Nanoscience and Nanotechnology

Yuehe Lin

What is Nanotechnology

Nanotechnology is the understanding and control of matter at dimensions of roughly ***1 to 100 nanometers***, where unique phenomena enable novel applications.

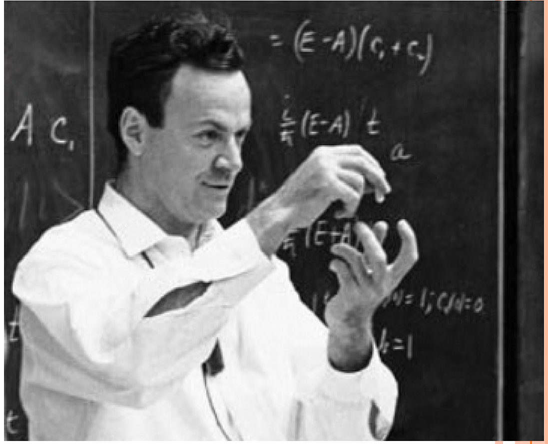
Nanoscience and nanotechnology are the study and application of ***extremely small things*** and can be used across all the other science fields, such as chemistry, biology, physics, materials science, and engineering.

Nanotechnology is distinguished by its interdisciplinary nature.

-National Nanotechnology Initiative

How it started

https://www.youtube.com/watch?v=_1Tq57MLHhc



The ideas and concepts behind nanoscience and nanotechnology started with a talk entitled "There's Plenty of Room at the Bottom" by physicist Richard ***Feynman*** at an American Physical Society meeting at the California Institute of Technology (CalTech) on December 29, 1959, long before the term nanotechnology was used.

In his talk, Feynman described a process in which scientists would be able to manipulate and control individual atoms and molecules.

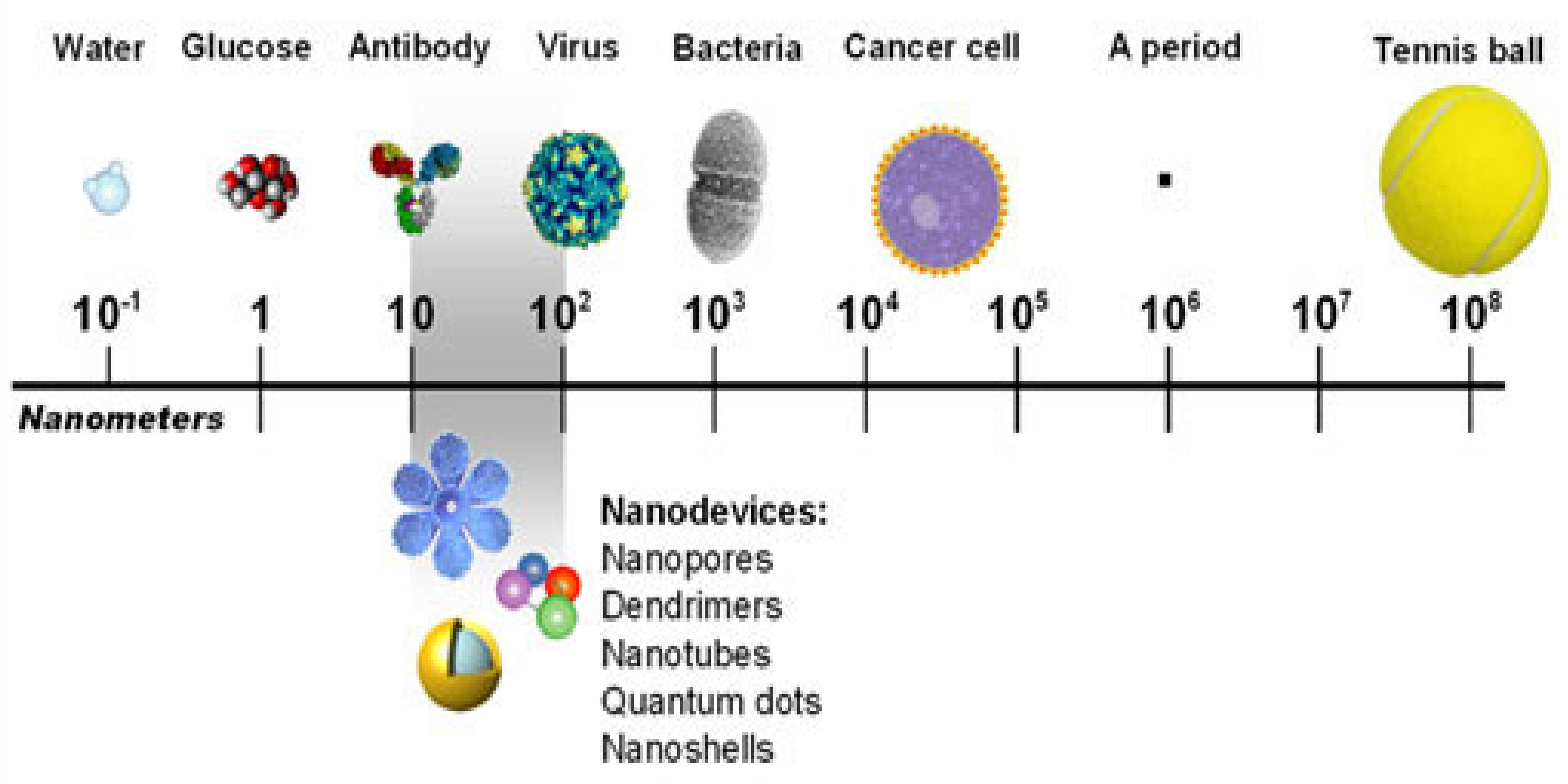
Over a decade later, in his explorations of ultraprecision machining in semiconductor processeses, **Professor Norio Taniguchi** (Tokyo Univ of Science) formulated and used the term nanotechnology. (1974)

VIEW AND MANIPULATE NANOSCALE PARTICLES, ATOMS, AND SMALL MOLECULES.

- Nanoscience and nanotechnology involve the ability to see and to control individual atoms and molecules.
- Everything on Earth is made up of atoms.
- But something as small as an atom is impossible to see with the naked eye. The microscopes needed to see things at the nanoscale were invented relatively recently—about 30 years ago.
- Once scientists had the right tools, such as the scanning tunneling microscope (STM) and the atomic force microscope (AFM), the age of nanotechnology was born.

How small is Nano?

- A nanometer (nm) = 1 billionth of a meter;
- 100,000 x's smaller than the diameter of a human hair.
- A line of 10 H atoms
- A strand of DNA has a diameter of 2.5 nm

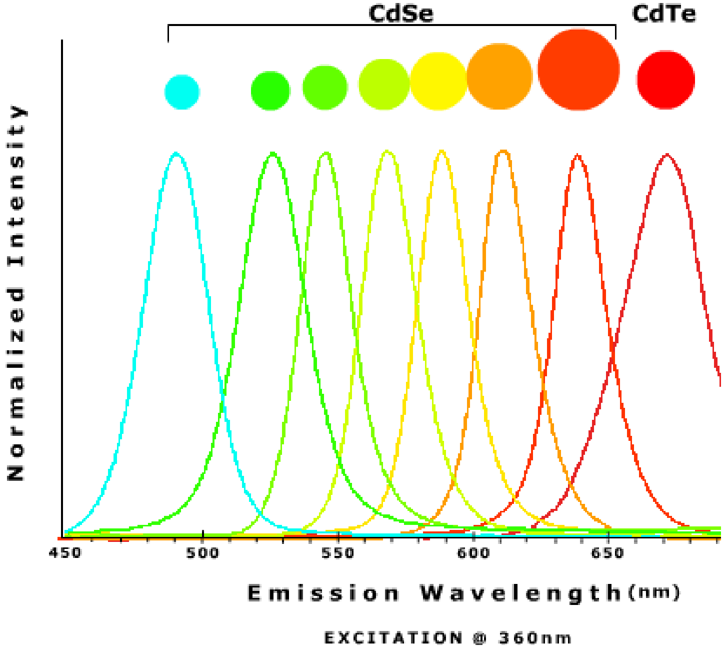


Why Nanotechnology?

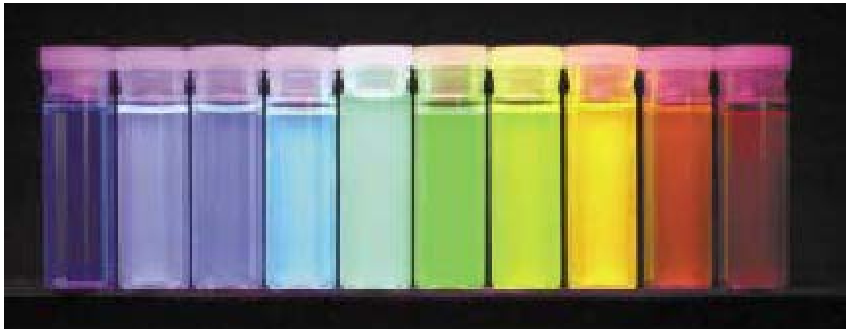
- At the nanoscale, the physical, chemical, and biological ***properties*** of materials ***differ*** from the bulk matter.

- Nanotechnology R&D is directed toward understanding and creating improved materials, devices, and systems that exploit these new properties.

Unique Property at Nanoscale:
I. Optical Properties Of Quantum Dots



a) Multiple colors



- Electronic characteristics of a QD are closely related to its size.
- The band gap in a QD which determines the frequency range of emitted light is inversely related to its size. Smaller size-> larger band gap.
- In fluorescent dye applications the frequency of emitted light increases as the size of the QD decreases.
- Consequently, the color of emitted light shifts from red to blue when the size of the QD is made smaller. This allows the excitation and emission of QDs to be highly tunable.

