Nanomaterials – Are they Engines of Creation?

"Living organisms are naturally – existing fabulously complex systems of molecular nanotechnology."
Dr. Gregory Faby

"What on earth would man do with himself if something did not stand in his way ?"
H. G. Wells

"To give less than your best is to sacrifice the gift."
Steve Prefontaine

"Life is an adventure and the worst of all fears is the fear of living."
Theodore Roosevelt

25th November 2007

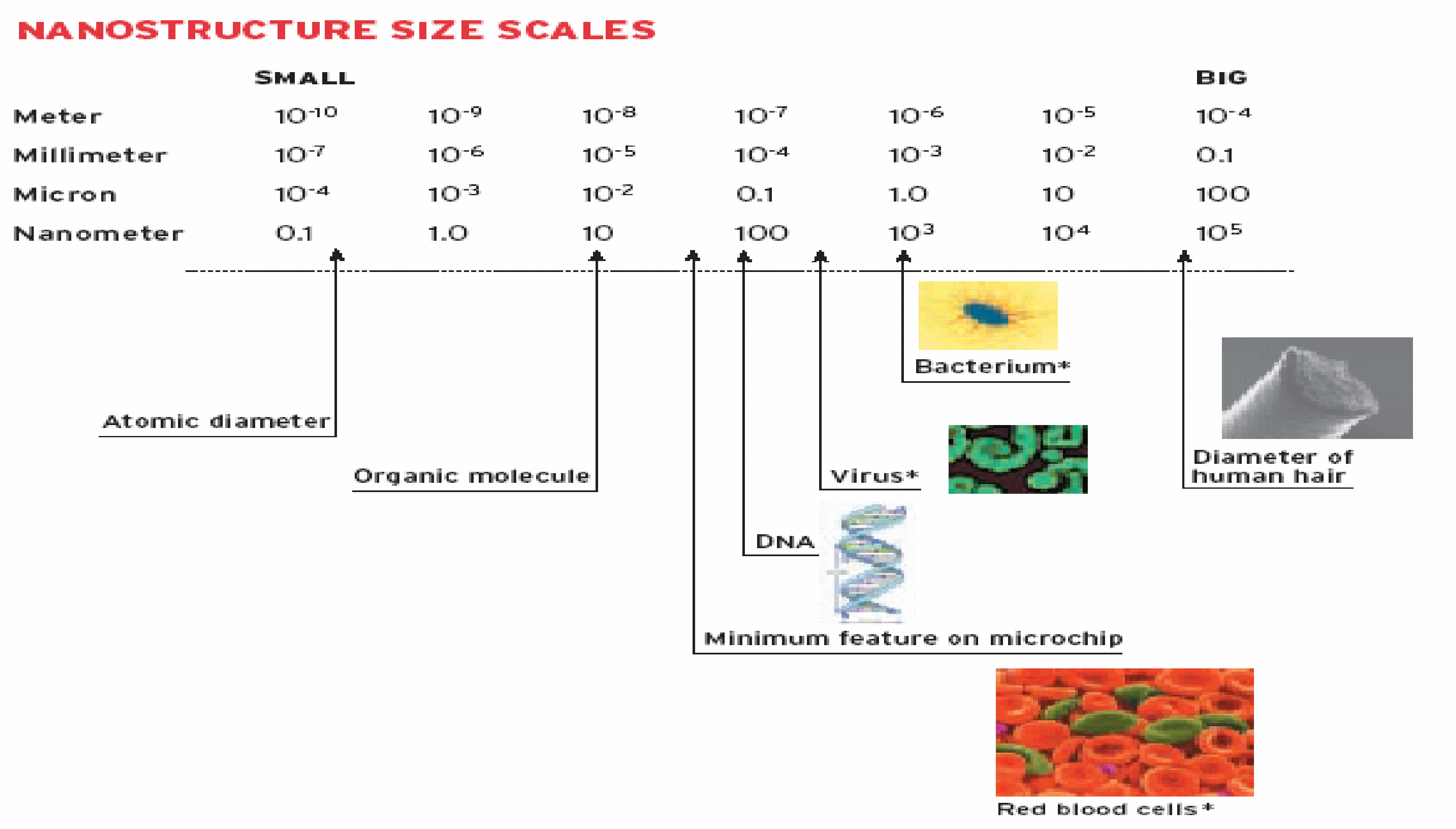
- What difference can arrangement of atoms (**The unruly herds**) make?
- What are nanomaterials?
- Why do we need nanomaterials?
- How to know about nanomaterials?
- What are the applications of nanomaterials?
- Long March from Nanoscience (Knowledge) [Academia] to nanotechnology (Application) [Business]

Is nanotechnology the greatest technological breakthrough in the history of mankind? Is this for good or bad?

