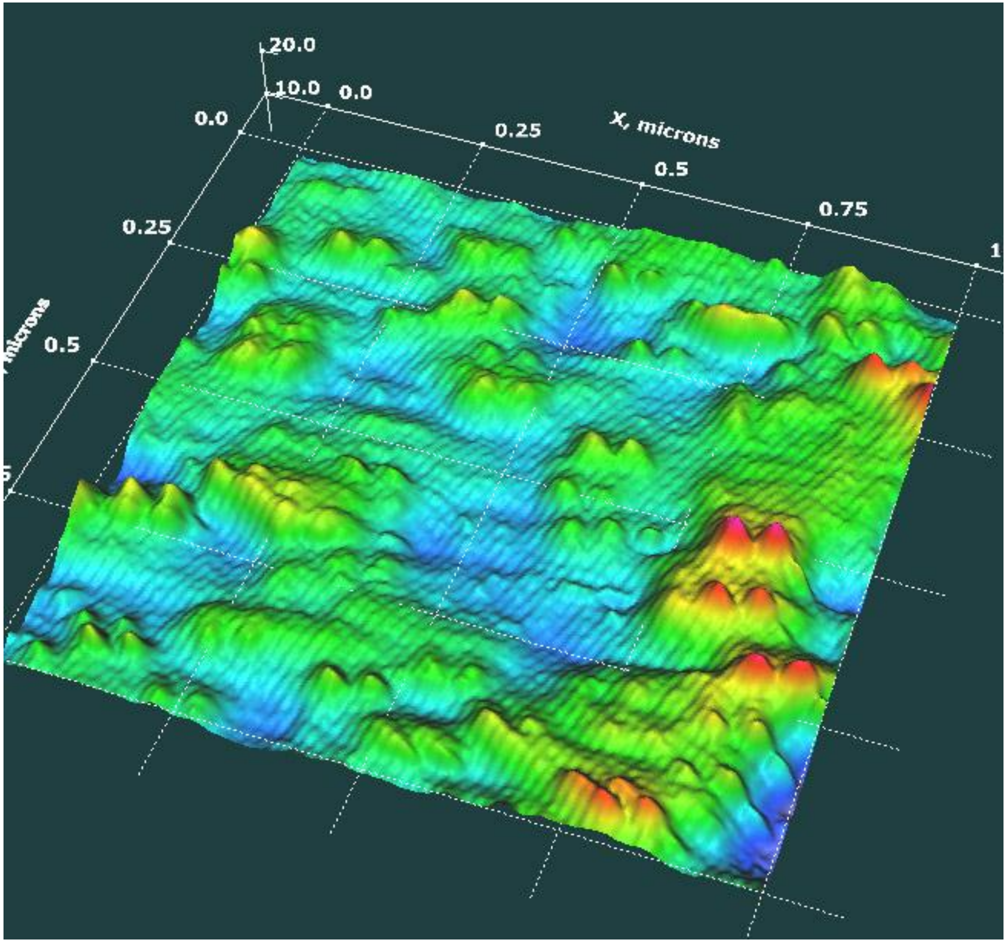




AFM analysis of particles

Interactive 3D visualization tools for nanoparticles amalgamation analysis.

ScienceGL Inc. has developed 3D AFM data visualization engine that provides researcher the set of interactive 3D measurement tools. These tools helps scientist to measure various important characteristics of the sample in real time. The 3D visualization software is also fast enough to work with live video AFM microscopes. For detailed comparison of the data obtained with AFM for different data acquisition modes we also offer **Multiple 3D surface analysis software.**

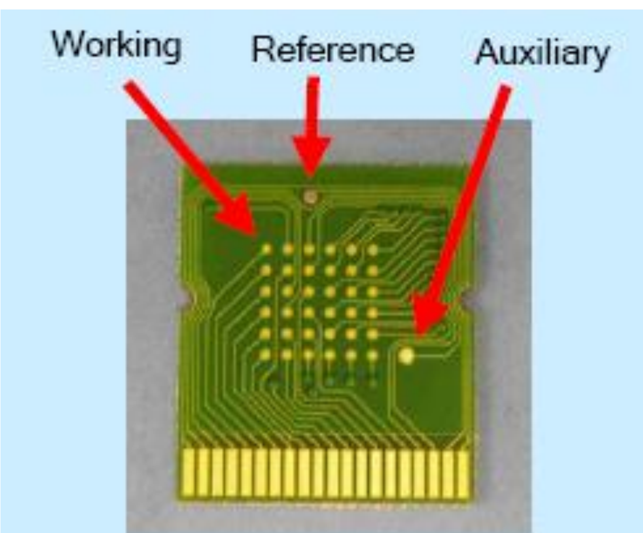


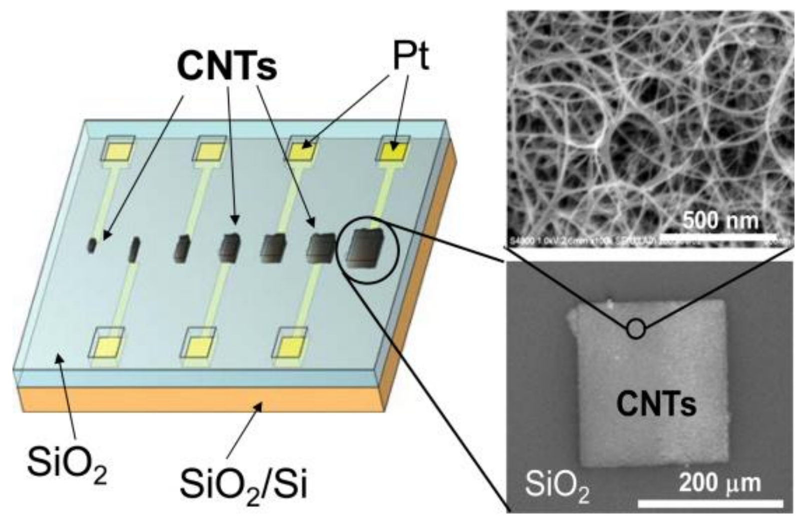
ELECTROCHEMICAL NANO SENSORS

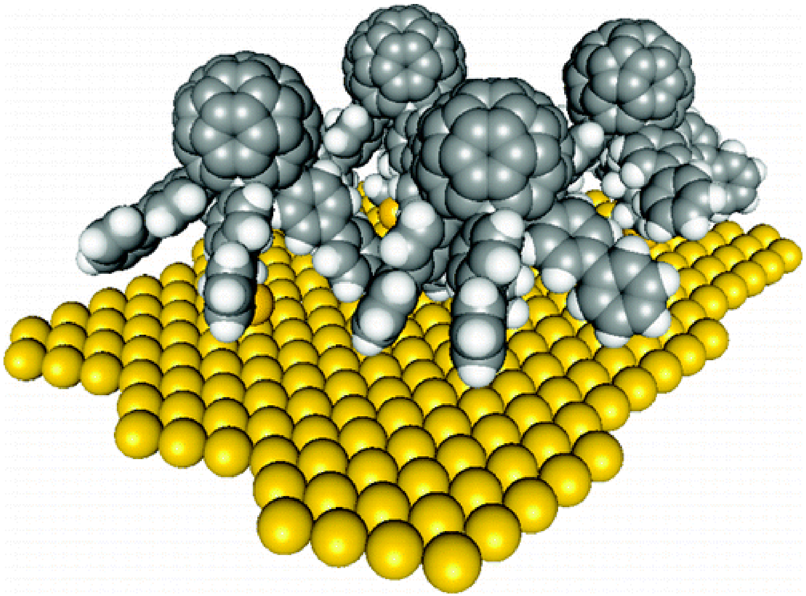
Mainly ***two strategies*** for detections of the analytes are used

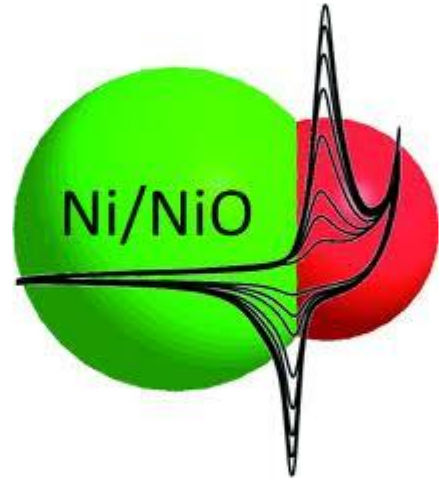
-***enhanced direct detection*** of many substrates
at nanoparticles modified electrodes

-***enhanced mediated detection*** of many substrates
at nanoparticles modified electrodes