Unique Property at Nanoscale:
II. Magnetic properties of nanoparticles

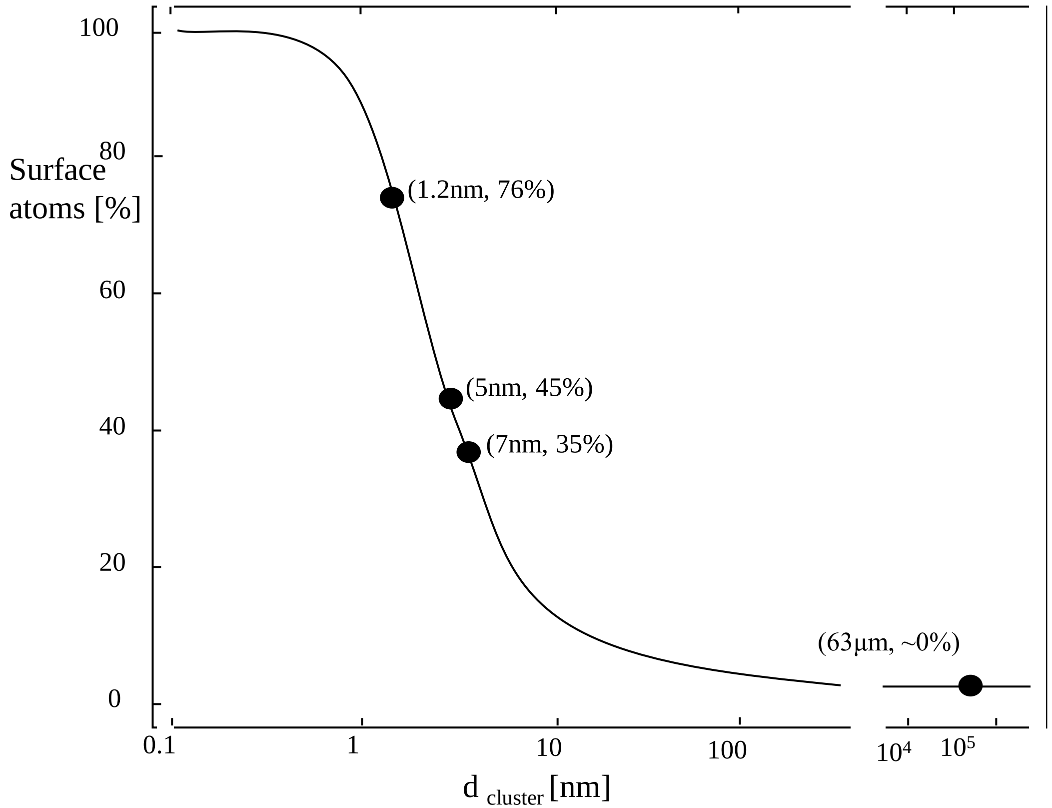
- Nano particles of magnetic and even non magnetic solids exhibit a totally new class of magnetic properties.
- Table gives an account of magnetic behavior of very small particles of various metals.
- Small particles differ from the bulk in that these atoms will have lower co-ordination number.
- The small particles are more magnetic than the bulk material

Metal	Bulk	Cluster (nm)
Na, K	Paramagnetic	Ferromagnetic
Fe, Co, Ni	Ferro magnetic	Super paramagnetic
Gd, Tb	Ferromagnetic	Super paramagnetic
Rh	Paramagnetic	Ferromagnetic

Magnetism in bulk and in nano particles

Unique Property at Nanoscale:
III. Catalytic activity of nanoparticles

- Surface atoms are more active for catalysis
- Pt Nanoparticles have higher catalytic activity for fuel cells
- Au particles are not good catalyst at micro-scale; but show high catalytic activity at nanoscale



SURFACE TO VOLUME RATIO

MANUFACTURING AT NANOSCALE--NANOMANUFACTURING

- Nanomanufacturing involves scaled-up, reliable, and cost-effective manufacturing of nanoscale materials, structures, devices, and systems.

- **Top-down:** lithography

  - **Top-down** fabrication reduces large pieces of materials all the way down to the nanoscale, like someone carving a model airplane out of a block of wood.

  - This approach requires larger amounts of materials and can lead to waste if excess material is discarded.

- The **bottom-up**: self-assembly, spontaneous growth

  - This approach creates products by building them up from atomic- and molecular-scale components, which can be time-consuming.

  -- Scientists are exploring the concept of placing certain molecular-scale components together that will spontaneously "self-assemble," from the bottom up into ordered structures.

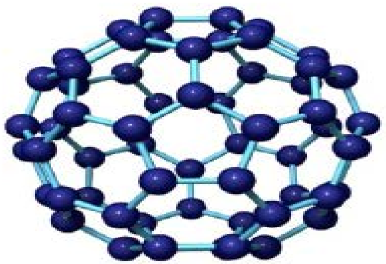
Nanostructures or nanomaterials

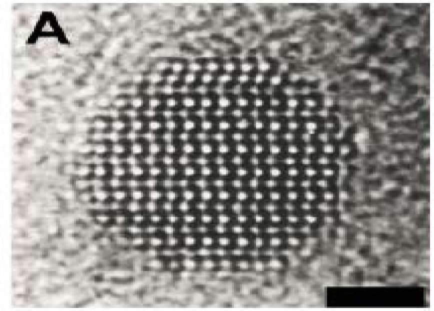
- **Nanoparticles (0 D)**
  - **Quantum dots; Au nanoparticles**
- **Nanorods, nanowires, nanofibers, and nanotubes (1 D)**
- **Thin-film, thin-layer (2 D)**

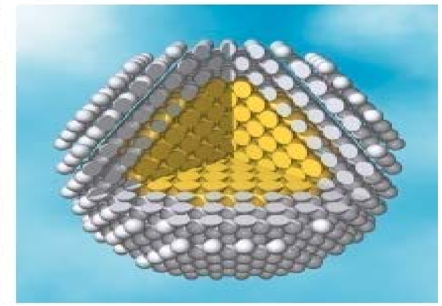
  Graphene
- **Bulk nanomaterials (3 D)**
  - **Mesoporous materials**
    - **Also aerogels, zeolites**
  - **Organic-inorganic hybrids**
  - **Nanograined bulk materials and nanocomposites**

Basic building blocks of nanoscale materials

0-D







Nanoclusters

Magic #'s of atoms

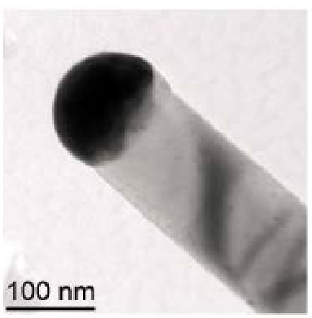
≤1 nm size

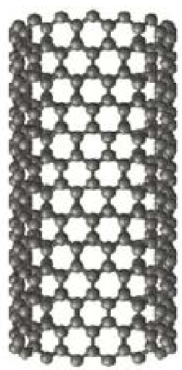
Nanoparticles

100's-1000's of atoms

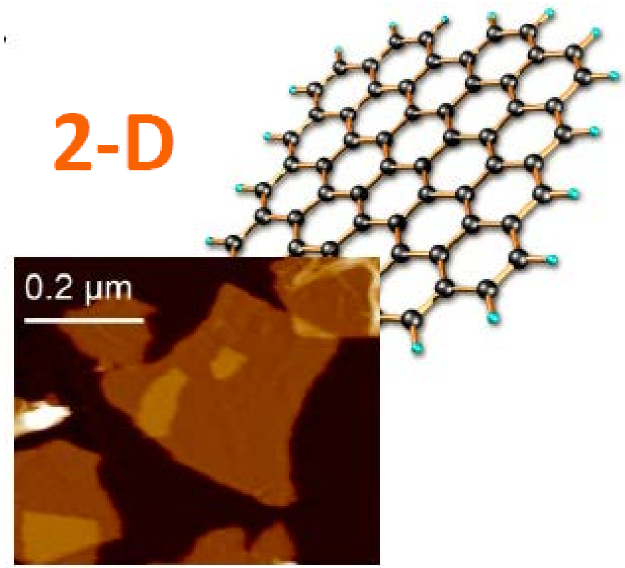
~1-100 nm diameter

1-D





2-D



Nanowires

Filled

Nanotubes

Hollow

~1-100 nm dia, up to mm long and beyond!

Nanosheets

~1 atom thick

Fullerene: 0-D Nanocarbon

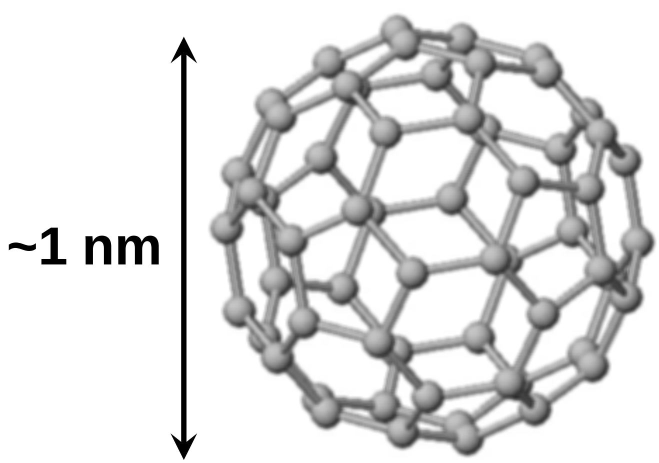
"The most symmetrical large molecule"

- Discovered in 1985

  - Nobel prize Chemistry 1996, Curl, Kroto, and Smalley

- **C_{60}, also 70, 76 and 84.**

  - 32 facets (12 pentagons and 20 hexagons)