Nanotechnology: Size Matters

Nanoscience refers to the world as it works on the atomic or molecular scale, from one to several hundred nanometers.

Nanometer = 10^{-9} meters: roughly the size of 10 hydrogen atoms lined up or the width of DNA.



Nomenclature

Nanoscience : The study of fundamental principles of molecules and structures with atleast one dimension roughly between 1 and 100 nanometers.

Nanotechnology : The application of nanoscience in technological devices.

Bottom-up nanofabrication : The building of nanostructures with small components such as atoms.

Top-down Nanofabrication : The process of making nanostructures starting with larger structures and taking parts aways.

Nanoscale : (phenomena that occur on) the length scale between 1 and 100 nm.

Nanoparticles : Aggregates of atoms bridging the continuum between small molecular clusters of a few atoms and dimensions of 0.2 – 1 nm and solids containing millions of atoms and having the properties of macroscopic bulk material.

Nanodots : Nanoparticles that consist of homogeneous material, especially those that are almost spherical or cubical in shape.

Nanostructure/Nanostructure materials : Structures whose characteristic variation in design length is at the nanoscale.

Nanorods : Nanostructures that are shaped like long sticks with a diameter in the nanoscale and a length very much longer.

Nanowires : Another term for nanorods, especially nanorods that can conduct electricity.

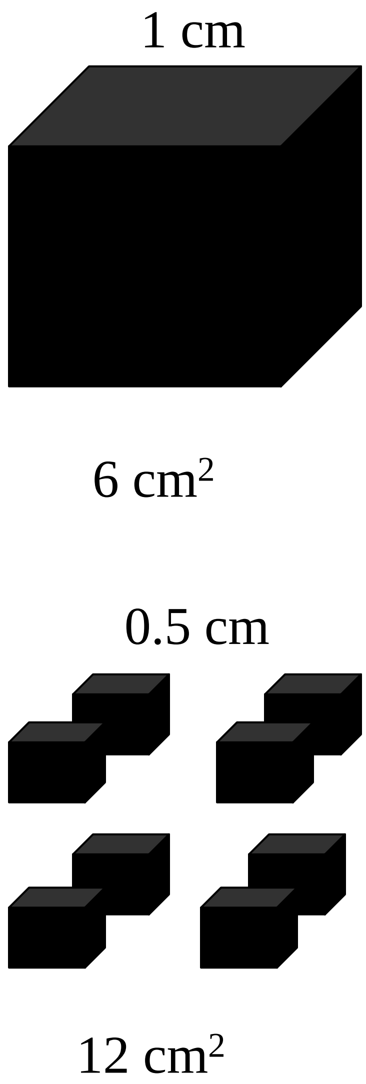
Nanotubes : Almost always carbon nanotubes, referring to the wires of pure carbon that look like rolled sheets of graphite or like carbon soda straws.

What is nanotechnology ?

Nanotechnology: The creation of functional materials, devices and systems through control of matter on the nanometer (1~100nm) length scale and the exploitation of novel properties and phenomena developed at that scale.

Why nano length scale ?