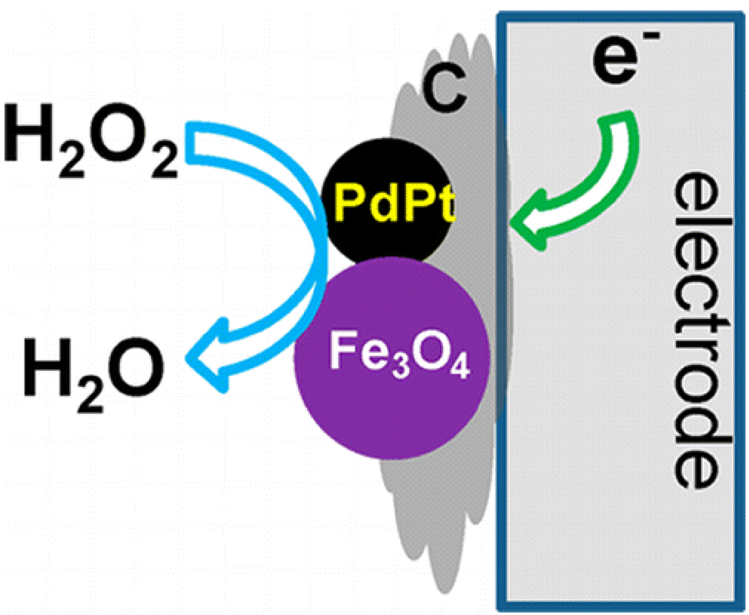


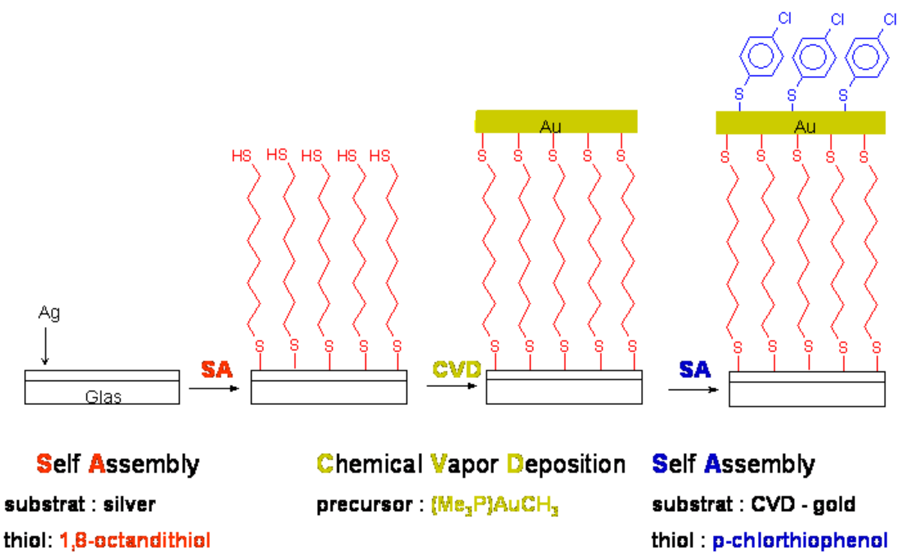




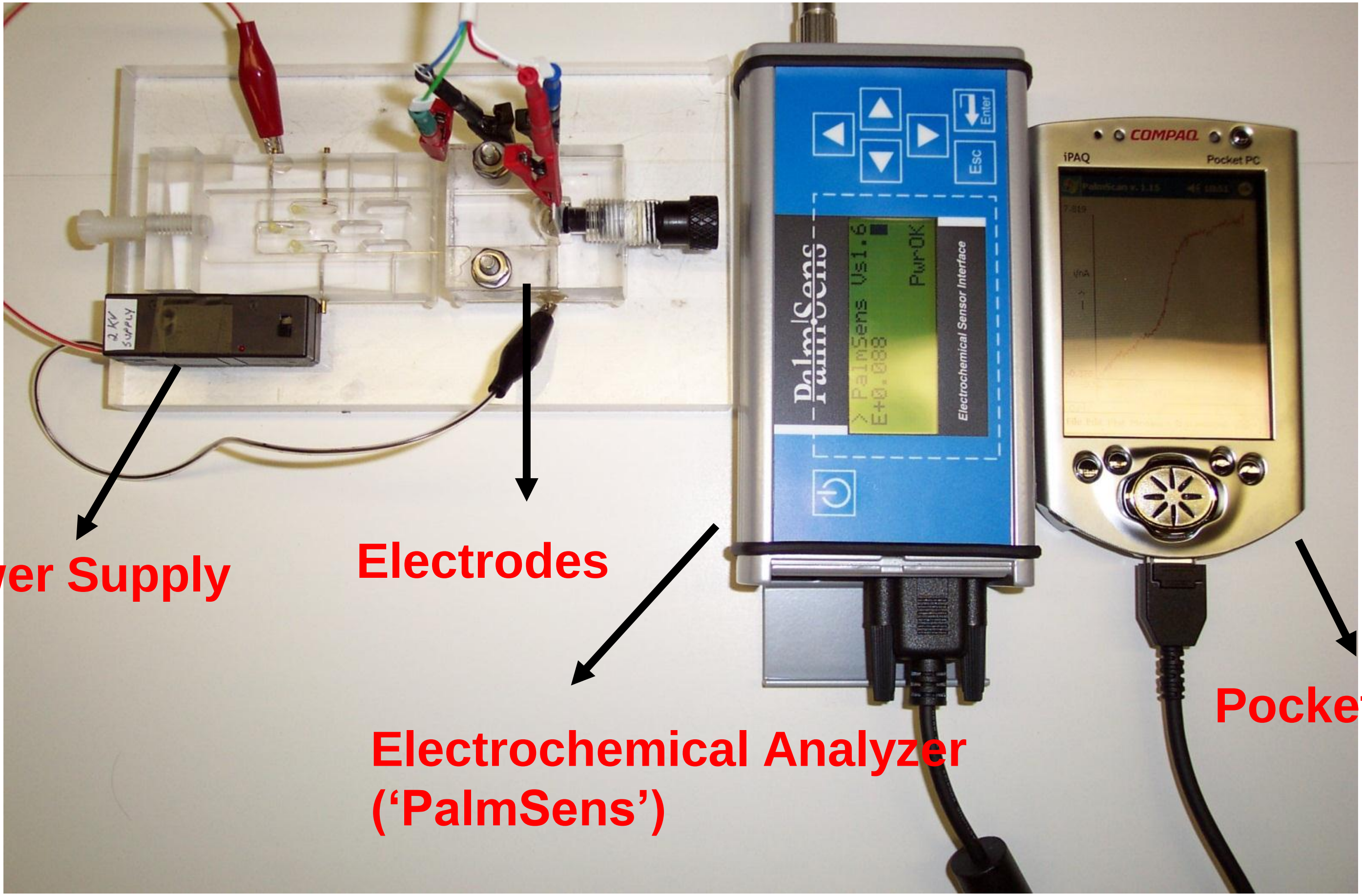


Organo-metallic CVD on SAMs





Electrochemical Nanoparticles Microsystem



Power Supply

Electrodes

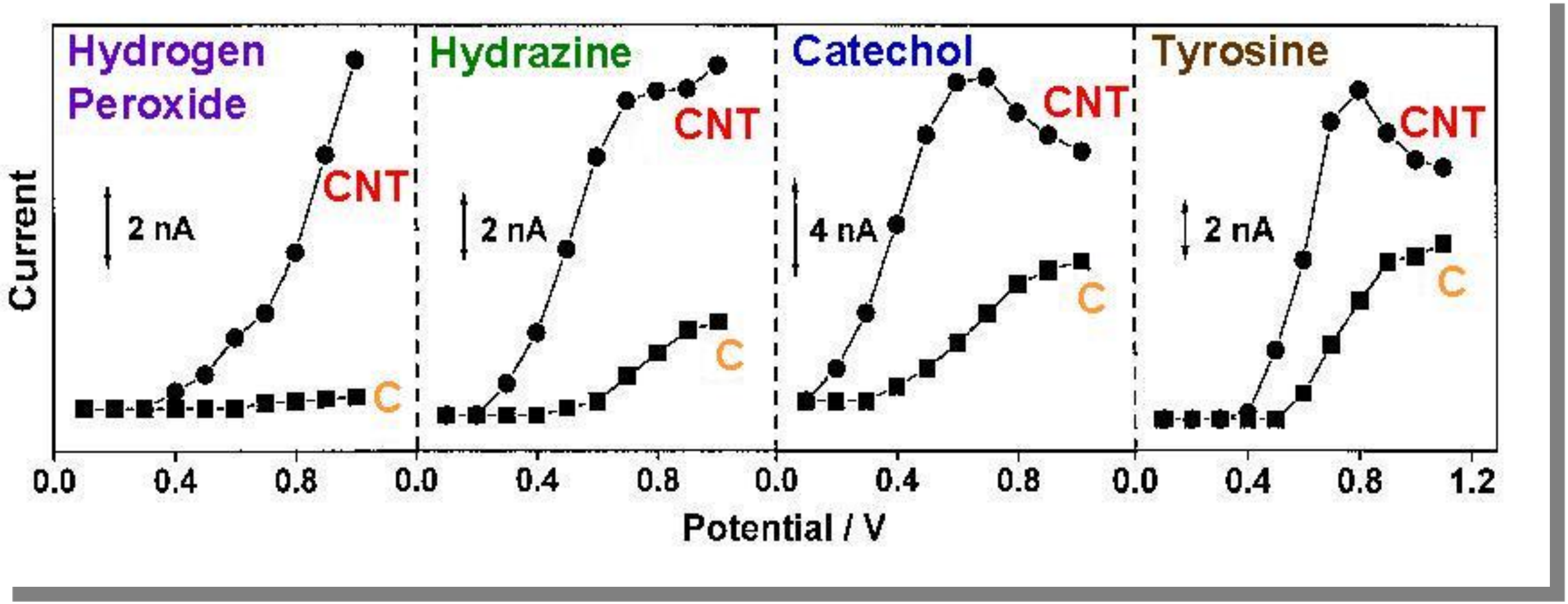
Electrochemical Analyzer ('PalmSens')

Pocket PC

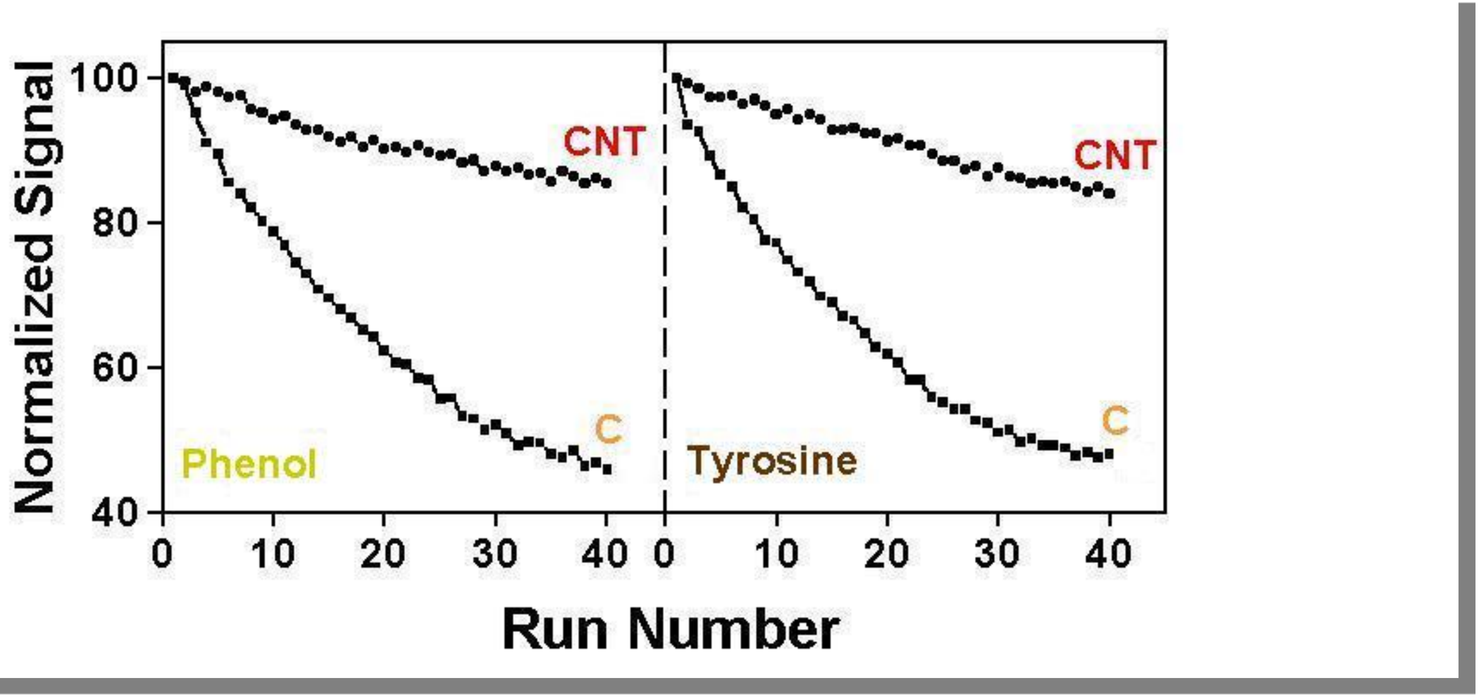
Use of Nano-modified electrodes
TOWARDS ENVIRONMENTAL MONITORING

- PHENOLIC COMPOUNDS
- HYDRAZINES
- NITROAROMATIC EXPLOSIVES
- PESTICIDES AND NERVE AGENTS

Carbon-Nanotube-based Electrochemical Detections

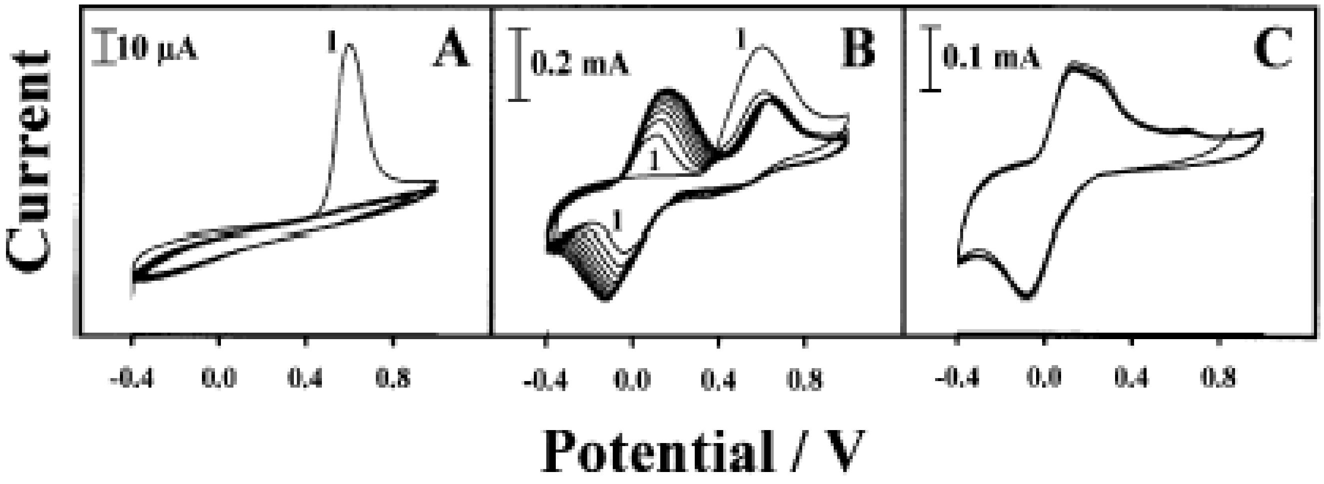


Stability of the response to phenol and tyrosine at the carbon-nanotube modified and unmodified electrodes



2,4-dichlorophenol

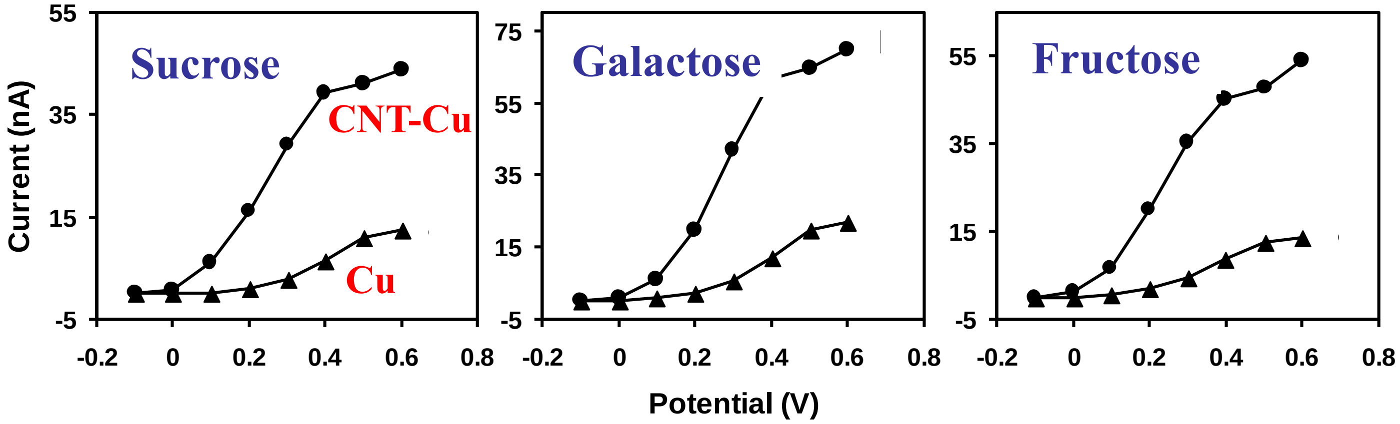
Bare GC CNT-GC CNT-GC



- CNT circumvents common surface fouling during the phenol oxidation; the redox process involves the formation of a surface-confined layer that promotes (rather than inhibits) the phenol oxidation.