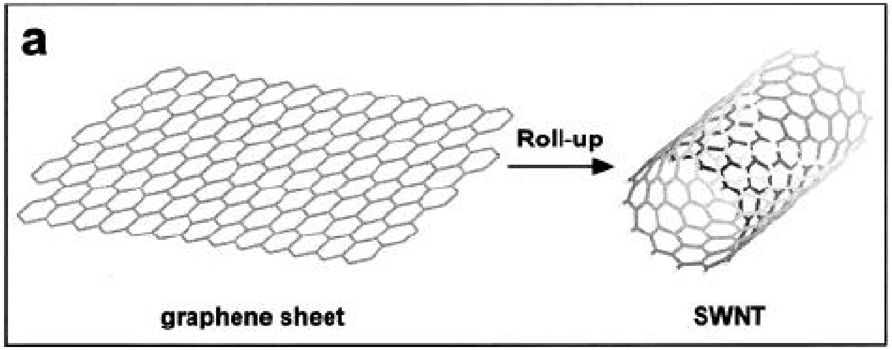


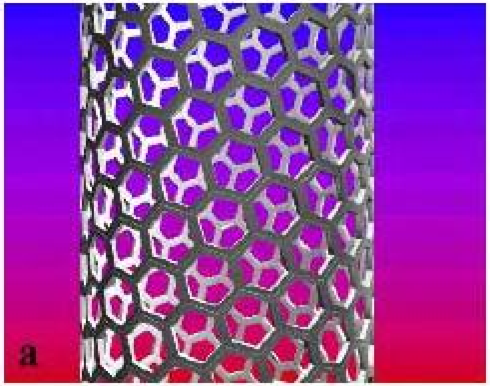
Epcot center, Paris

Architect: R. Buckminster Fuller

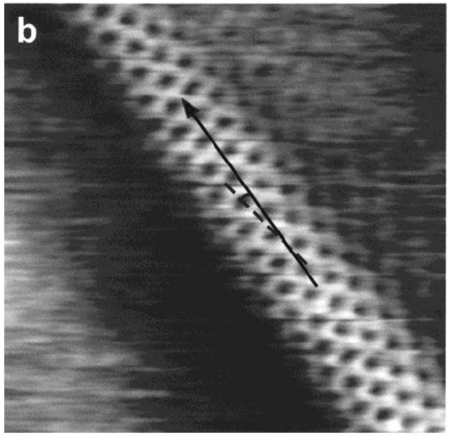
Carbon nanotube: 1-D Nanocarbon

CNT: Rolling-up a graphene sheet to form a tube





Schematic of a CNT



STM image of CNT

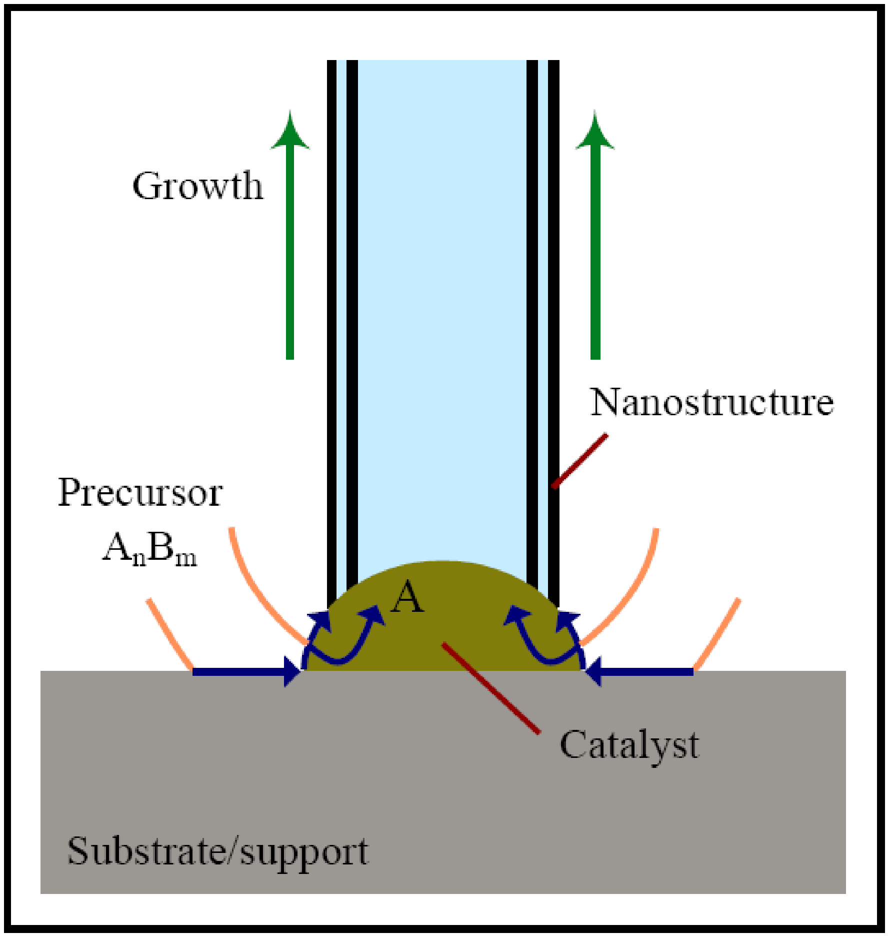
Carbon nanotube properties: *Mechanical*

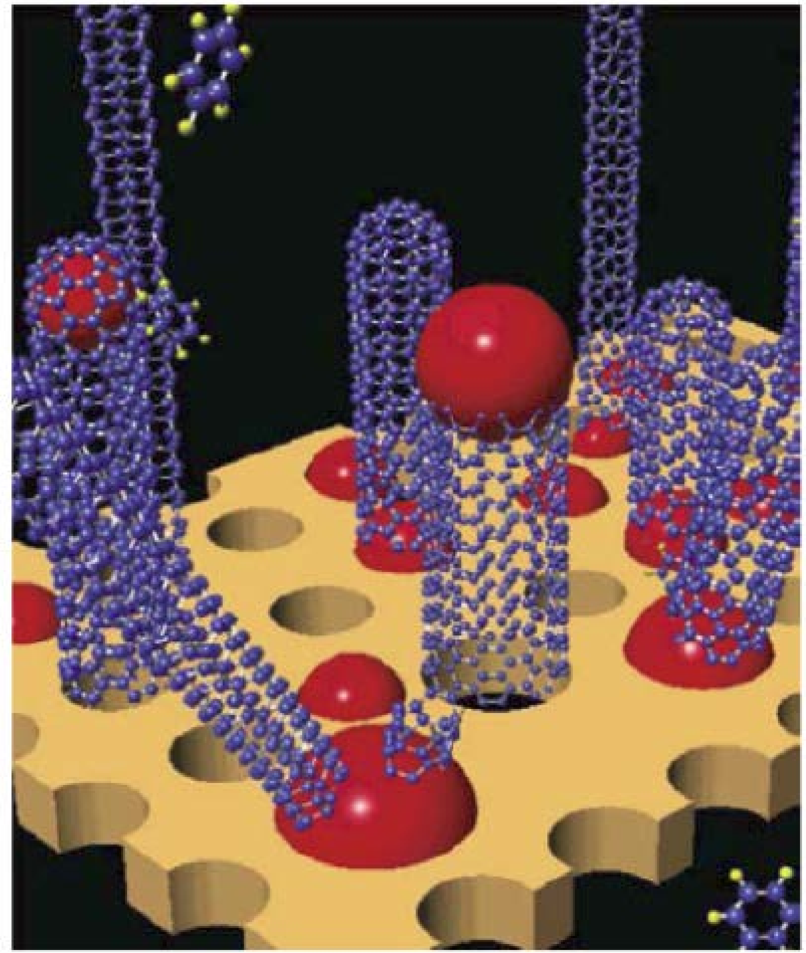
- Carbon-carbon bonds are one of the strongest bond in nature
- Carbon nanotube is composed of perfect arrangement of these bonds
- Extremely high Young's modulus

Material	Young's modulus (GPa)
Steel	190-210
SWNT	1,000+
Diamond	1,050-1,200

Synthesis of Carbon Nanotube: Catalytic Chemical Deposition

Base vs. tip growth (CNTs)





https://www.youtube.com/watch?v=B099DRAX_X4

Hayashi et al., *Nano Letters* 3(7):888, 2003.

Applications

- ➢ Electrical

1. Field emission in vacuum electronics

- ➢ Energy

1. Lithium ion batteries
2. Fuel cells

- ➢ Biological

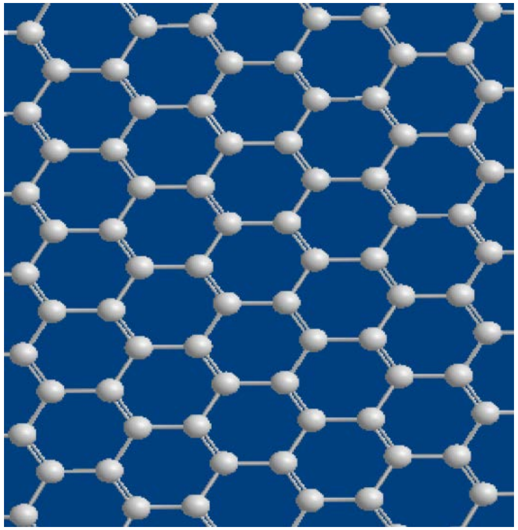
1. Bio-sensors
2. Functional AFM tips
3. Drug delivery

Graphene: 2-D Nanocarbon

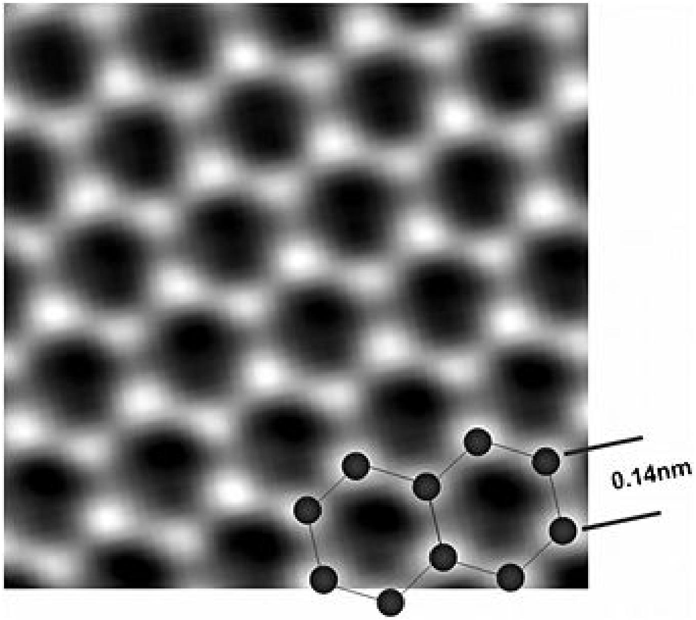
In late 2004, graphene was discovered by Andre Geim and Kostya Novoselov (Univ. of Manchester).
- 2010 Nobel Prize in Physics

Graphene is a one-atom-thick planar sheet of sp^2-bonded carbon atoms that are densely packed in a honeycomb crystal lattice

The name 'graphene' comes from graphite + -ene = graphene

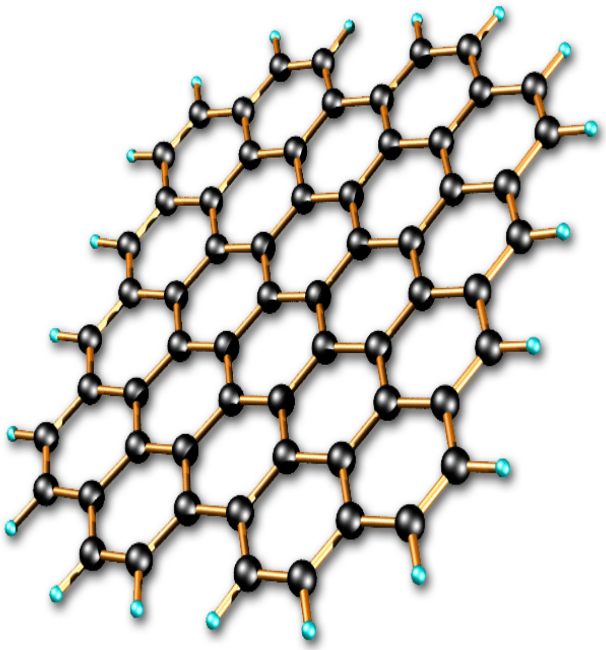


Molecular structure of graphene



High resolution transmission electron microscope images (TEM) of graphene

Properties of Graphene



Q1. How thick is it?
→ a million times thinner than paper
(The interlayer spacing : 0.33~0.36 nm)

Q2. How strong is it?
→ stronger than diamond
(Maximum Young's modulus : ~1.3 TPa)

Q3. How conductive is it?
→ better than copper
(The resistivity : 10^{-6} Ω·cm)
(Mobility: 200,000 $cm^2 V^{-1} s^{-1}$)

Q4. Optical Property?
-> Monolayer graphene absorbs 2.3% of white light (97.7 % transmittance).