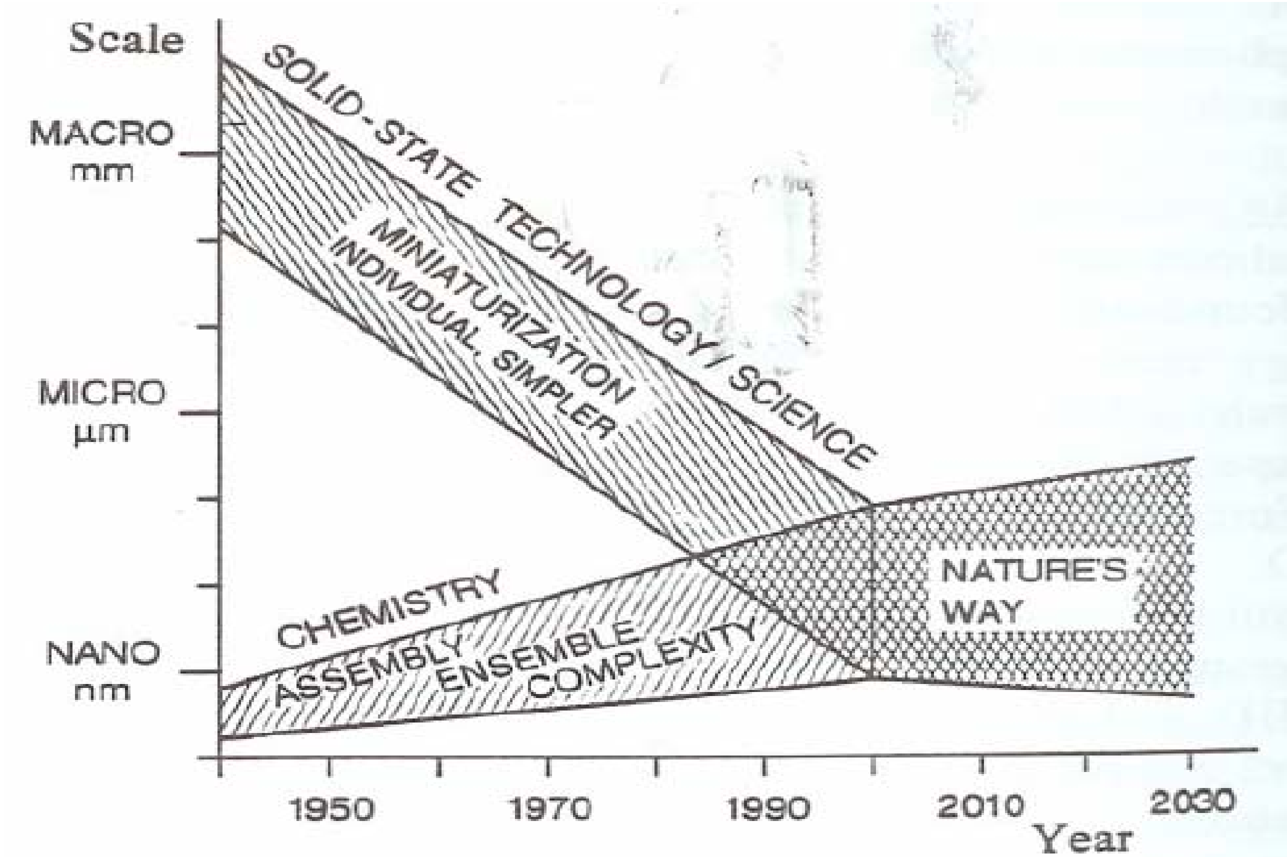
- By patterning matter on the nano scale, it is possible to vary fundamental properties of materials without changing the chemical composition



What is the Importance of Nano Research ?