Coupling of CNT with metal NP catalysts: Cu/CNT composites

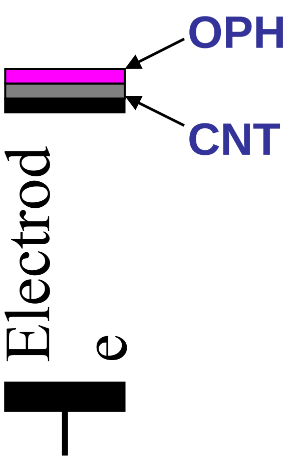
for determination of some carbohydrates



Hydrodynamic voltammograms for different sugars

CNT FOR ENHANCED BIOSENSING OF ORGGANOPHOSPHORUS (OP) PESTICIDES THROUGH CATALYTIC DETECTION OF THE p-NITROPHENOL PRODUCT

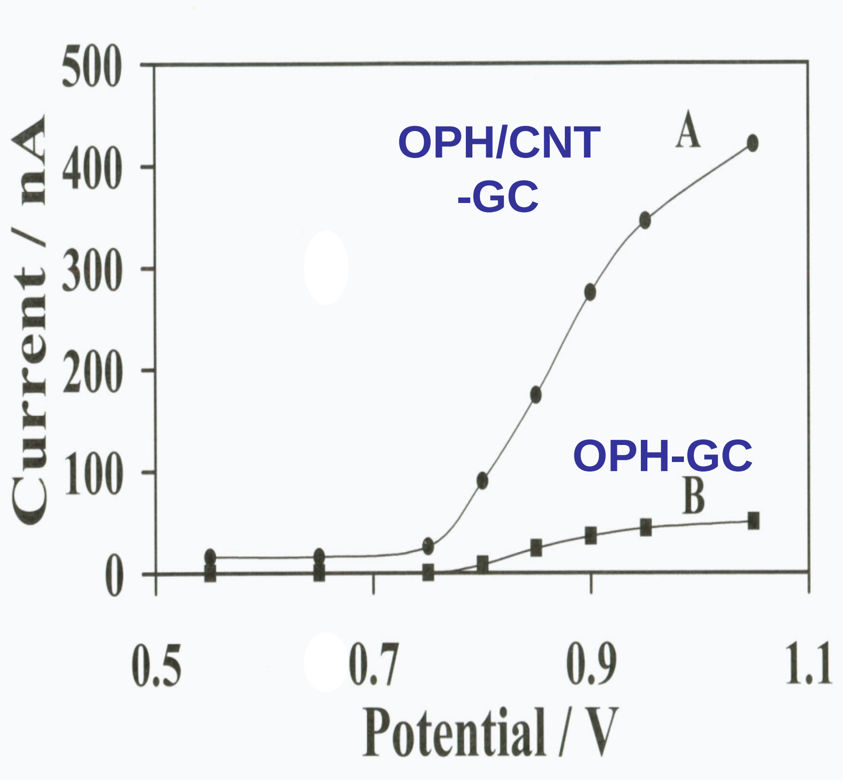
- **Organophosphorus compounds**
  - **neurotoxic**



Optimized condition: 5mg CNT; 0.5% Nafion;