Preparation of Graphene
1. Mechanical process
(Scotch-tape method)

- https://www.youtube.com/watch?v=a60xAjM4spo

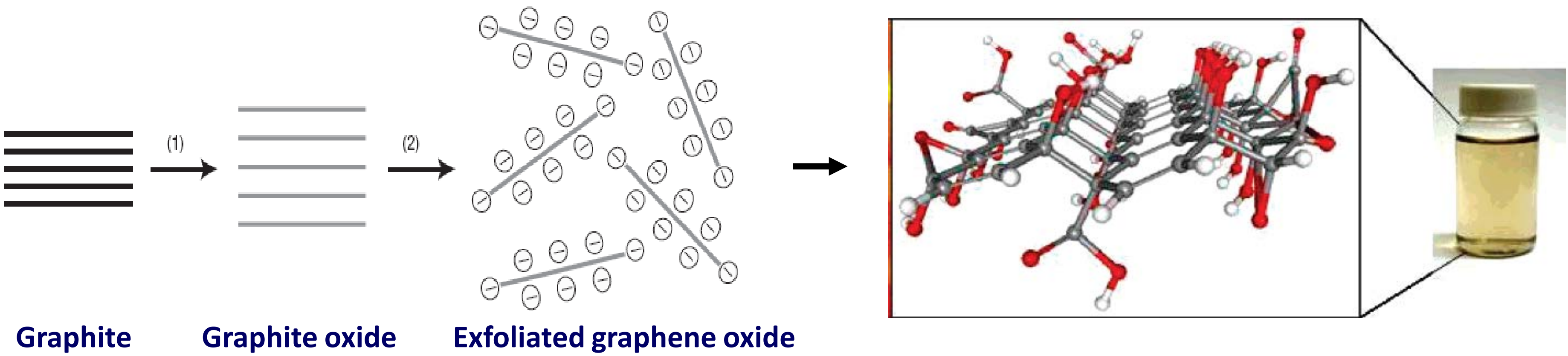
In 2004: Andre Geim and Kostya Novoselov at Manchester University managed to extract single-atom-thick crystallites (graphene) from bulk graphite:

Pulled out graphene layers from graphite and transferred them onto thin silicon dioxide on a silicon wafer in a process sometimes called micromechanical cleavage or, simply, the Scotch tape technique.

Novoselov, K. S.; Geim, A. K.; Morozov, S. V.; Jiang, D.; Zhang, Y.; Dubonos, S. V.; Grigorieva, I. V.; Firsov, A. A. *Science* 2004, 306, 666.

Graphene Preparation: 2. Chemical Method

Graphene Oxide Production with Hummers Method



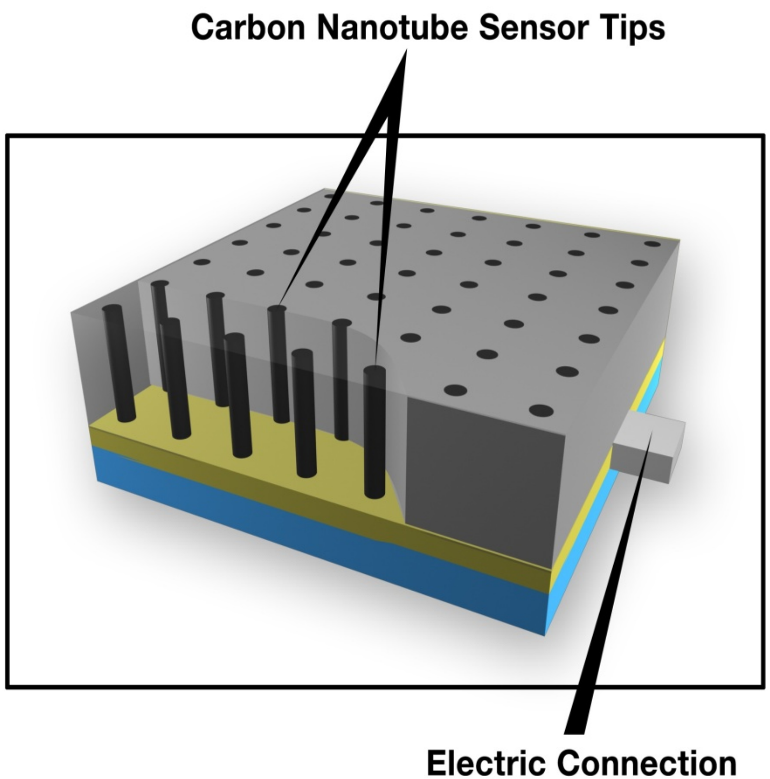
1. Pre-oxidation with H_2SO_4, $K_2S_2O_8$, and P_2O_5
2. Secondary Oxidation with H2SO4 + $KMnO_4$
3. Sonication for splitting
4. Using chemical reduction to convert Graphene oxide to graphene

Graphene Applications

- OLED Techonologies
- Body Armour
- Lightweight Aircraft/vehicles
- Photovoltaics
- Superconductor/battery
- Filtration
- http://www.graphenea.com/pages/graphene-uses-applications#.U1c1hFVdV8E

Biomedical Applications of Nanotechnology

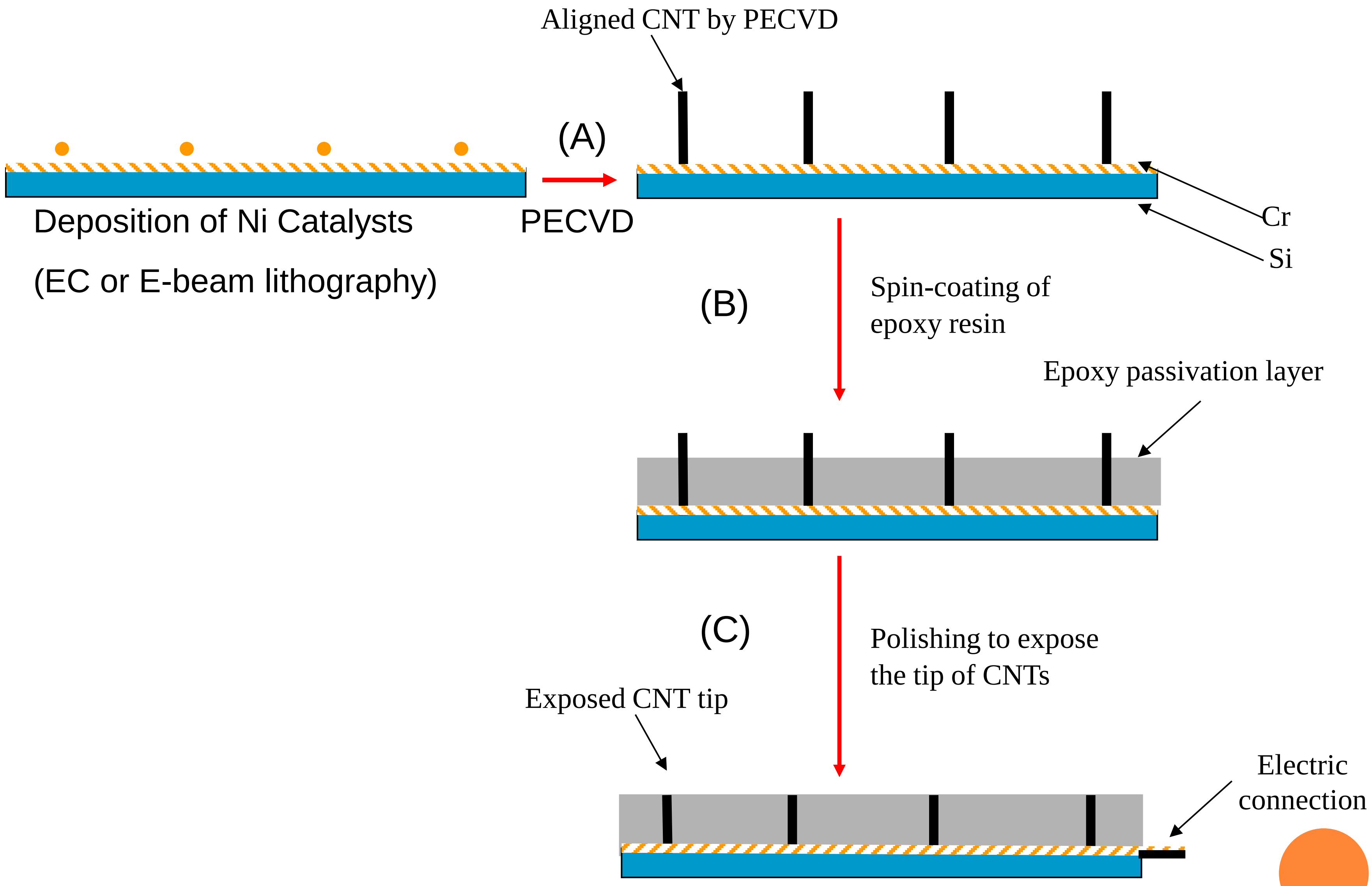
Nanotechnology Applications: Biosensors Based On Carbon Nanotube Arrays



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

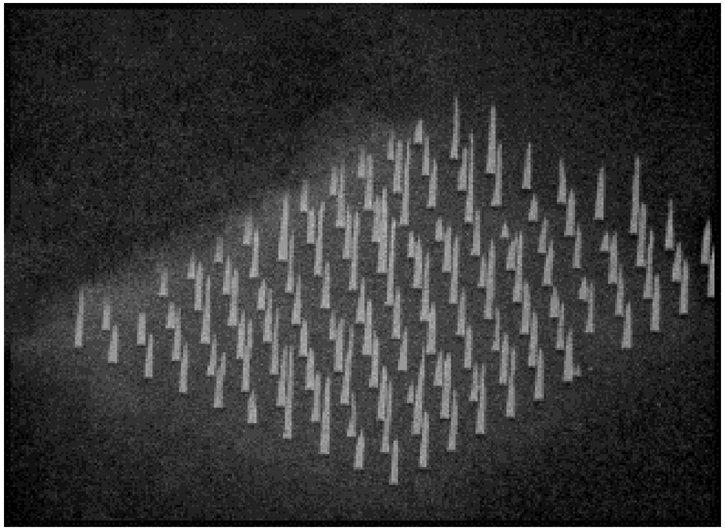
Lin, Lu, Ru, Ren, Nano Lett. 4, 191-195, 2004

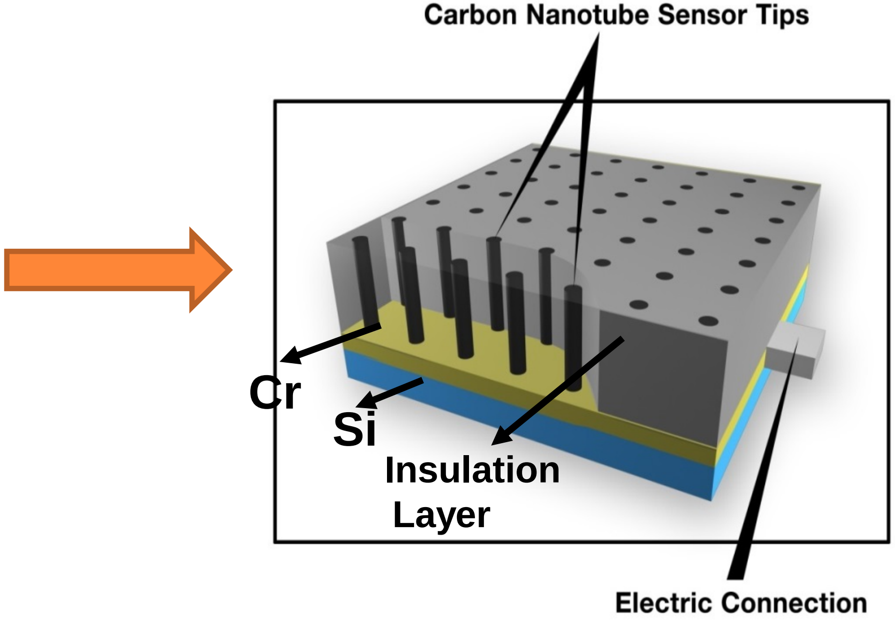
Fabrication of CNT Nanoelectrode Array



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

Control Density of Carbon Nanotubes by Controlling Density of Catalyst Nanoparticles