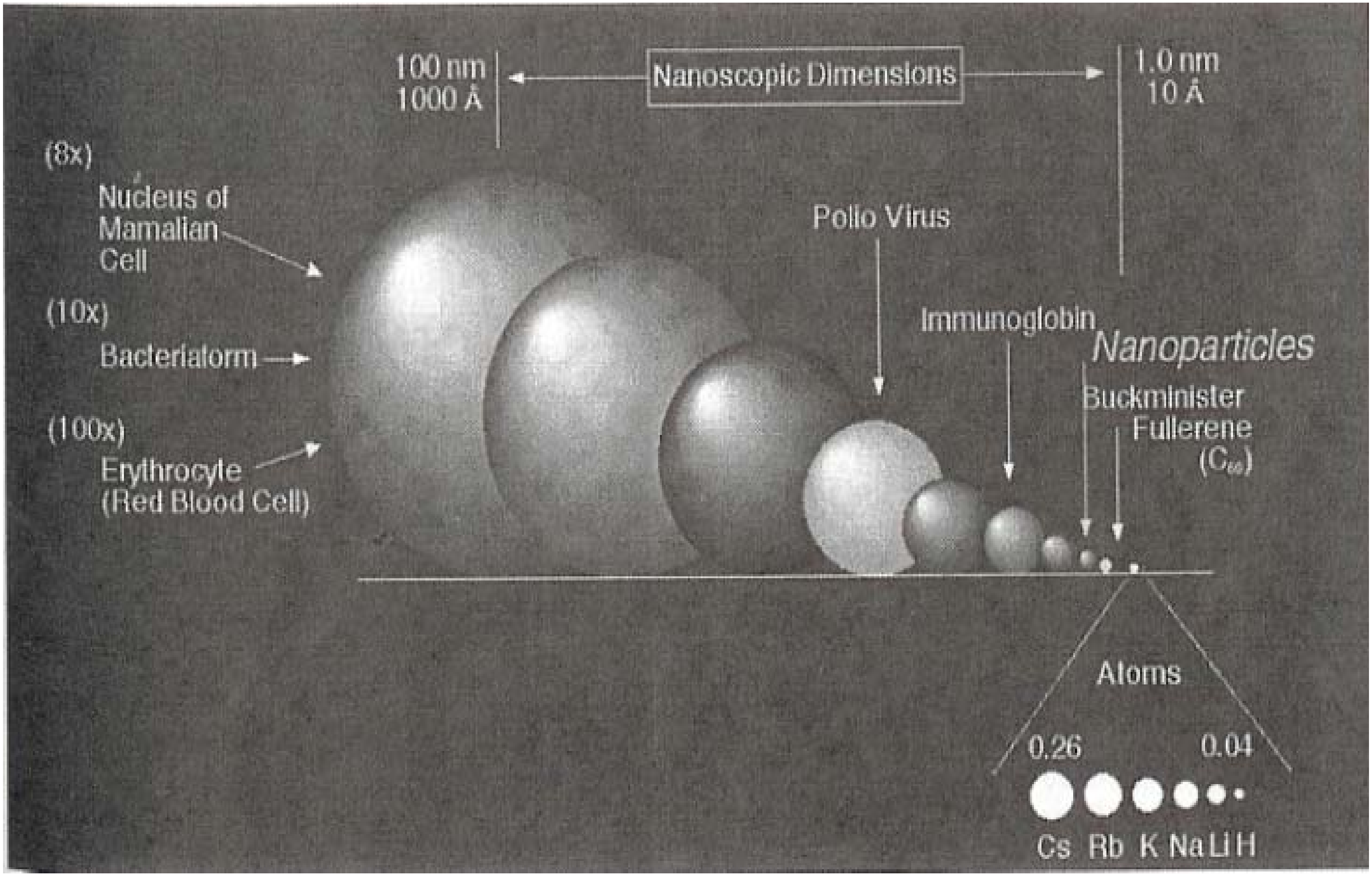
Nanoparticles exhibit size dependent properties that are profoundly different from the corresponding bulk material.

Electrical	higher electrical conductivity in ceramics and magnetic nanocomposites; higher resistivity in metals
Magnetic	increase in magnetic coercivity down to a critical size in the nanoscale regime; below critical crystalline size, decrease in the coersivity leading to the superparamagnetic behavior
Mechanical	increase in hardness and strength of metals and alloys; enhanced ductility, toughness and formability of ceramics; super strength and superplasticity
Optical	blue shift of optical spectra of quantum-confined crystallites; increase in luminescent efficiency of semiconductors
Chemical	fundamental understanding of heterogeneous catalytic properties



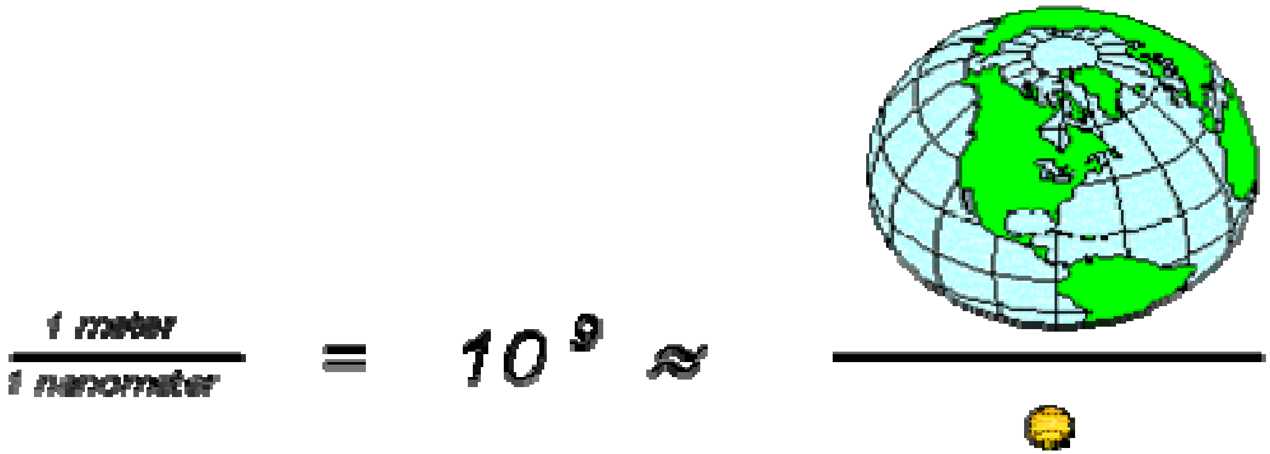
Schematic suggesting the convergence of solid state science and technology And supramolecular assembling chemistry after year 2000