48 IU/μL OPH

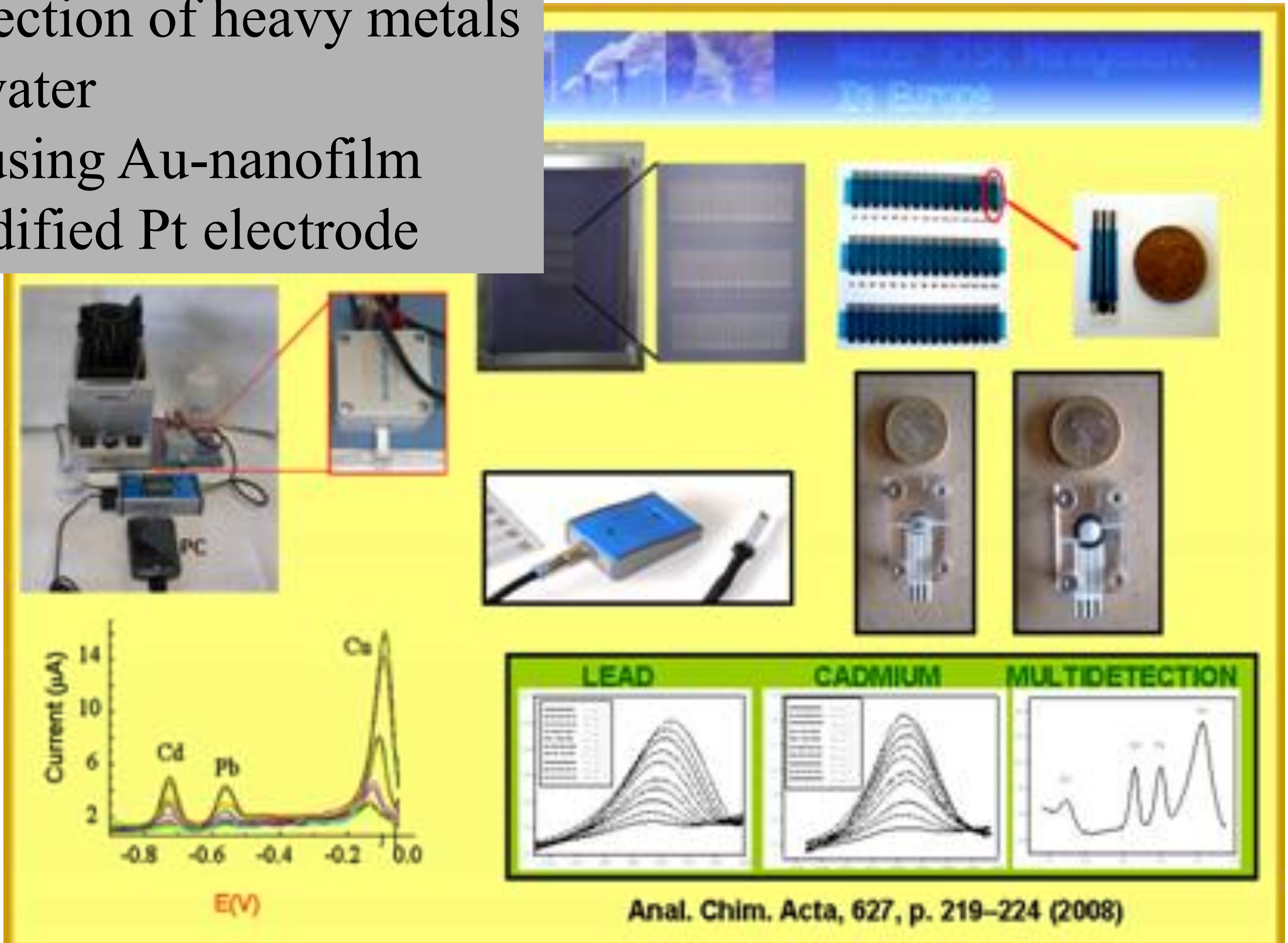
Pesticides



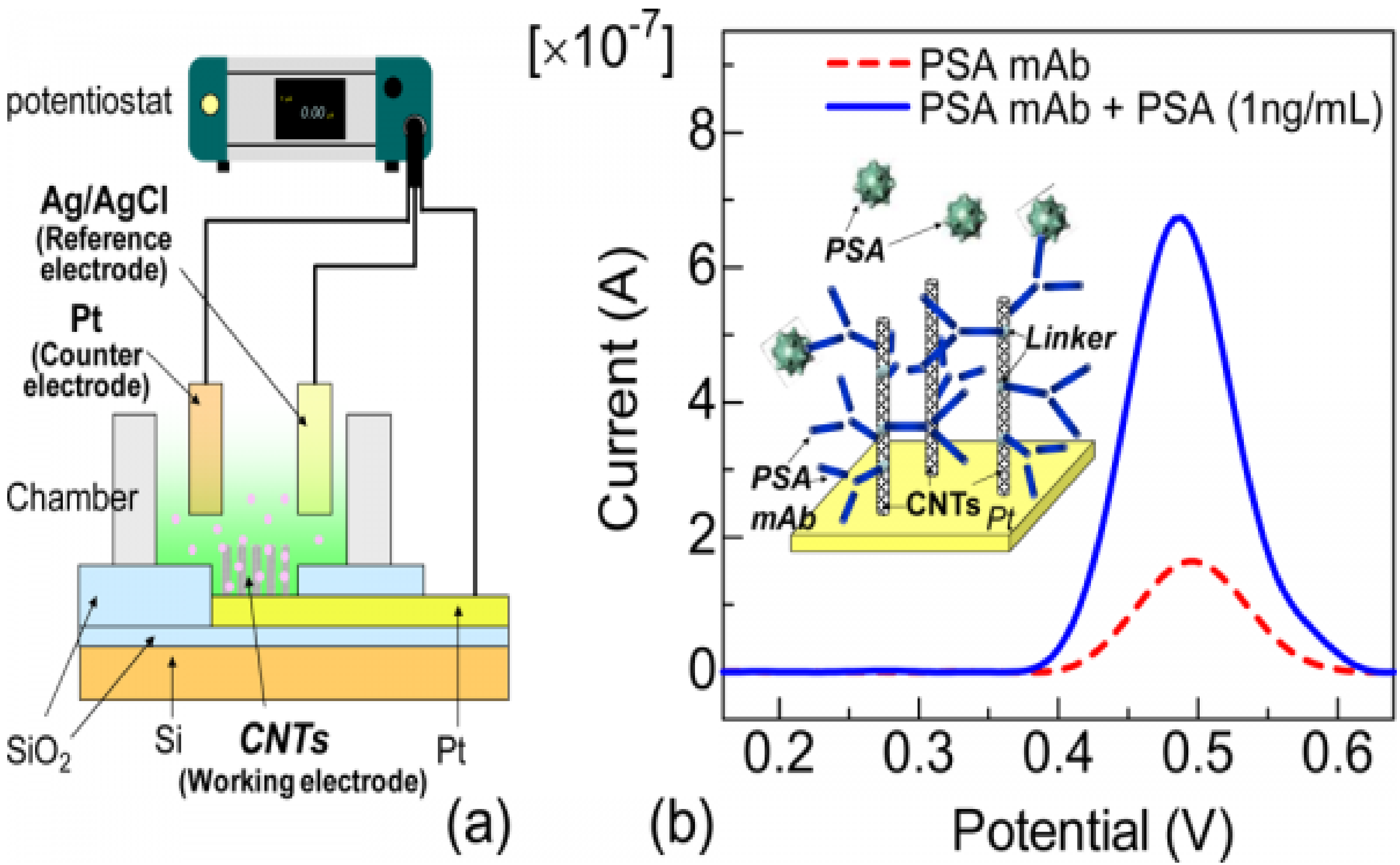
HDV for 10 µM paraoxon

Potential: +0.85 V

Detection of heavy metals in water by using Au-nanofilm Modified Pt electrode

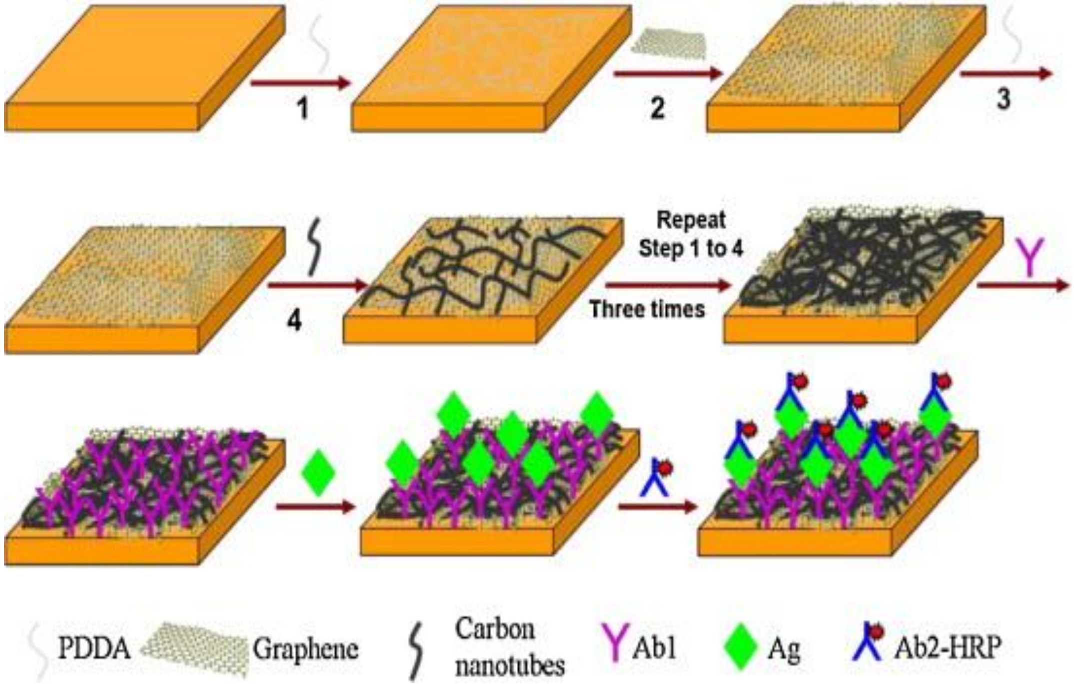


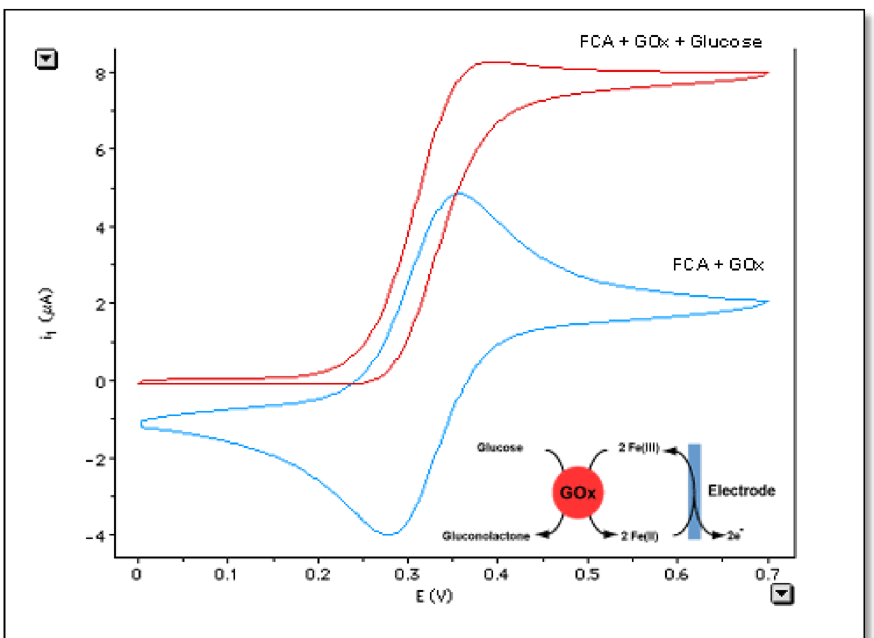
Detection of some Biospecific Agents by Nanotubes modified electrodes

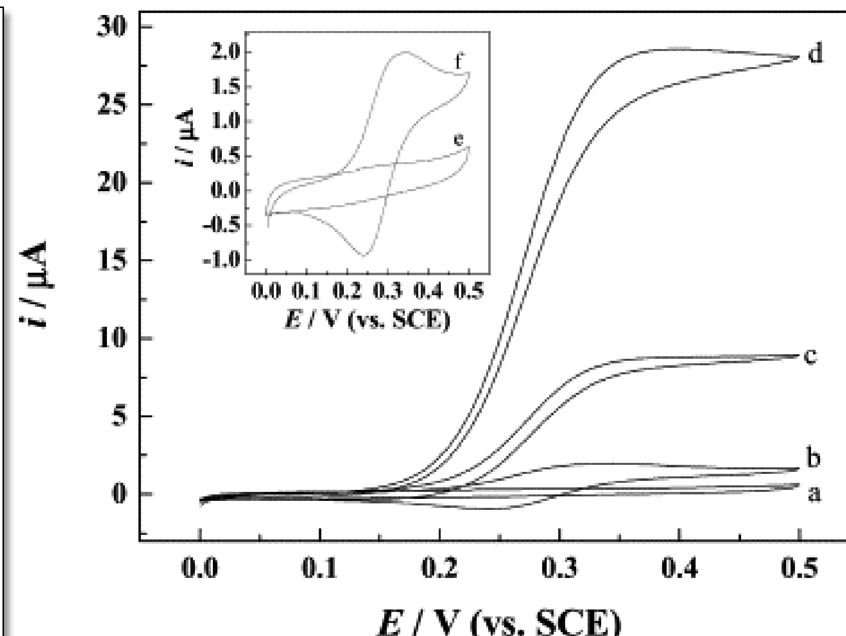


PSA-Prostate Specific Agent
mAB-monoclonal antibodies

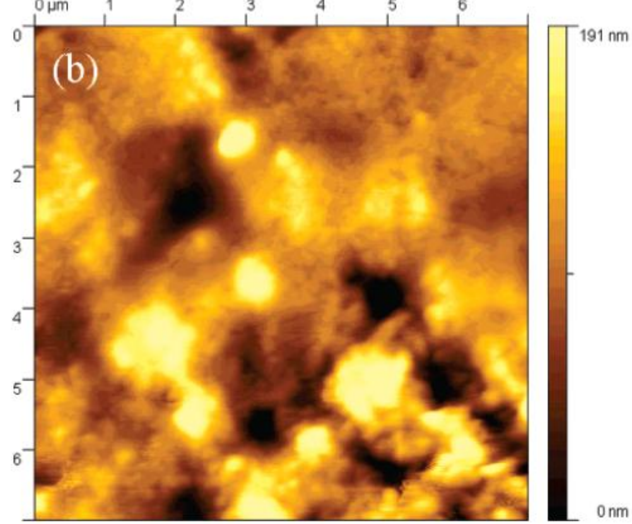
Glucose Determination at CNT modified electrodes







Detection of Vitamin E at Au-nanoparticles graphite Modified electrode



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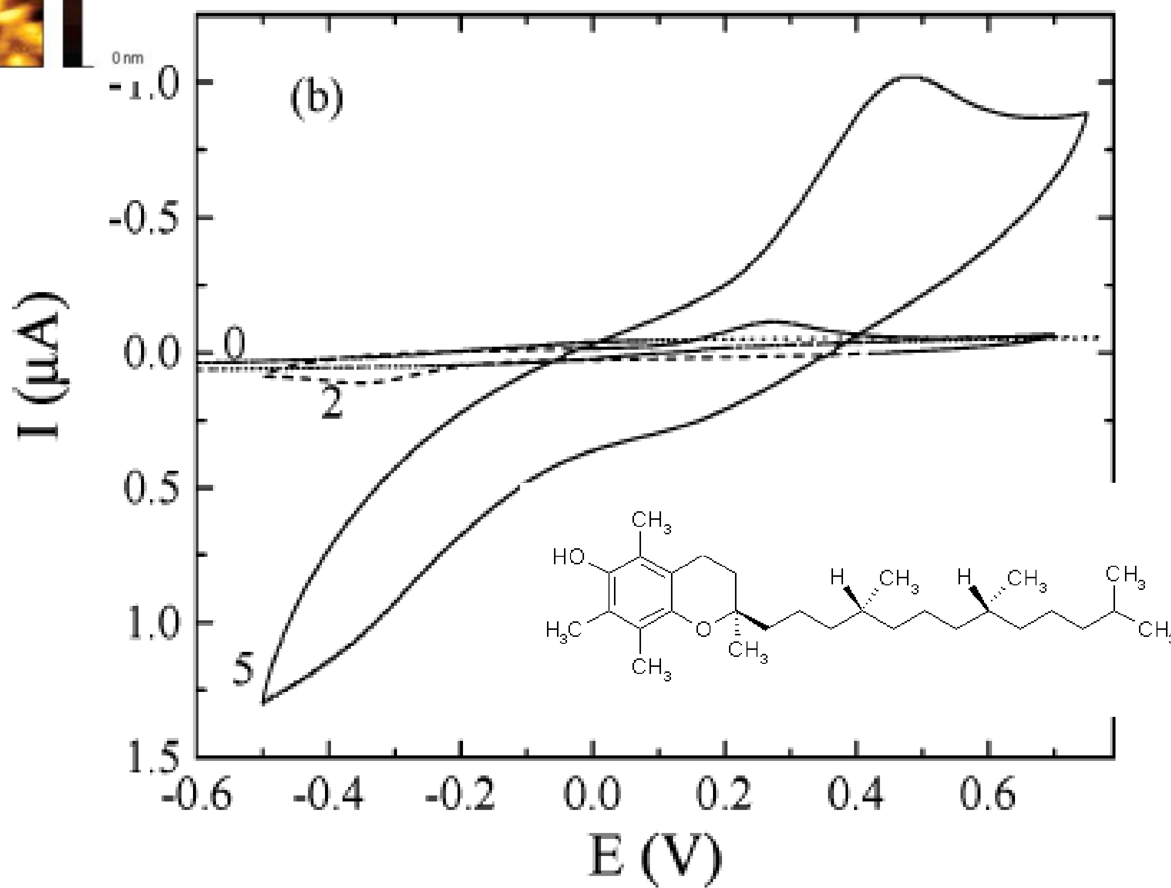
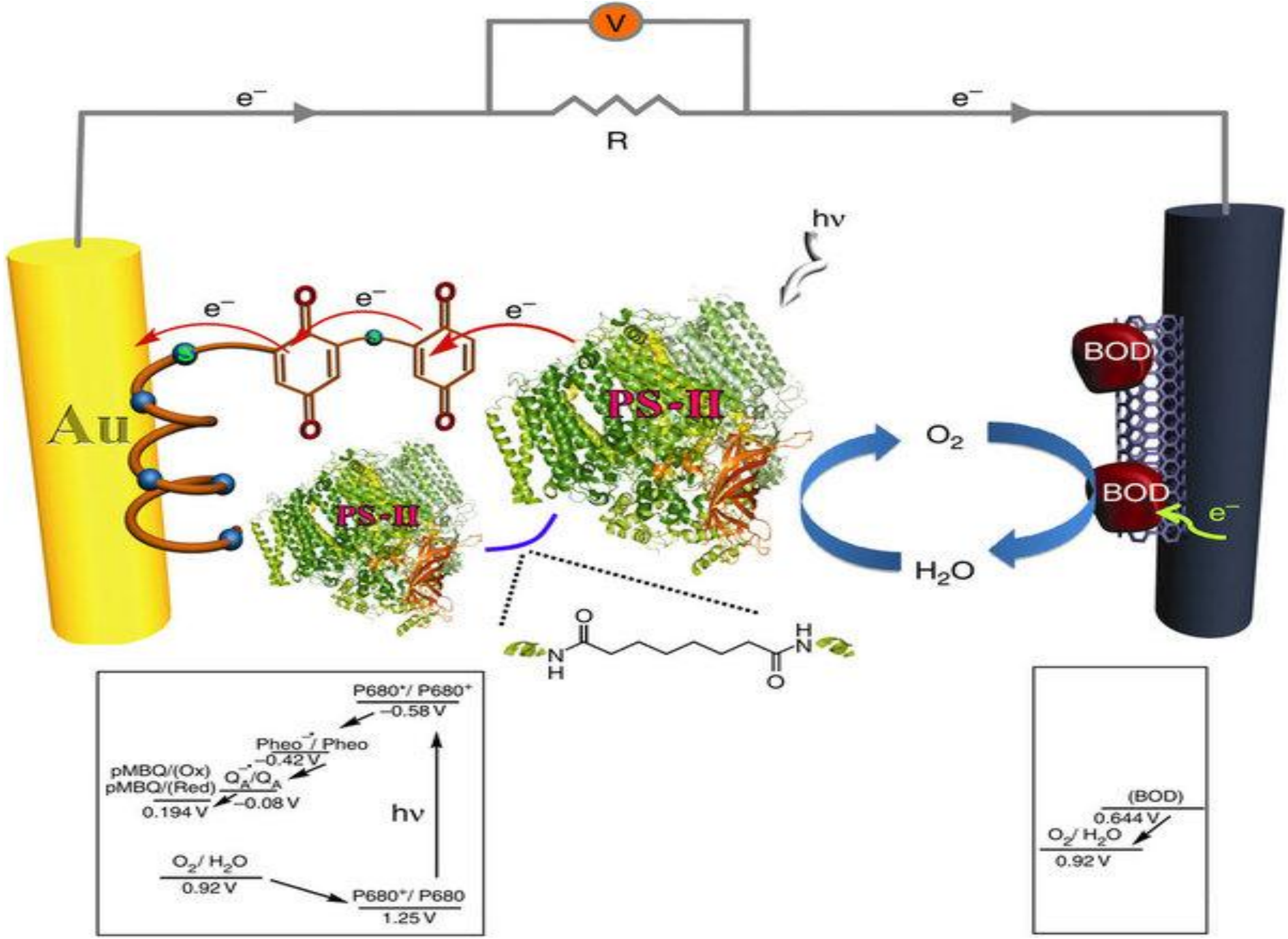
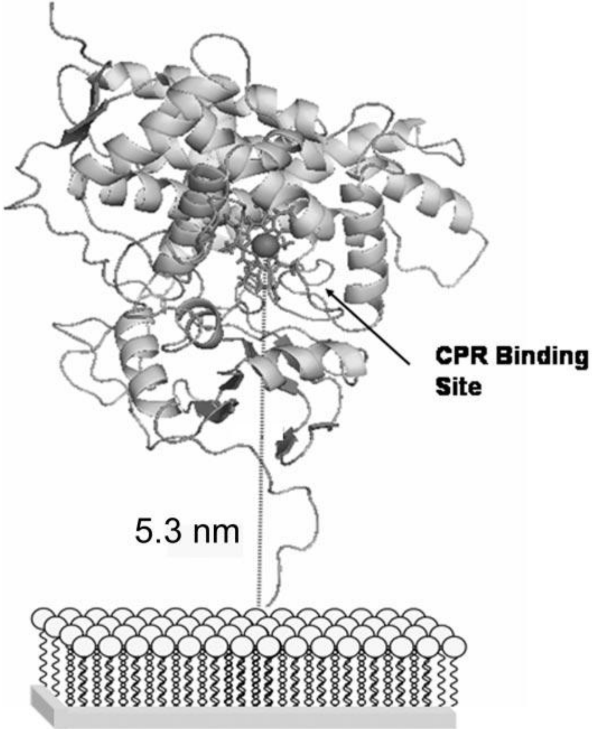