Electron beam lithography Ni dots

• **Precisely control the density of Ni dots with regular arrays**

Unique properties of CNT-Tip nanoeletrode array:

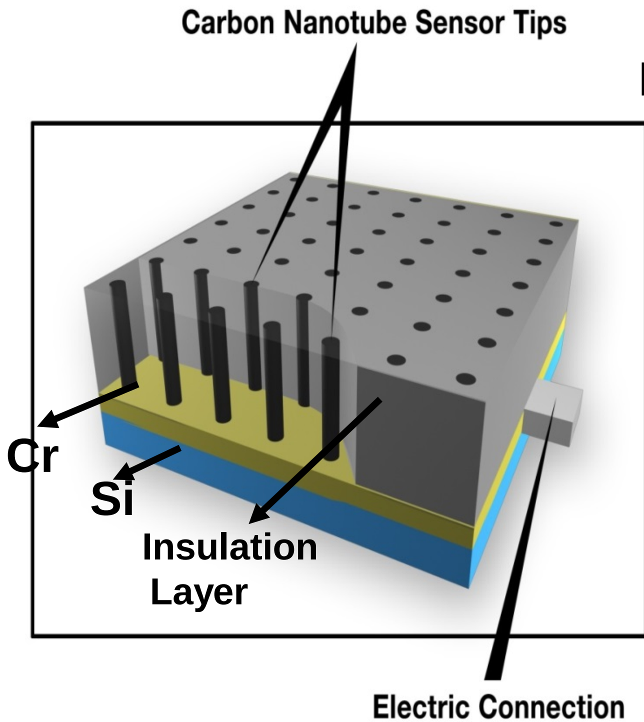
- **High S/N ratio**

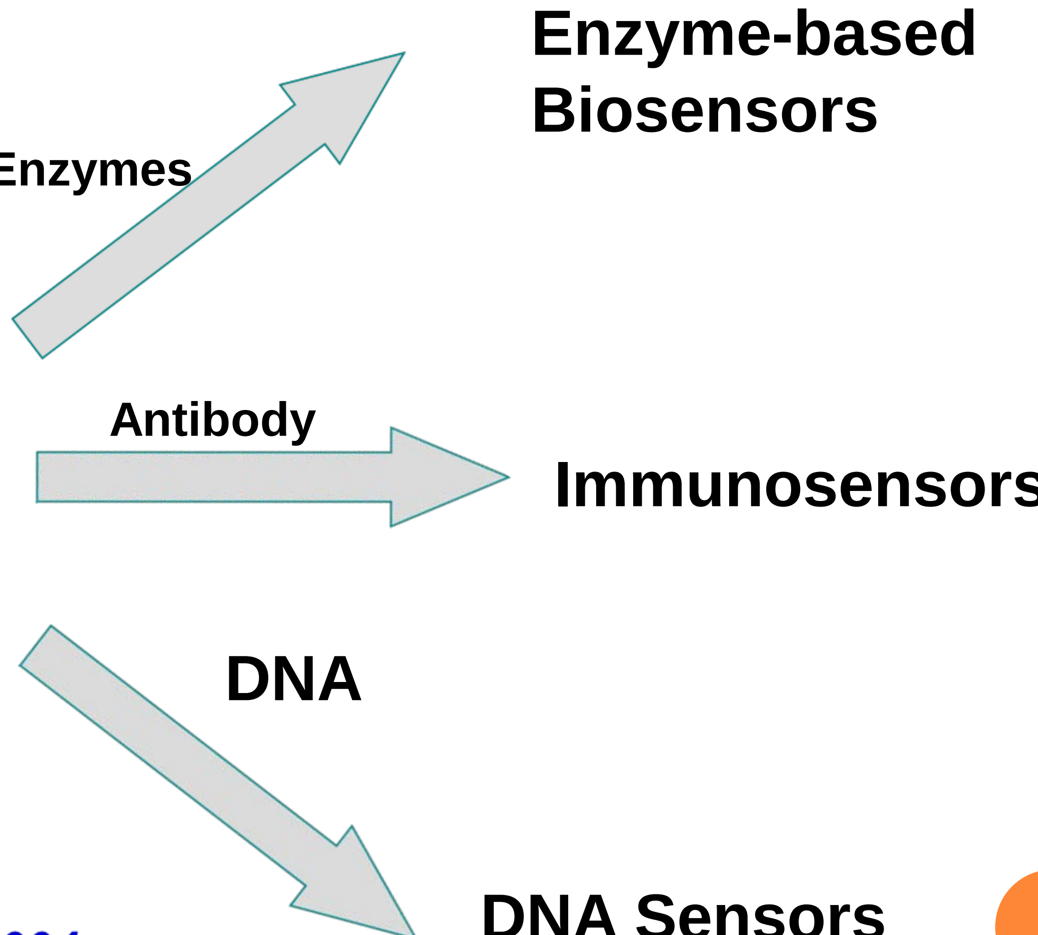
  Only sensitive part, CNT-tip is exposed to solution for sensing, side-wall are insulted to reduce capacitance background current

- **High sensitivity**

  1-2 millions vs. single CNT

Nanotechnology Applications: Biosensors Based On Carbon Nanotube Arrays





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

US Patent issued 2008

Nanoprobes for Imaging

Quantum Dots

Gold Nanoparticles

functionalized to achieve biocompatibility and cell targeting

Carbon materials

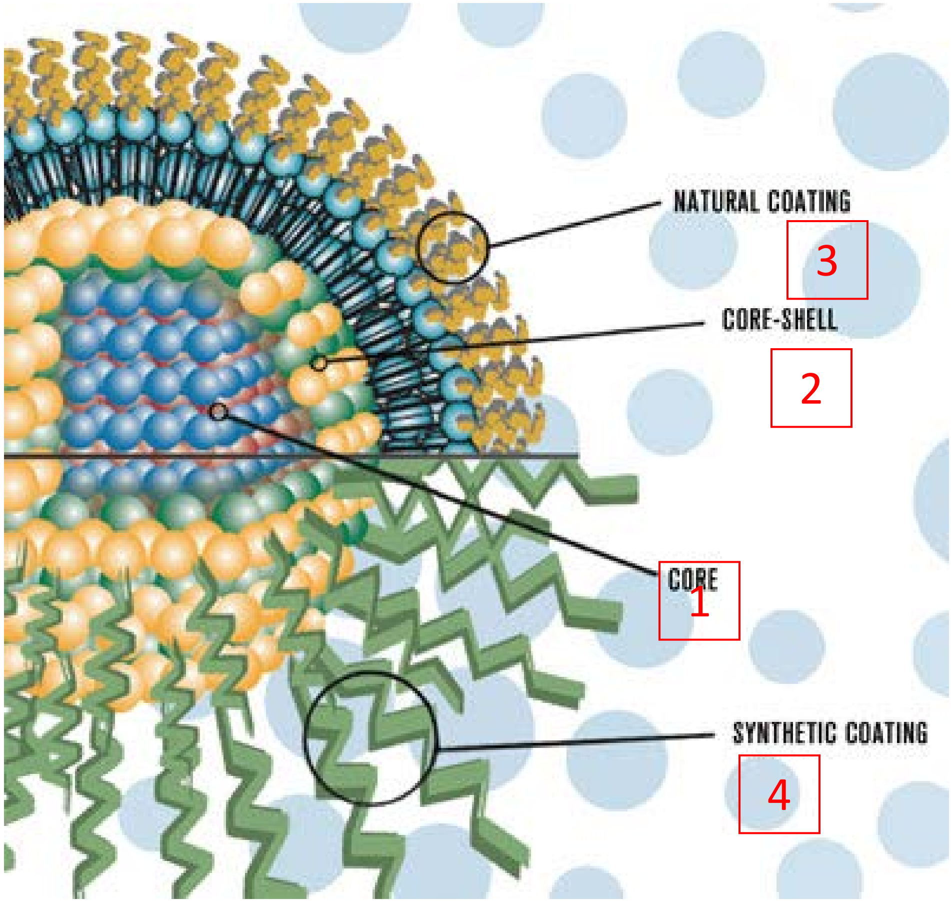
Magnetic nanoparticles

Liposomes

Polymeric Nanoparticles

A Quantum Dot Nanoparticle

The quantum dot itself (the semiconductor nanoparticle) is toxic. Therefore some typical modifications has to be made for it to become biocompatible.



Source: The scientist (2005), Vol. 19, p. 35

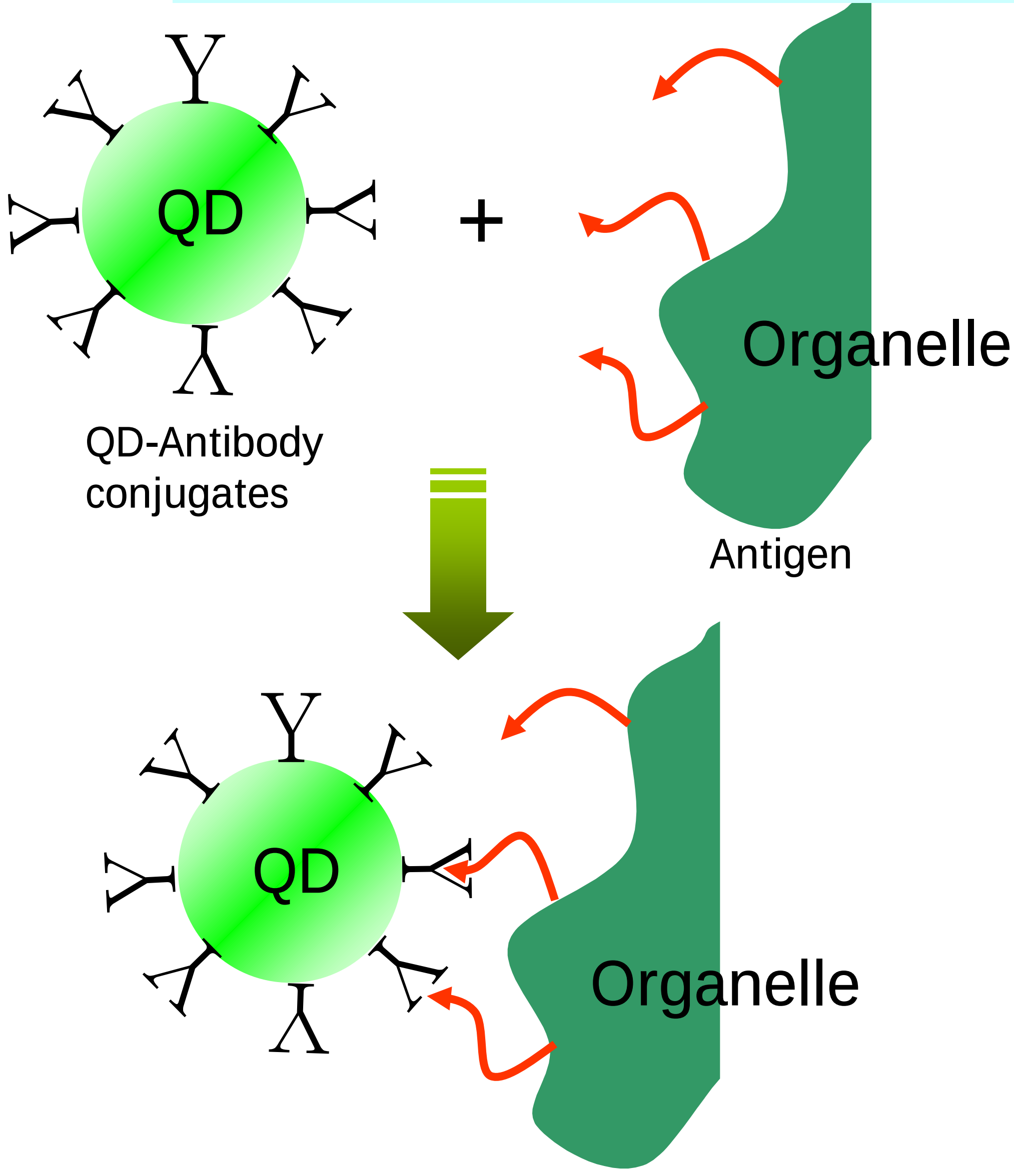
1) The core consist of the semiconductor material that emits lights