Nanostructured mateirals Science and Technology, Gan-Moog Chow and Nina Ivanovna Noskova, Kluwer Academic Publishers, 1997.



Size comparisons of nanocrystals with bacteria, viruses and molecules

Nanometer : A magical point on length scale



Nanotechnology :

Research and technology development at the atomic, molecular, or macromolecular levels, approximately 1-100 nm in length.

❖Ability to control or manipulate on the atomic scale.

❖Creation and use of structures, devices, and systems that have novel properties and functions because of their small and/or intermediate size.

❖A technology based on the manipulation of individual atoms and molecules to build structures to complex atomic specifications.

Three eyes for this new millennium

1. Information technology

2. Biotechnology

3. Nanotechnology

The are expected to find wide, novel and new applications
In all fields of science and technology.

Nanostructured Materials

- Metals
- Ceramics
- Semiconductors
- Biomolecular materials
- Polymers

Nanomaterials – Dispersion and Coatings

Current commercial Applications:

Printing
Sunscreens
Photography
Pharmaceuticals

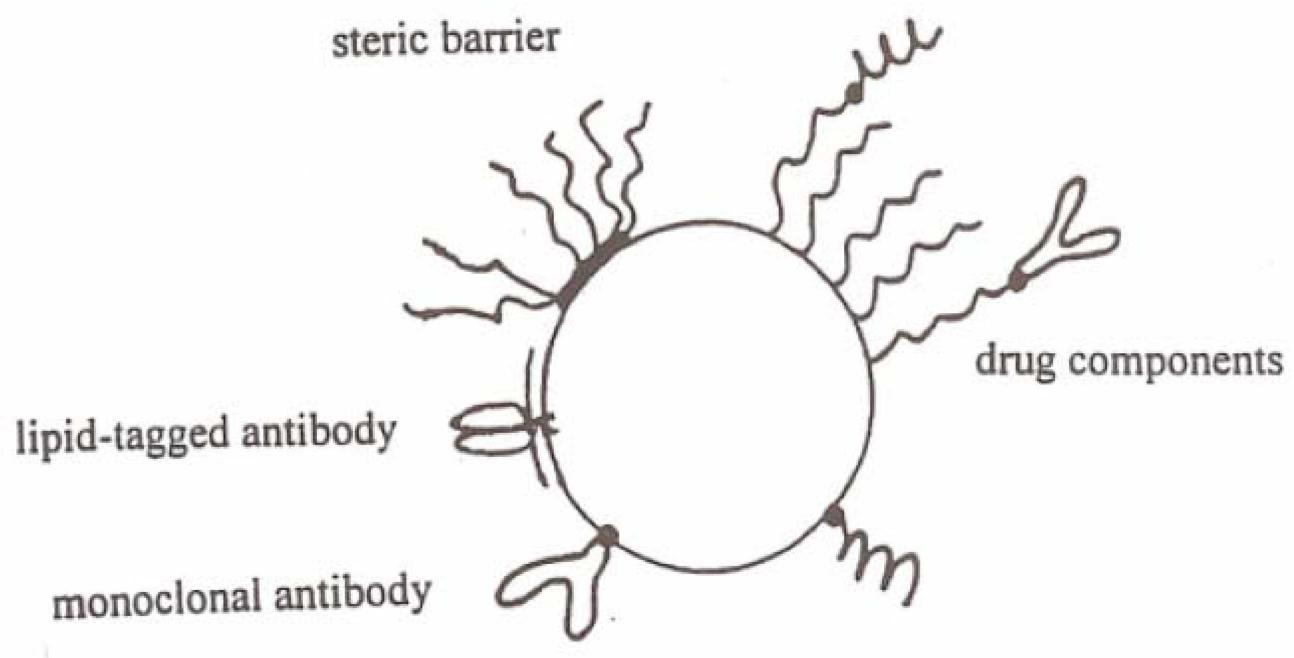
Areas with very strong potential impact:

Targeted drug delivery
Gene Therapy
Multifunctional coatings

❖ For nanoscale dispersions to be successful they should have freedom from agglomeration

Nanostructure Science and Technology (WTEC Panel Report)
Richard W. Siegel, Evelyn Hu and M. C. Roco, Kluwer Academic Publishers

Drug delivery systems in biomedicine



Schematic diagram of an engineered particle for biomedical applications

A particle prepared for a medical application, including doping with Monoclonal antibody, lipid-tagged antibody, steric barrier, and the drug components.

Nanostructured mateirals Science and Technology, Gan-Moog Chow and Nina Ivanovna Noskova, Kluwer Academic Publishers, 1997.

Nano materials – High surface area

❖ Nanostructured material building blocks possess inherently high surface area values.
For example, a nanoparticle 5 nm in diameter has about half of the atoms on its surface.

Applications:

Chemical and electrical energy storage
Sensors (molecule specific sensors)
Absorption/desorption materials
Tailored catalysts
Drug delivery
Porous membranes
Molecular sieves (large hydrocarbon or bacterials filters)
Solar cells (Gratzel-type)

Functional Nanoscale Devices

- Need for ever smaller devices

Major focus areas:

Single Electron Transistor (SET)
Magnetic devices using Gaint magnetoresistance
Carbon nanotubes for high-field-emission displays

Potential Areas on the Horizon

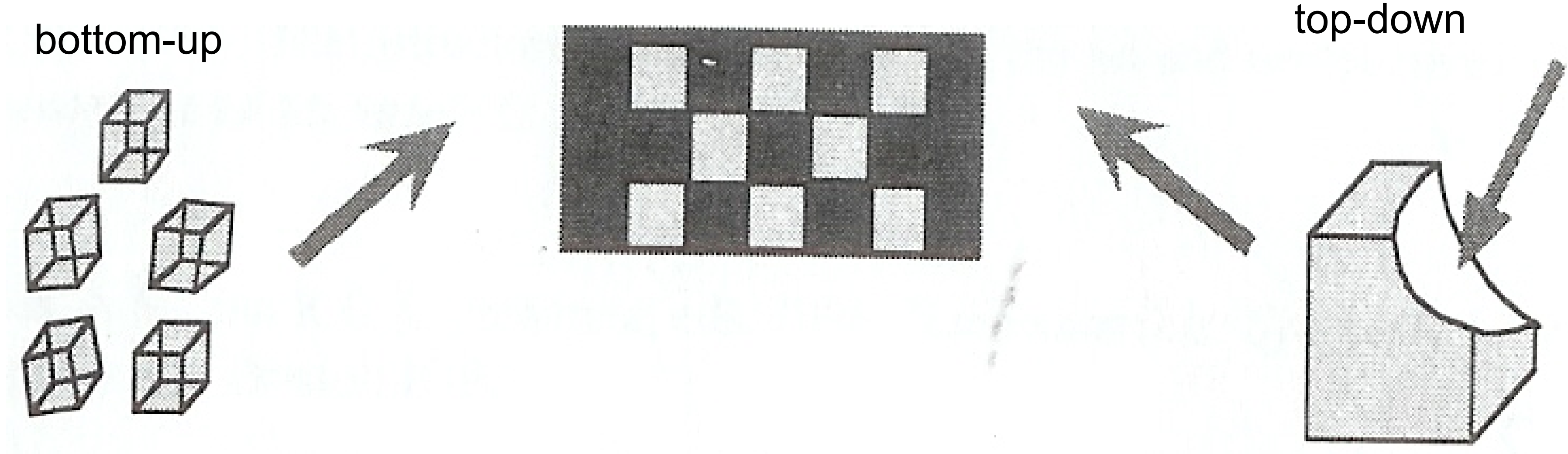
- Terabit memory
- Microprocessing
- Single molecule DNA sizing and sequencing
- Biomedical sensors
- Low-noise, low-threshold lasers
- Nanotubes for high brightness displays