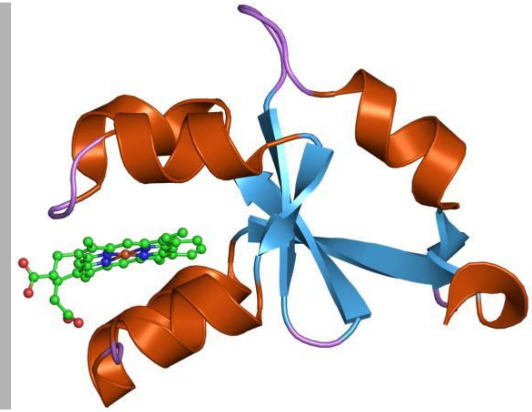
Detection of Proteins at CNT modified electrode

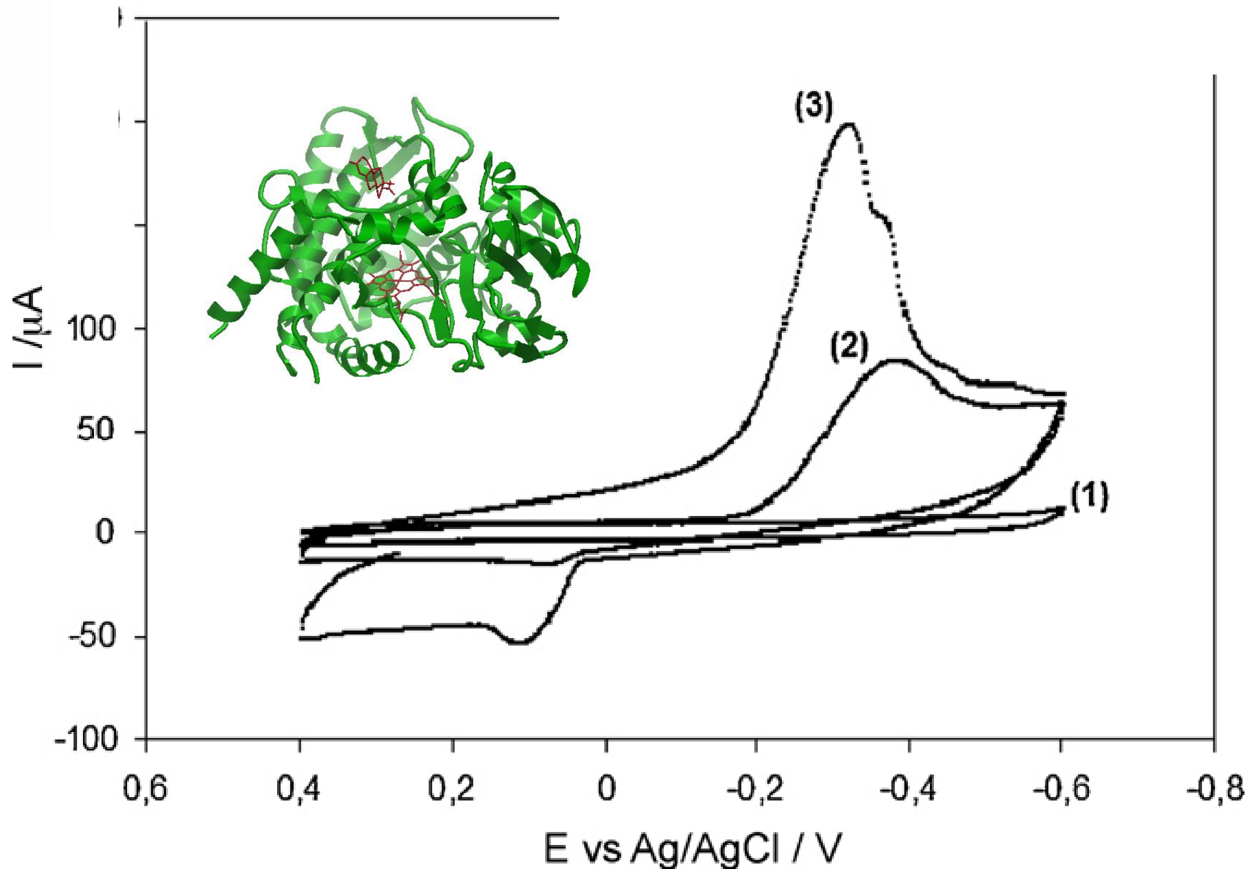


Detection of Photosystem II at CNT modified electrode

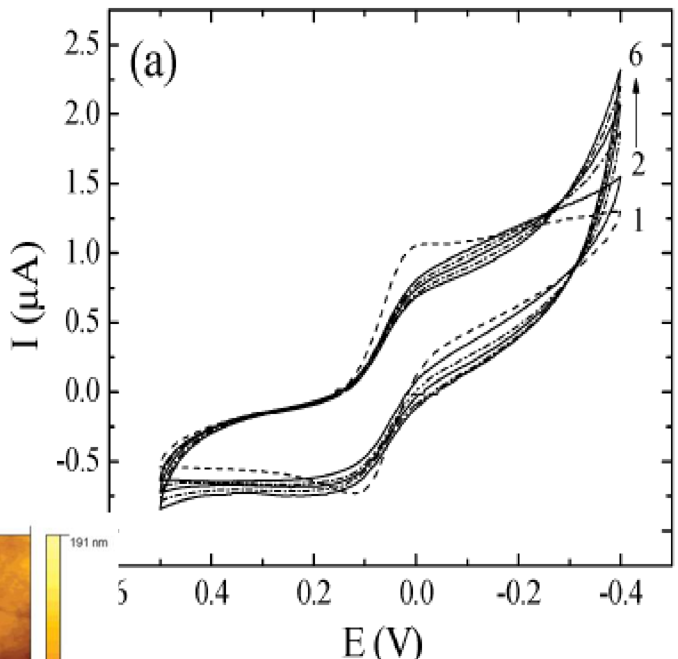
Determination of Cytochrome ***P-450*** at CNT Modified electrode

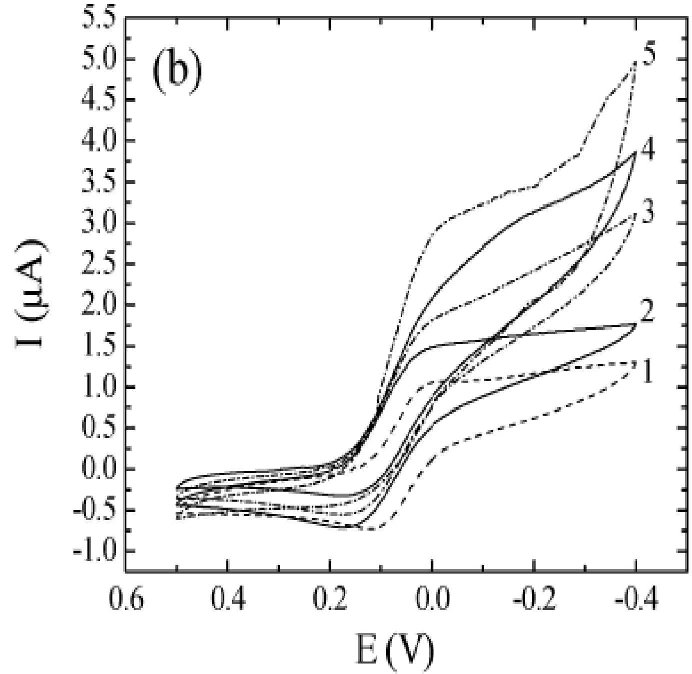


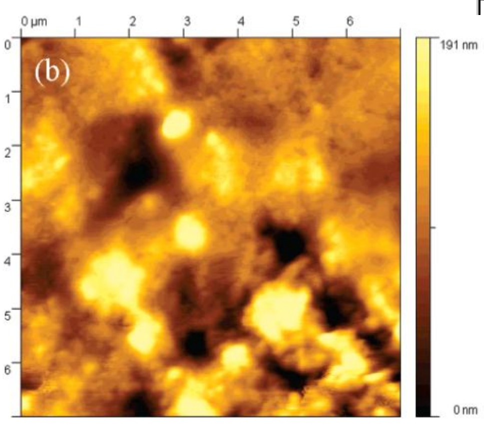




DETECTION OF HYDROGEN PEROXIDE in pH of 7.00
at graphite electrode (a) and at
Au-nanoparticles modified graphite electrode (b)
(hexacyanoferrate is used as redox mediator)







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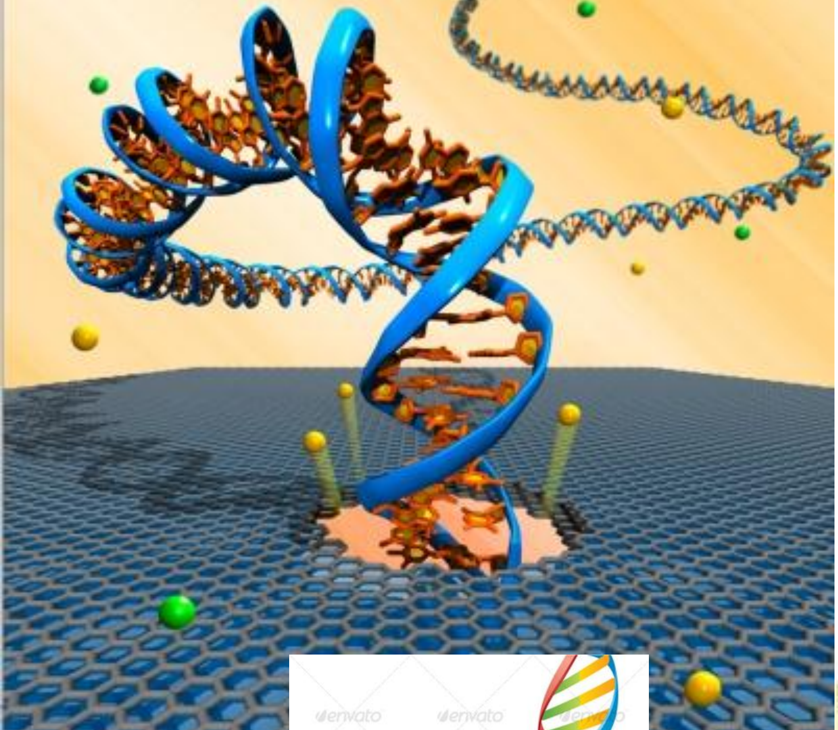
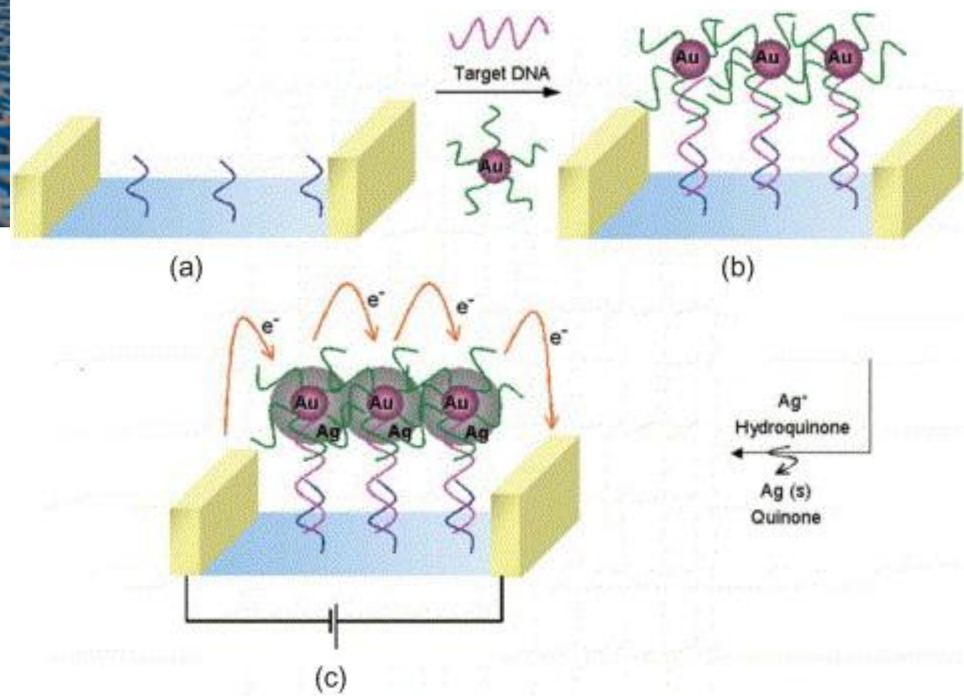