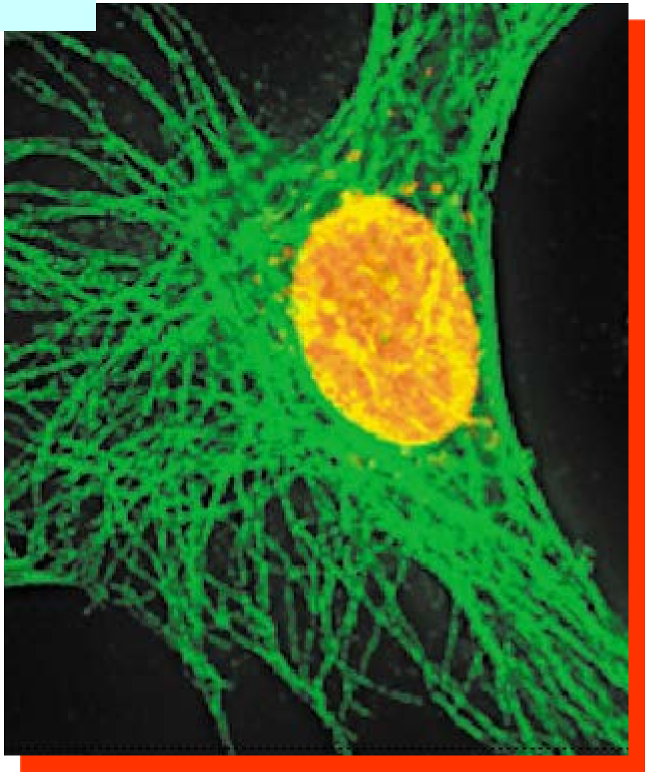
2) The shell consist of an insulator material that protects the light emitting properties of the QD in the upcoming functionalization

3) The shell is functionalized with a biocompatible material such as PEG or a lipid layer

4) Additional functionalization can be done with several purposes (e.g. embed a drug for drug delivery, or assemble an antibody to become the QD target-specific)

Nanotechnology Applications: In Vivo Cell Imaging





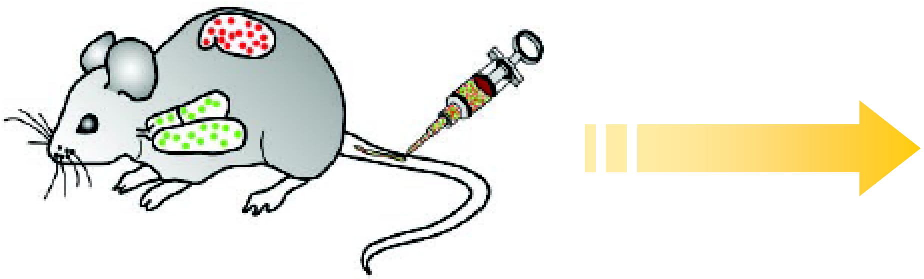
▲ 3T3 cell nucleus stained with red QDs and microtubules with green QDs

- Multiple Color Imaging
- Stronger Signals

Wu *et al. Nature Biotech.* **2003** 21 41

Nanotechnology Applications: In Vivo Tumor Imaging

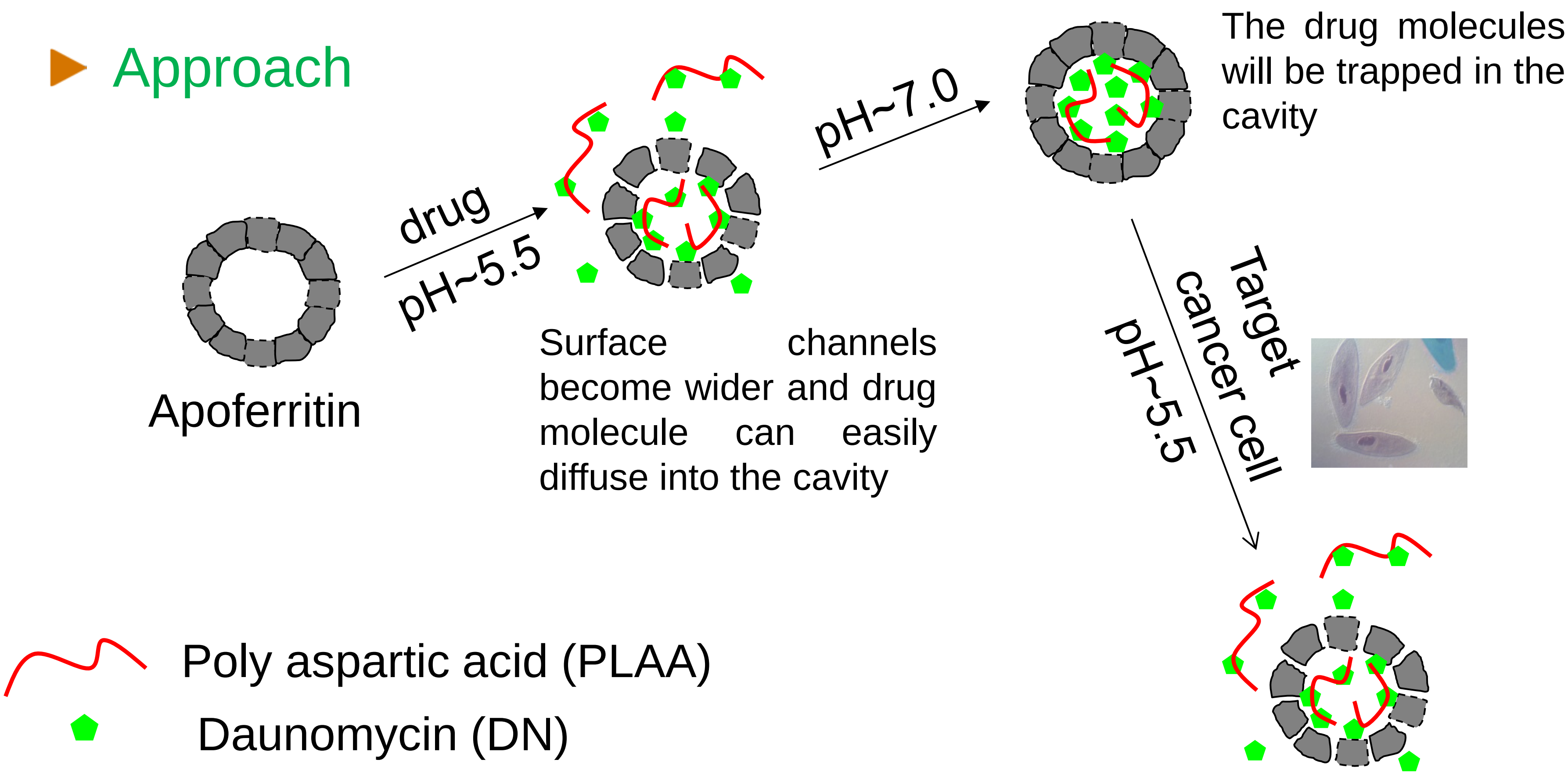
Quantum Dot Injection



▶ **Red Quantum Dot locating a tumor in a live mouse**

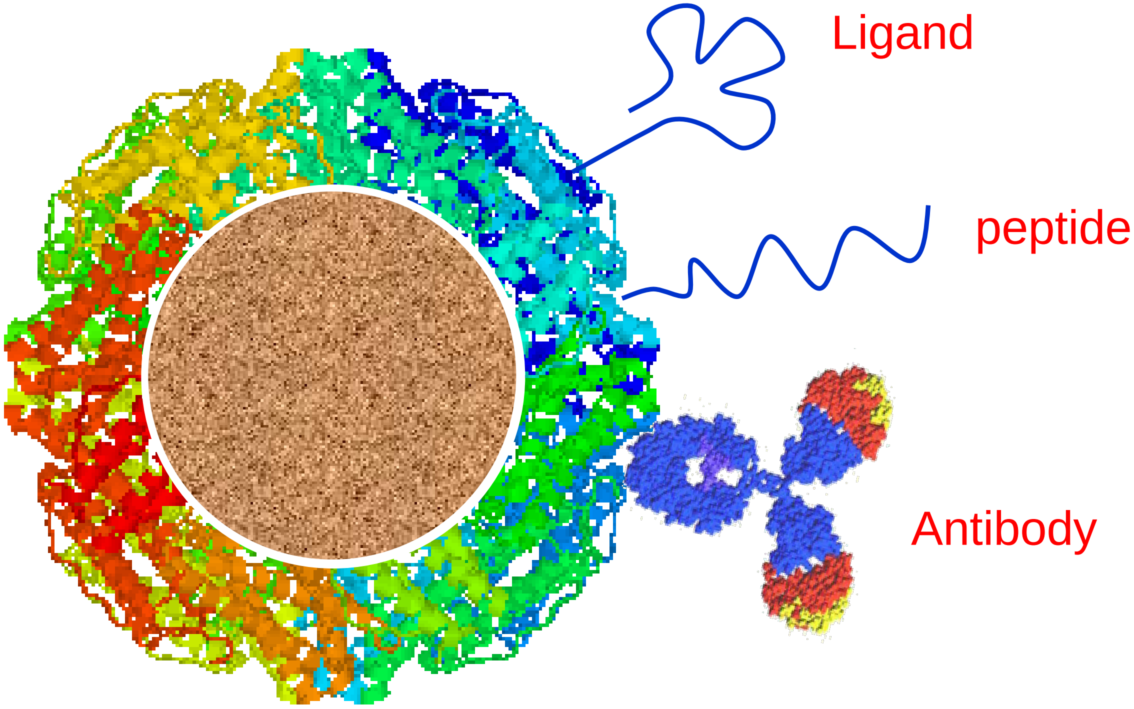
Protein-Cage Based Platform for Drug Delivery and Release