Target DNA
Au
(a)
(b)
e⁻
Ag
Ag⁺
Hydroquinone
Ag (s)
Quinone
(c)

Nanoparticle-based DNA detection

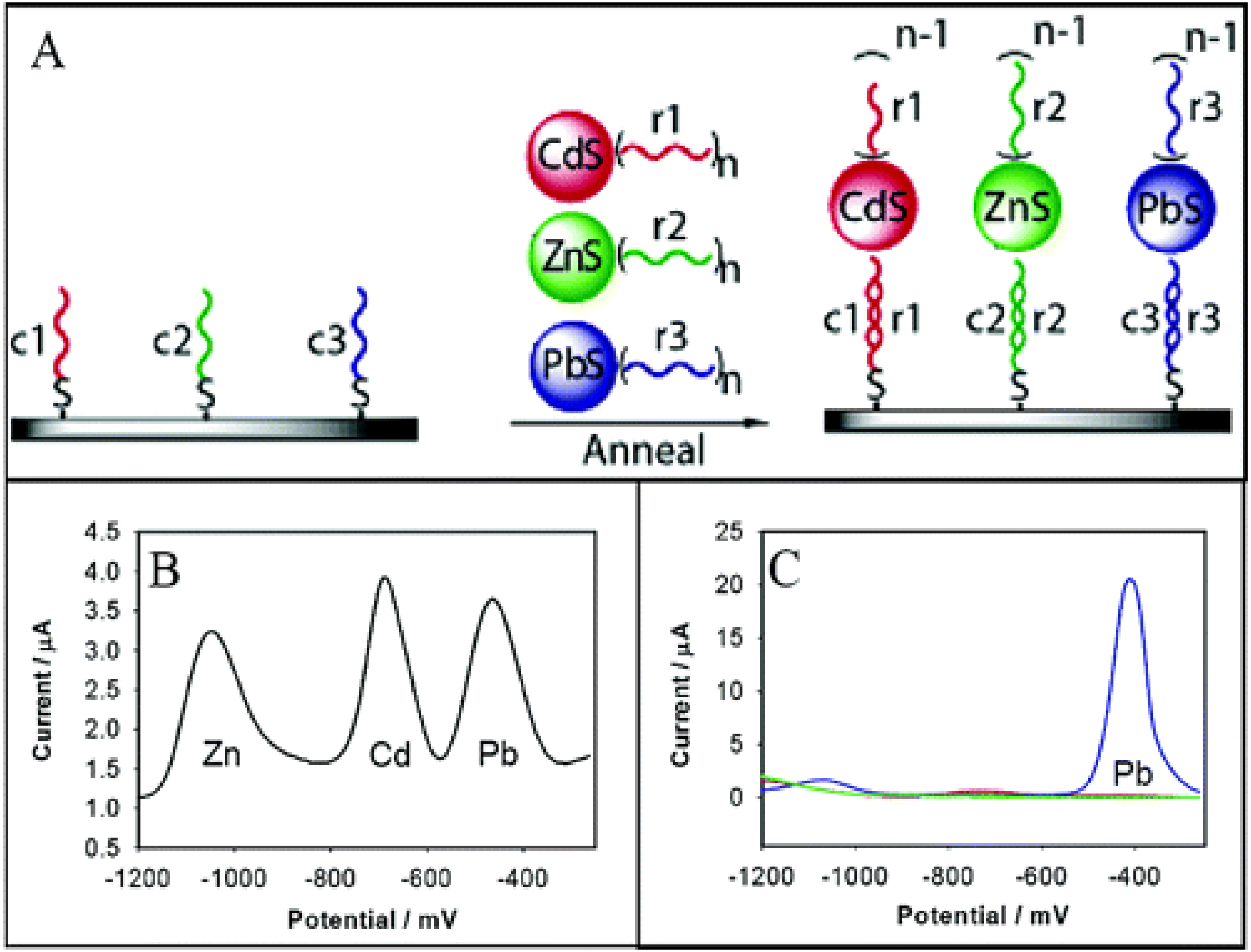
- **Example**: detection of DNA using metal sulfide nanoparticles

- 5’-thiolated capture sequence DNA c1, c2, c3 on the gold substrate

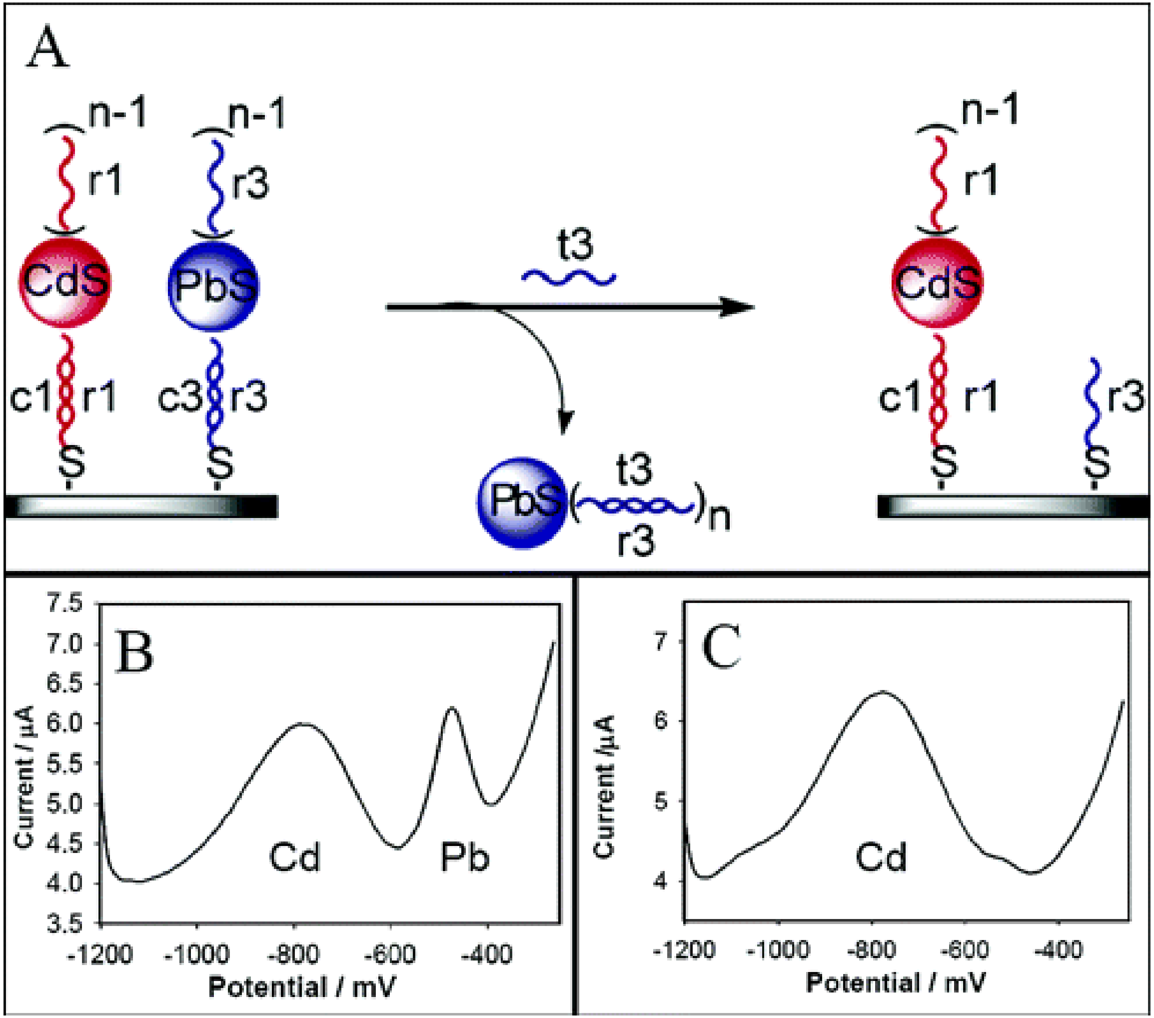
- CdS, ZnS, PbS nanoparticles (3nm, 5nm)

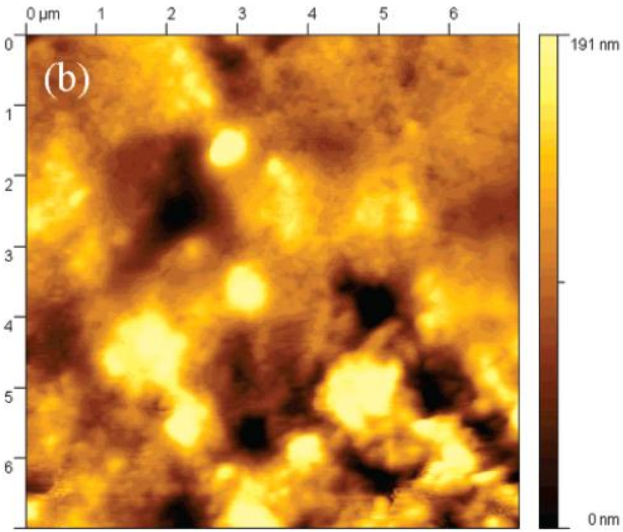
- Conjugated with 5’-thiolated DNA reporter sequences r1, r2, r3

Multi-target Detection



Competitive Binding





DIRECT Detection of DNA at Au-nanoparticles graphite Modified electrode in 1 M HNO_3

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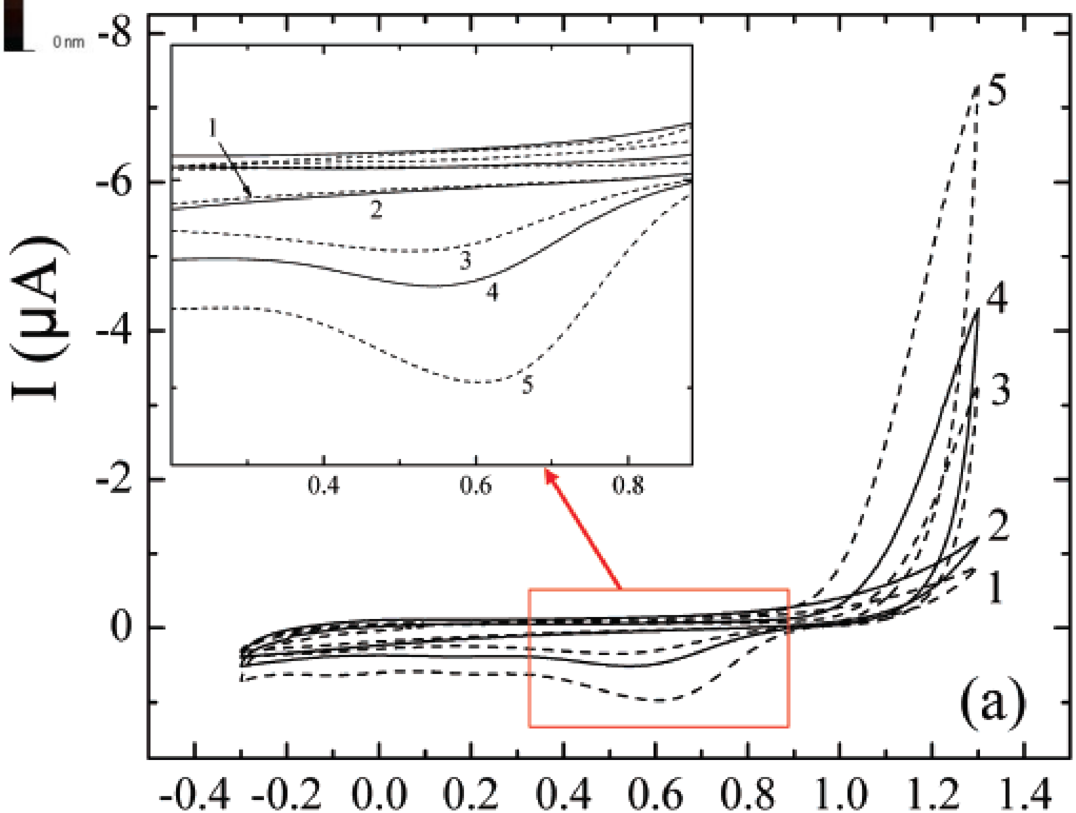