▶ Approach



J. Mater. Chem. 2011

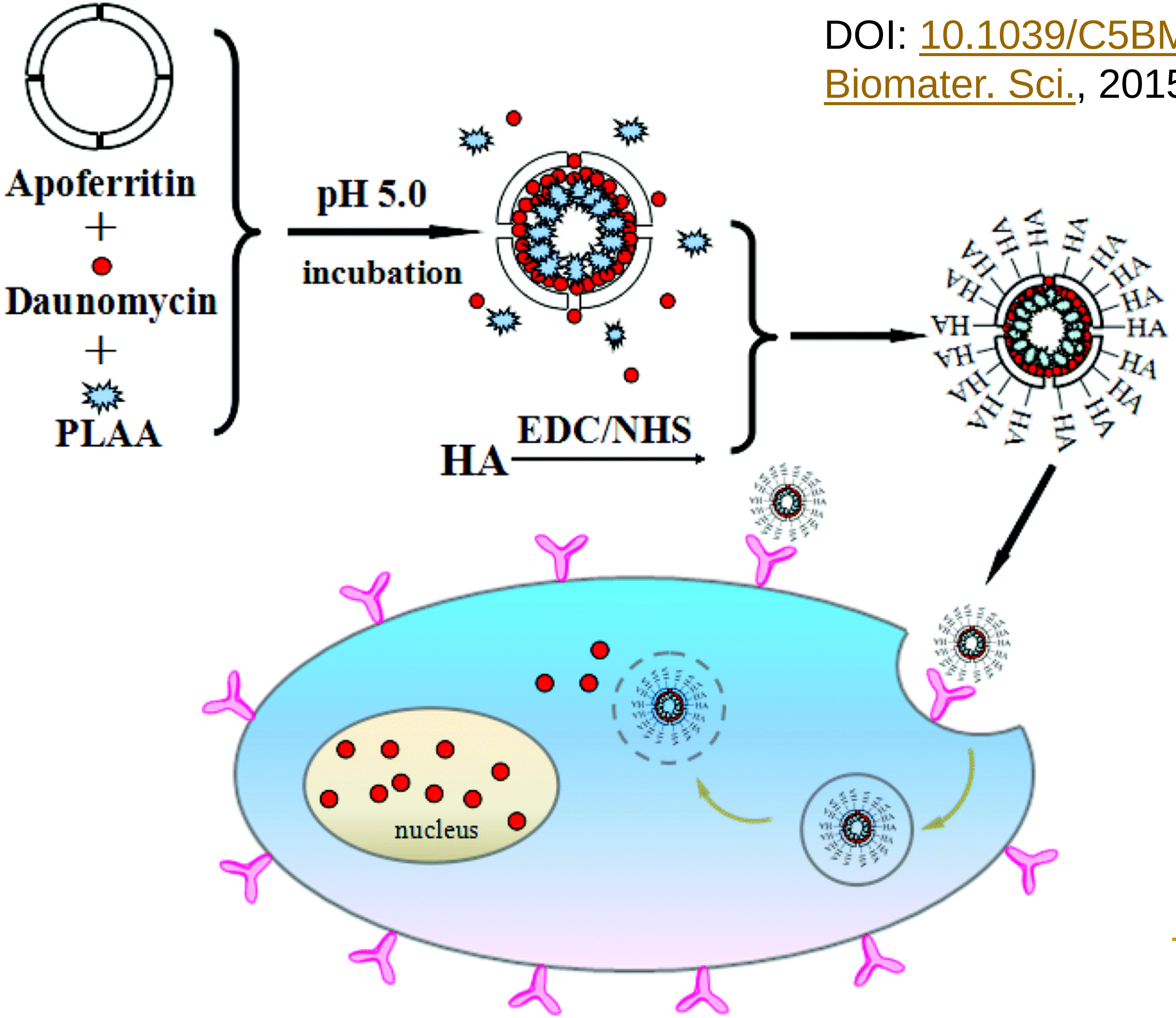
Biosensing and Bioimaging Based on Protein-Cage Nanoparticles



- Protein cage surface can be easily modified with biomolecules

Schematic illustration of the synthesis of the hyaluronic acid–apoferritin–daunomycin–poly-L-aspartic acid (HA–Apo–DN–PLAA) drug delivery system.

DOI: 10.1039/C5BM00067J (Paper)
Biomater. Sci., 2015, **3**, 1386-1394

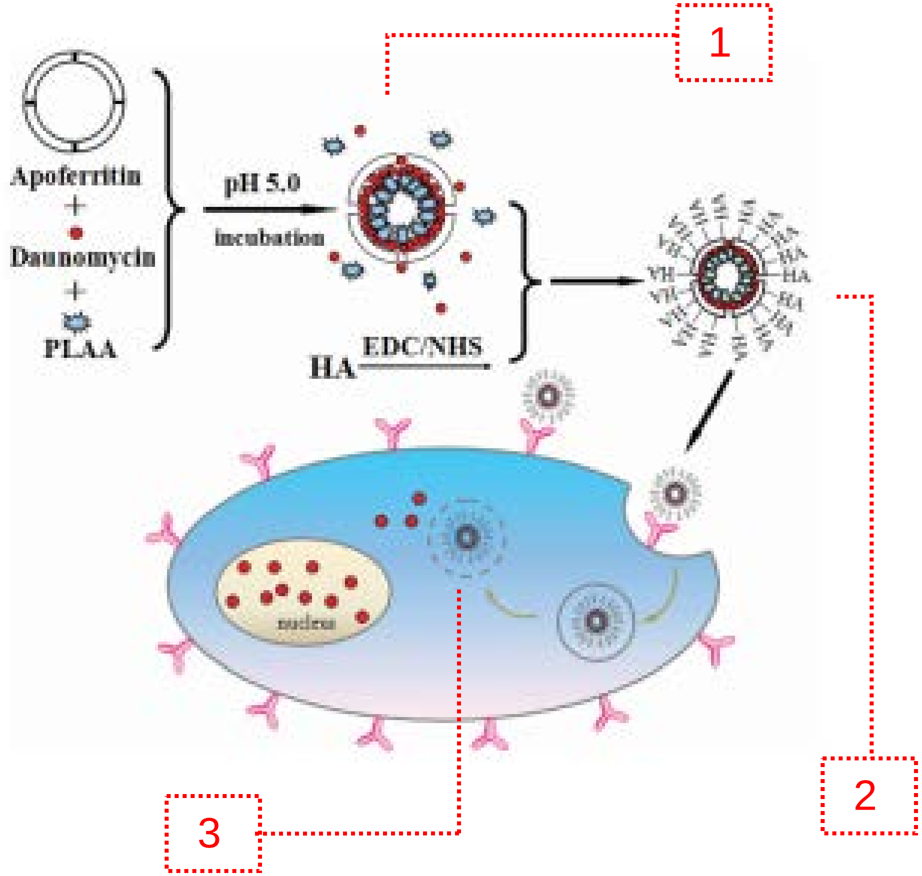


Protein Cage for Drug Delivery

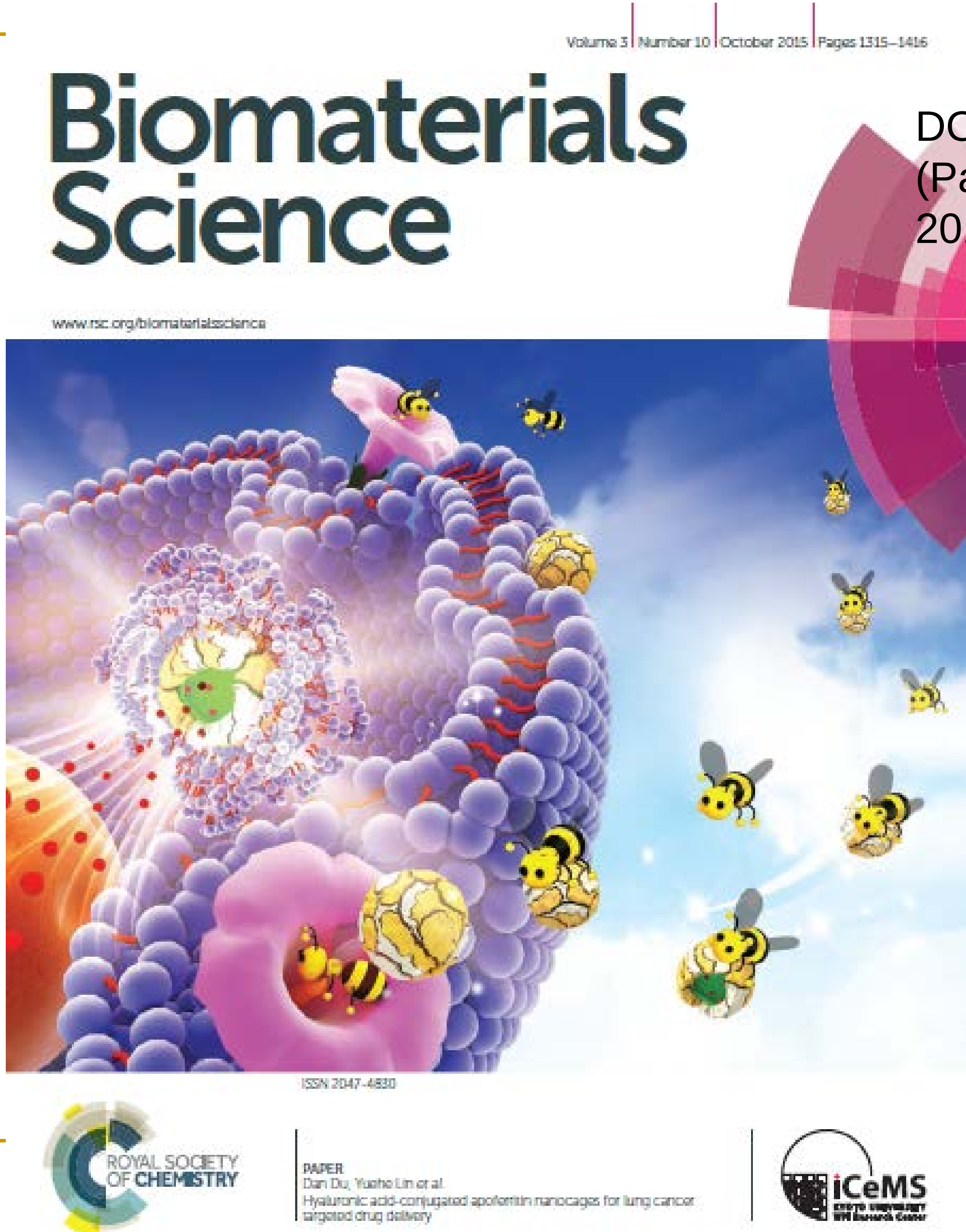
1) Apoferritin is a naturally derived protein cage and it is composed of 24 subunits. We have used apoferritin’s ability to disassemble and reassemble under pH control to load the therapeutic compound.

2) HA has been used as a targeting moiety to recognize overexpression CD44 in A549 lung cells.

3) Endosomes break and drug release.



Biomater. Sci., 2015, 3, 1386–1394

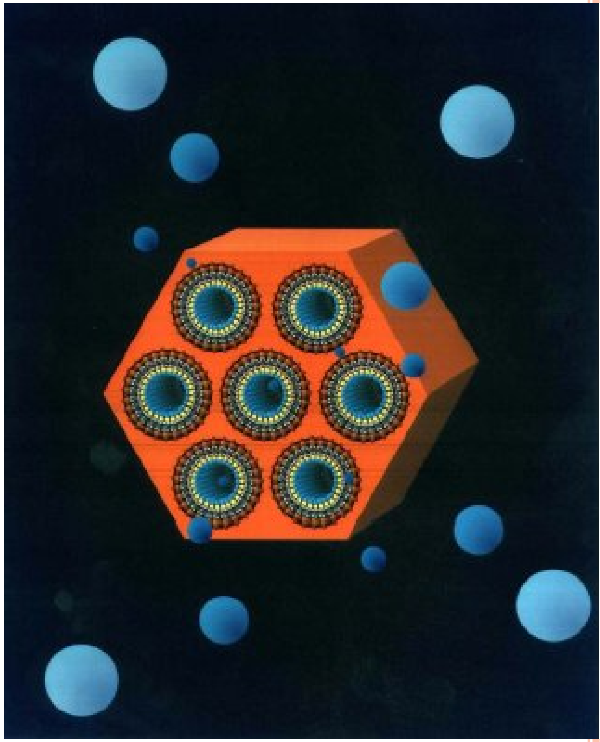


DOI: 10.1039/C5BM00067J
(Paper) Biomater. Sci., 2015, **3**, 1386-1394

Environmental Applications of Nanotechnology

1. Functionalized Mesoporous Silica for Water Treatment

High capacity due to high surface area (1000 m2/g)
and high-density of functional groups



a. Toxic heavy metals: Hg, Cd, Pb, As Cr

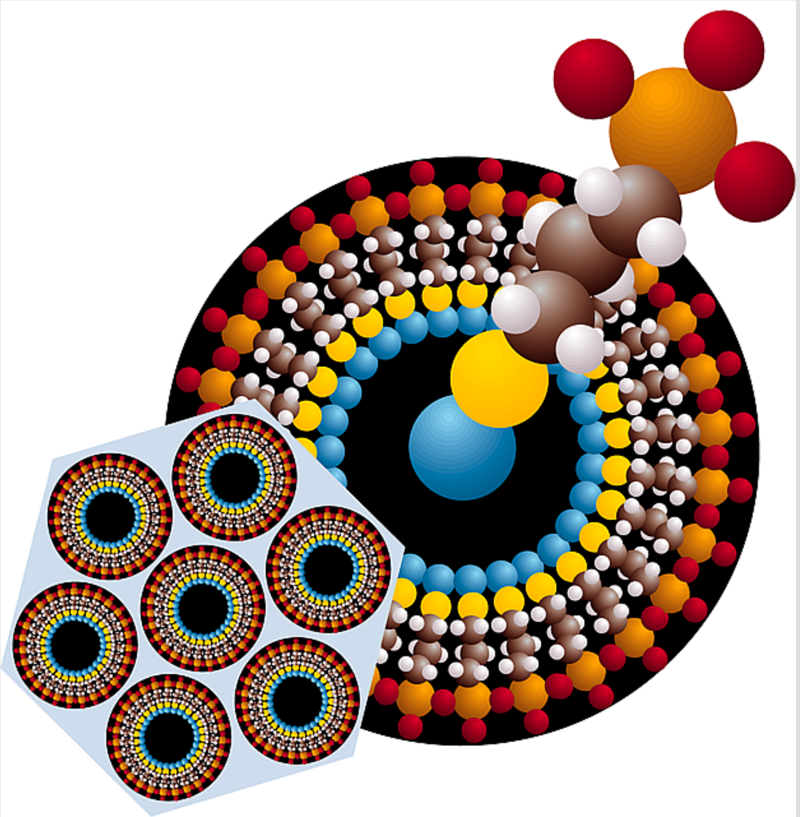
b. Radioisotopes: Cs-137; U, Pu

2. Sensors Based on Functionalized Mesoporous Silica for Environmental Monitoring

Environmental Science & Technology, 2005, 39, 1324-1331

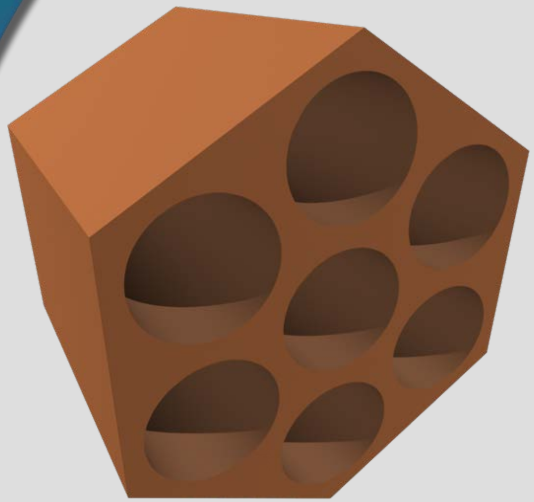
SAMMS: Self-Assembled Monolayer on Mesoporous Silica

For Environmental Applications

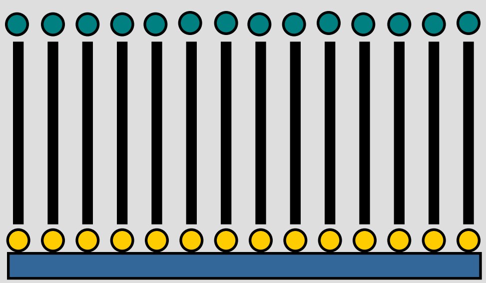


Synthesis of SAMMS

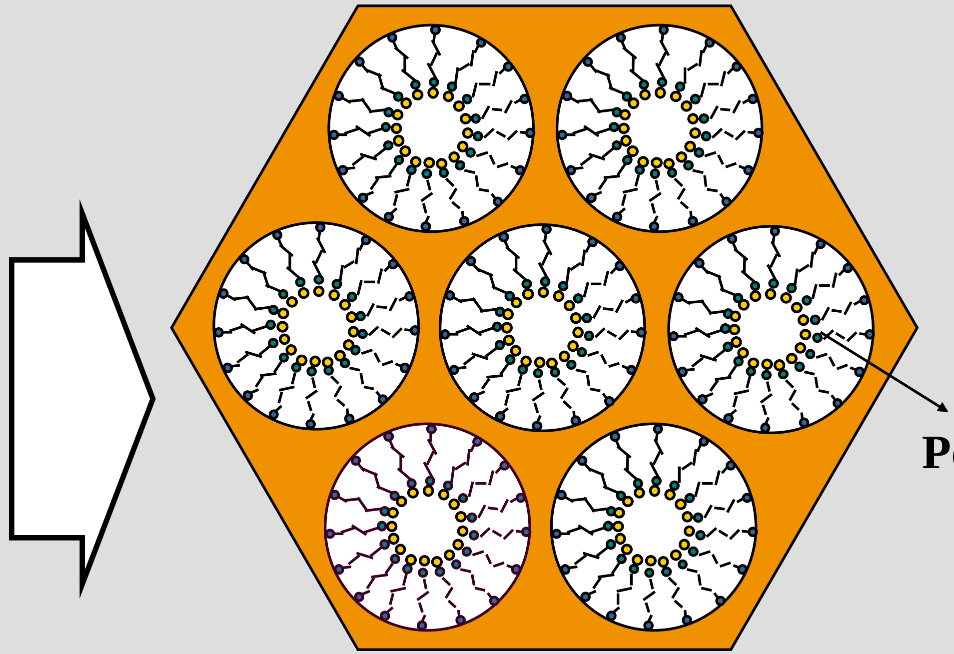
A. Ordered mesoporous silica



B. Self-assembled monolayers



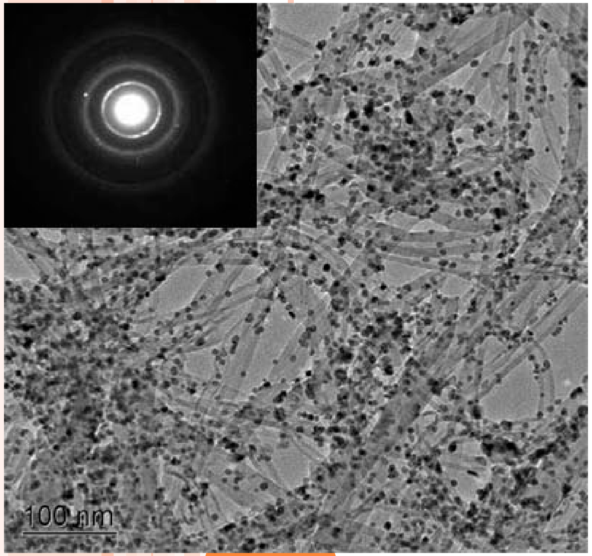
C. Self-assembled monolayers on mesoporous supports (SAMMS)



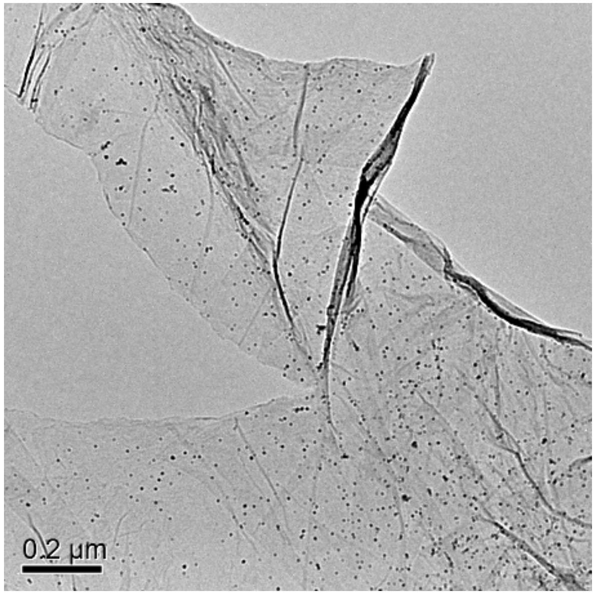
One end group of the functionalized monolayers is covalently bonded to the silica surface and the other end group can be used to bind metal ions

Nanotechnology Application:
Nanocatalysts for Fuel Cells

Supercritical fluid deposition and wet chemical methods to prepare well-dispersed Pt, Pt-Ru, Pt-Au, Au, on nano-carbon supports (CNTs, mesoporous C, graphene)



CNTs



Graphene