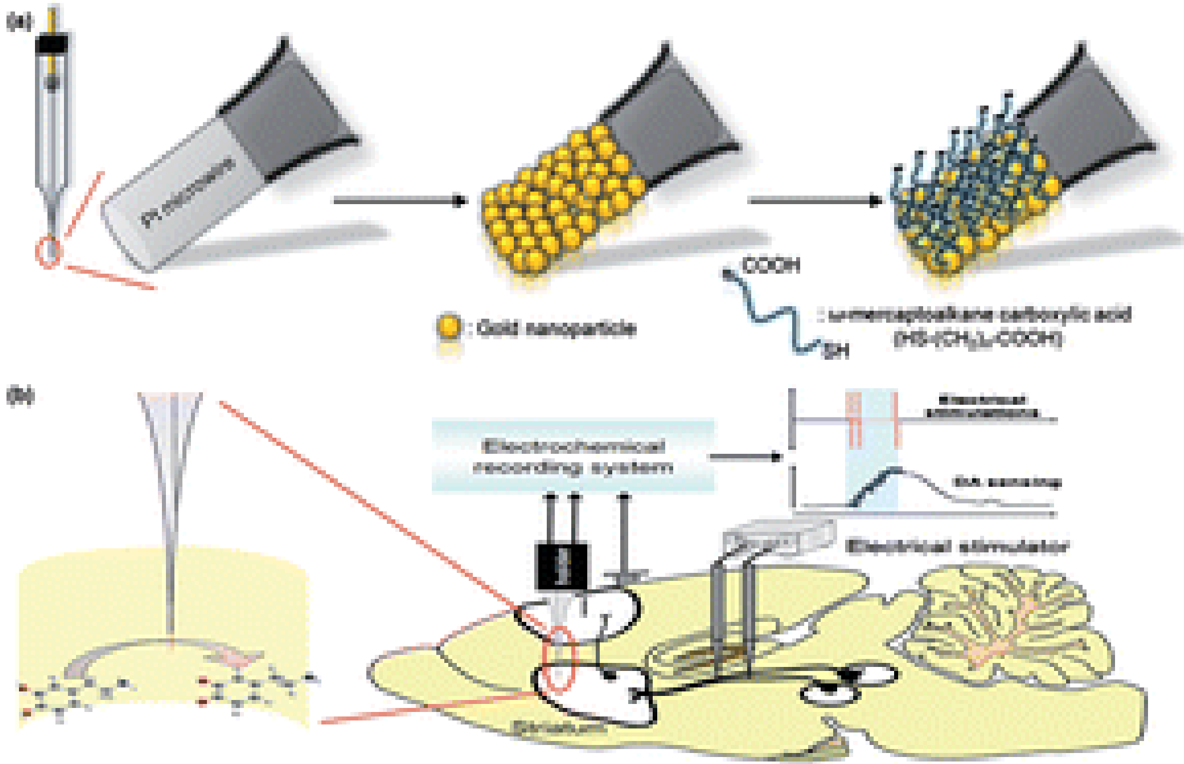

Monitoring Parkinson's disease with implantable Au-nano modified microelectrodes

………… numerous of other nano-applications as sensors

 Chem. Rev. **2008,** *108,* 2688–2720

Nanoelectrochemistry: Metal Nanoparticles, Nanoelectrodes, and Nanopores

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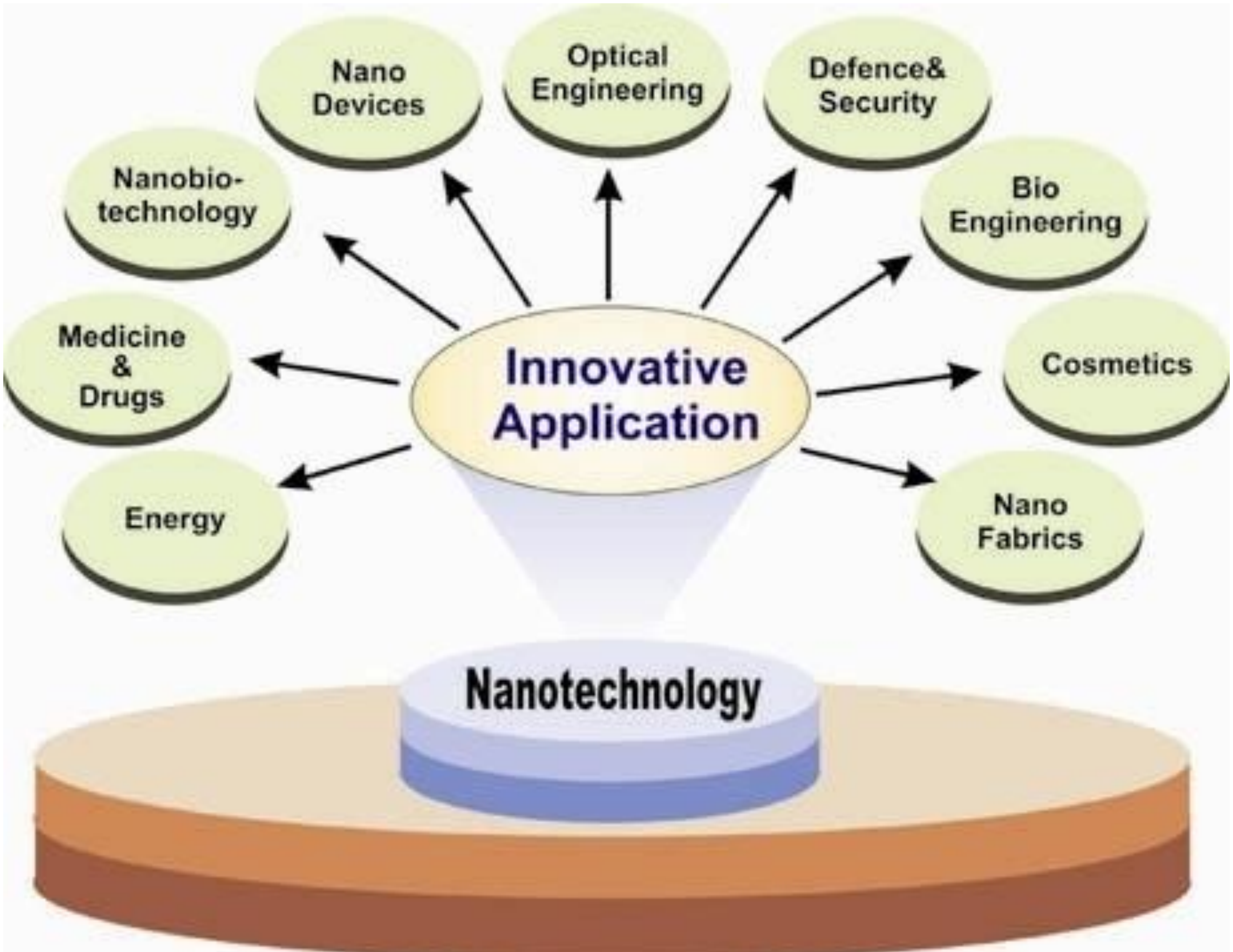
Contents

1. Introduction and Nanoboundaries 2688
2. Electrochemistry of Metal Nanoparticles 2688
3. Voltammetry of Solutions of Isolatable Nanoparticles 2689
   - 3.1. Bulk-Continuum Voltammetry 2691
   - 3.2. Quantized Double Layer Charging Voltammetry 2693
   - 3.3. Voltammetry of Molecule-like Nanoparticles 2696
   - 3.4. Electron Transfer Chemistry of Nanoparticle Solutions 2699
   - 3.5. Voltammetry of Nanoparticles with Molecular Redox Labels 2701
4. Electrochemistry of Films of Nanoparticles 2702
   - 4.1. Electrochemistry of Monolayers of Nanoparticles 2703
   - 4.2. Nanoparticle Films Made by Langmuir Methods 2703
   - 4.3. Electrochemistry of Multilayer Films of Nanoparticles 2704

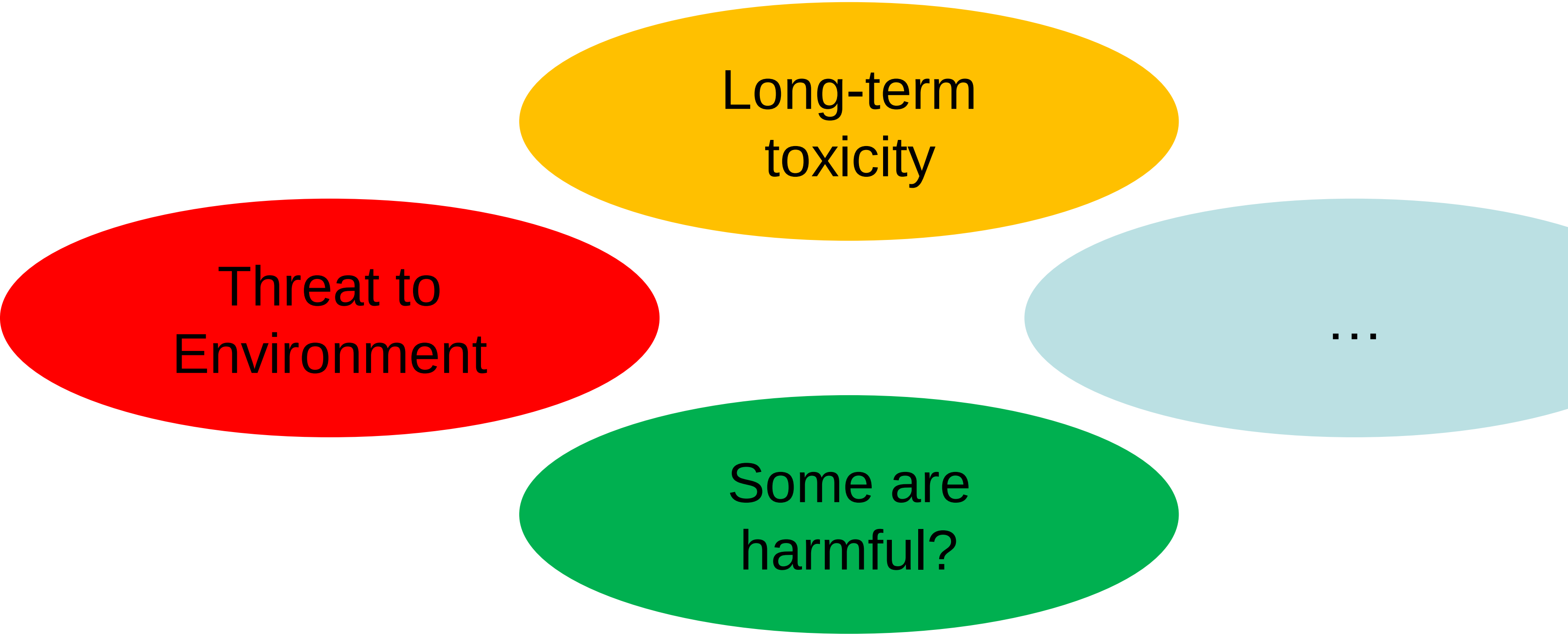
as are nanoparticle applications in bioanalysis, catalysis, and electrocatalysis, and nanomaterials such as fullerenes, carbon nanotubes and networks, semiconductor nanoparticles, and arrays of nanoelectrodes and nanopores. With apologies to those topics, I have chosen to whittle the scenery down to the electrochemistry of nanoparticles, and single nanoelectrodes and nanopores. Within these, attention will be biased toward metal nanoparticles having dimensions of only a small number of nanometers, because it is in the 10 nm and lower size range where many significant recent advances have been made. Similarly, I will focus mainly on single nanoelectrodes and nanopores, as opposed to arrays thereof. The literature cited here is predominantly not over a decade old; a lot has happened, and quickly. I hope the reader will find it an interesting decade.

What has promoted the rapid advances in the 1−10 nm range of dimensions? For nanoparticles, progress has been stimulated by synthetic innovations; for single nanoelectrodes and single nanopores, similarly by advances in methods of fabrication. Further, while making something that is really

Applications of Nanoparticles



Unsolved issues



Safety

- Nanoparticles present possible dangers, both medically and environmentally. Most of these are due to the high surface to volume ratio, which can make the particles very reactive or catalytic They are also able to pass through the cell membranes in organisms, and their interactions with biological systems are relatively unknown.

- A recent study looking at the effects of ZnO nanoparticles on human immune cells has found varying levels of susceptibility to cytotoxicity

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Any Questions ?

That’s it!

1. What kinds of biological objects have sizes similar to nanoparticles?

2. Define what are nanocoloids, nanoparticles and nanoclusters:

3. What is the cause for bigger reactivity of nanoparticles compared to the bulk material?

4. How can nanoparticles be roughly divided?

5. Application of carbon nanotubes:

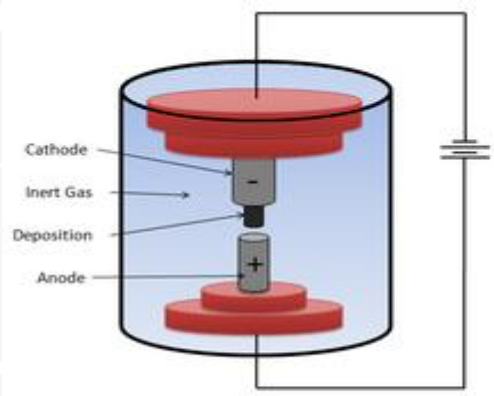
Additional useful slides

Arc discharge –a method to obtaind CNT

first and simplest method to synthesize Carbon Nanotubes.
Two pure graphite electrodes are connected to DC generator in atmosphere of helium.
An inert gas is added to the chamber which does not react with carbon.
Electric current is run thorough electrodes and therefore Carbon is deposited into cathode from anode and CNT are shaped in the middle .
quite perfect about few micro meters long
inner tube is 1-3 nm and outer tube in MWNT 10 nm in diameter.

Drawback

If both of the electrodes are made of graphite (mixture of CNTs along with fullerene, sheets of graphite, amorphous carbon)
more work to separate CNTs from its **undesirable by-products**.
4000 °C which is an extremely high temperature .
Electric arc method good for scientific study but not for industrial use .



- **Magnetic field in arc discharge synthesis**

applying a magnetic field around the arc plasma for alignment purposes
a magnetic field have a high purity and fewer defects
electronic devices as nanowires for device fabrication .

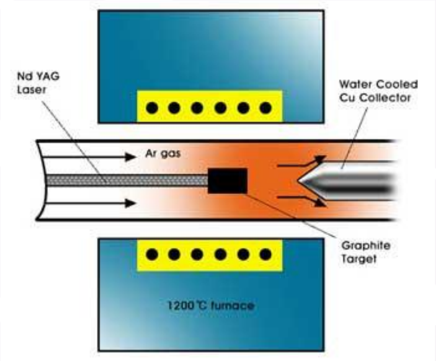
- **Plasma rotating arc discharge**

In this method the arc discharge technique is done by plasma rotating. As a result increased plasma volume more stable and homogenous plasma has been observed.

The rotation speed is 5000 rpm and temperature is found to be 1025°C which is high.
No catalyst is used in this method and after purification yield is increased to 90% .

Laser ablation

laser is used to vaporize carbon from graphite ,a high temperature reactor at 1200 °C
inert gas is helium or argon
The process of laser ablation is like arc discharge method but in a lower temperature.



- Continuous Laser
- Pulsed Laser

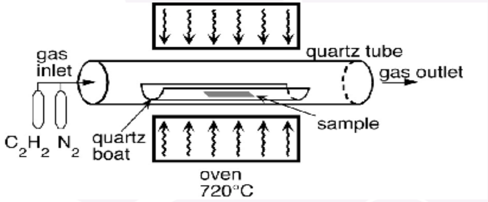
difference is that pulsed laser requires much higher light density.

If we use pure graphite electrodes we can obtain MWNTs ,but to have uniform SWNTs, a mixture of graphite with Co, Ni, Fe or Y

The yield of this process is low and contains carbon Nanotubes along with Carbon Nanoparticles which is not ideal for industrial applications.

have a very high quality 10-15 μm in length.
Research to scale up the yield of this process.

Chemical vapor deposition



The other common method is called Chemical vapor deposition (CVD)

several gases such as methane (CH_4), carbon monoxide (CO) and acetylene (C2H2)
Heated substrate which is coated by catalyst like Ni, Al_2O_3, and SiO_2
Inert gas such as nitrogen and hydrogen.

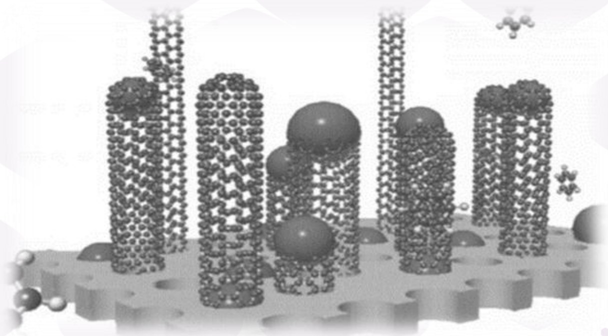
The energy source decomposes the molecule into active carbon atoms which then will be diffused on the substrate and CNTs begin to grow

The temperature 650–1000 ^{o}C which is quite high. The diameter of each nanoparticle defines the diameter of grow .

it is possible to have control over the diameter and length of grown CNT.

CVD process has mostly two main steps which first is preparing substrate by sputtering then to use thermal annealing to have catalyst nanoparticles on the substrate .

- ✓Large scale production and high yield production
- ✓Low cost
- ✓Continuous production instead of batch production
- ✓Control of the quality and CNT
- ✓Ability to manipulate
- ✓No separation of unwanted by-products



CVD process is extremely sensitive to the condition parameters .
Continues reactor and discontinuous reactor.
According to the original work done by Izaskun Bustero an optimal condition for CVD process for best yield

Optimal operating conditions	
Reaction time	10 min
Temperature	1000 °C
Catalyst mass	0.5 g
Ratio H_2/CH_4 in gaseous stream	1

Purification techniques

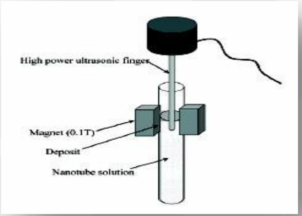
Oxidation
By oxidation we can partially purify CNTs from impurities (time and temperature of exposure of the process are very important) .
While oxidation –COOH or –OH groups are generated which help the attachment of organic or inorganic material to increase solubility.
Best way is to mildly oxidize them with H_2O_2 and H_2SO_4 which only causes oxide defects.

Acid treatment
By acid treatment mostly metal catalysts are removed by the reaction with **Nitric acid or Sulfuric acid** or a mixture of both.

Annealing
In this method a very high temperature is applied (800-1800 °C) in a vacuum atmosphere which caused CNT atoms to rearrange and form a perfect CNT very high temperature ,metal is melted and also can be removed from the reaction

Ultrasonication
Ultrasonic created a low pressure and high pressure waves in the liquid and it improves the reaction and causes reactants to be mixed it forces particles to vibrate and disperse in the liquid evenly.

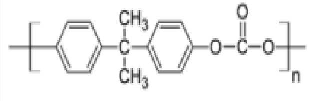
Magnetic Purification

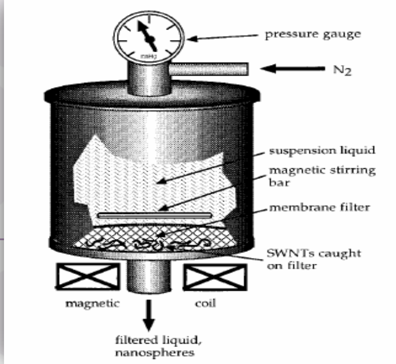


Ultrasonic while ferromagnetic catalyst will be removed from SWNT.
Suspension is mixed with **Zirconium Dioxide (ZrO_2) or *Calcium Carbonate* ($CaCO_3$)** and the bath is trapped among a magnet

Micro filtration
By this method while we have a mixture of materials along with carbon nanotubes by using a membrane.

Purification step
1. Purification process sample was used in **HCl, Acid Nitric HNO_3, and Hydrofluoric Acid HF**
2. Sonication (Ultra Sonication) in HF for 30 minutes and filtrated by **polycarbonate**
3. Immersed in HCl and HNO_3 solution
4. Washed in pure water
5. Put in 600 °C pure air to remove amorphous carbon





They could be added to polyethylene
They can be synthesized in a fiber

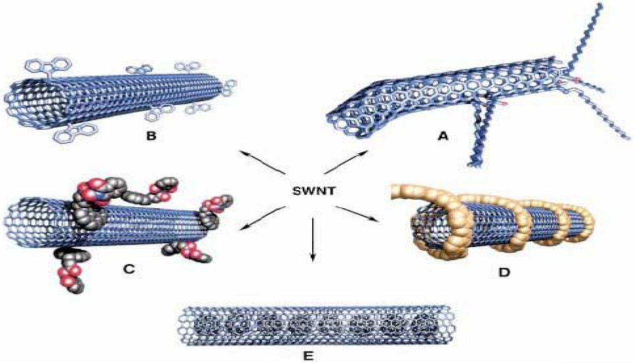
Functionalization of Carbon Nanotubes

B) covalent sidewall functionalization

C) Noncovalent with surfactants

A) Covalent defect-group functionalization

D) Noncovalent exohedral polymers



E) endohedral functionalization

CNTs have **high mechanical strength, thermally and electrically conductive, extremely light** with low mass and **high aspect ratio** (surface to volume ratio).

To use these phenomenal properties homogeneously dispersed in nanocomposites to preserve their characteristics.

As CNTs have a hydrophobic structure and agglomerate because of vandervalse forces ,they do not disperse evenly in the liquid .

Need to align CNTs and prevent them from agglomerating so that they can be even evenly distributed in nanofluids. .

Chemical Functionalization Methods

Endohedral Functionalization

Endohedral Functionalization
Modification of CNT by putting nanoparticles **inside** the tube.

Change the hydrophobic structure to hydrophilic and make them as solvents.
Filling Nanotubes with nanoparticles to add the characteristics of the Nanoparticles inside the Carbon Nanotubes to fantastic phenomenal of CNT.

This method itself is sub categorized to two methods:

1. Putting CNT inside the suspension **containing nanoparticles so that it can penetrate** the tube internal site and stay inside the CNT
   Depends on surface energy(surface tension) of the liquid.
   Experiments show that if surface tension of the liquid is more than 200 mN/m, liquid can fill the Nanotubes

2. Are filled with a material **which reacts with it and then produces nanoparticles which are trapped**

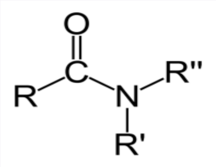
Chemical functionalizations

There are also several chemical functionalizations which we briefly mention in the following :

1. **Amidation – Formation of Carbon Nanotube-Acyl Amides**
2. **Fluorination of Nanotubes**
3. Chlorination of Carbon Nanotubes
4. Bromination of MWCNTs
5. Hydrogenation of Carbon Nanotubes.
6. Addition of Radicals
7. Addition of Nucleophilic Carbenes
8. Sidewall Functionalization through Electrophilic Addition
9. Addition of Nitrenes
10. Nucleophilic Cyclopropanation
11. Azomethine Ylides .
12. Diels-Alder Reaction
13. Sidewall Osmylation of Individual SWCNTs
14. Aryl Diazonium Chemistry –
15. Electrochemical Functionalization
16. Cathodic Coupling
17. Anodic Coupling

Amidation of CNTs

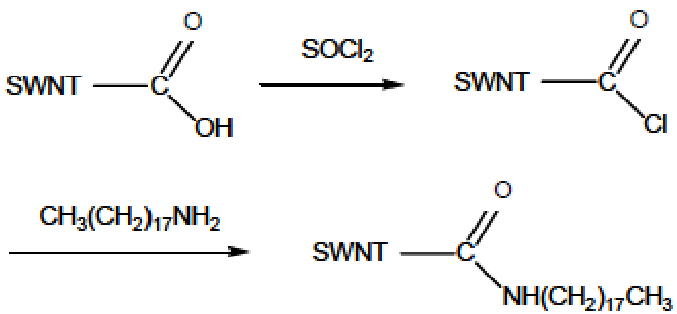
Amid is an organic compound as a functional group that has **(R-C=O)** attached to a nitrogen atom



This kind of functionalization can only be done of the CNTs which are already are **carboxyl-functionalized (-COOH).**

to treat it with Thionyl chloride ($SOCl_2$) to substitute the (-OH)with chlorine and then add octadecylamine as shown in figure 18.

Thionyl chloride to substitute the (-OH)

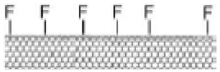


octadecylamine

Fluorination of MWNT

This process can be done on already functionalized CNTs by carboxyl group then they can be functionalized by fluorine .
further functionalization meaning that we can remove the fluorine and attach other functional groups.
This process can be continues by removing fluorine and replacing it with other functional group .

By this process there will be no damage imposed to CNT sidewalls and temperature is low about 150 °C to 500 °C. In this case for maximum fluorination can be achieved using iodine **pentafluoride IF_5**, which leads to composition of C-F bonds .



Experiments show electrical resistance of fluorinated SWCNTs has dramatically increased.

Further functionalization ,substituting fluorine can be done in the group of f-CNT.
Like adding functionalized groups .