Approaches for the synthesis of Nanostructured Materials

Nanostructured Material

bottom-up

top-down



Assemble from
Nano-building Blocks

Power/aerosol compaction
Chemical Synthesis

'Sculpt' from Bulk
Mechanical attrition
(ball milling)
Lithography/etching

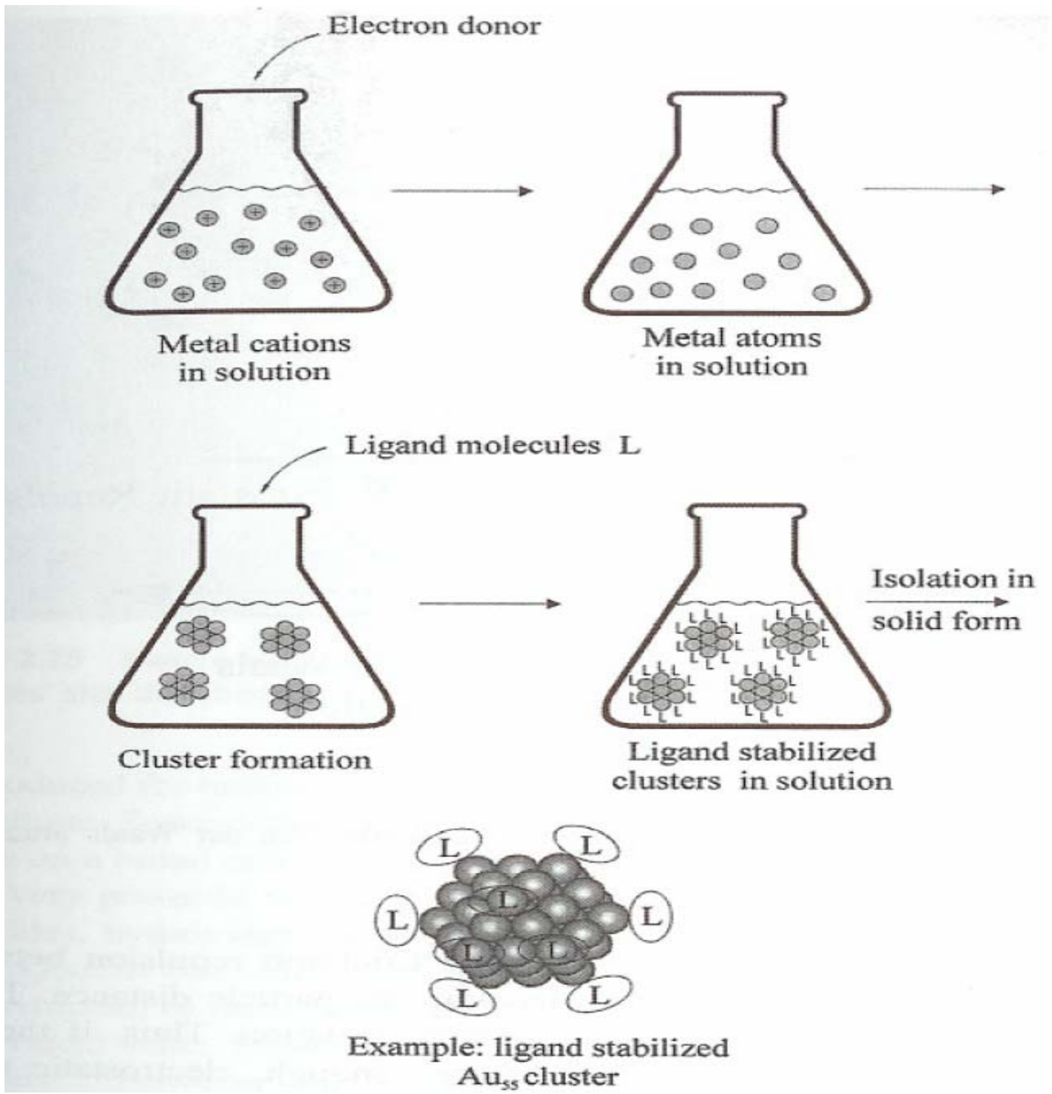
❖ In bottom-up approach the nanostructured building blocks first formed are then assembled into the final material (ex. Formation of powder components through aerosol Techniques and then the compaction of the components into the final material.

❖ Bottom up approaches were extensively employed for the formation of structural Composite materials

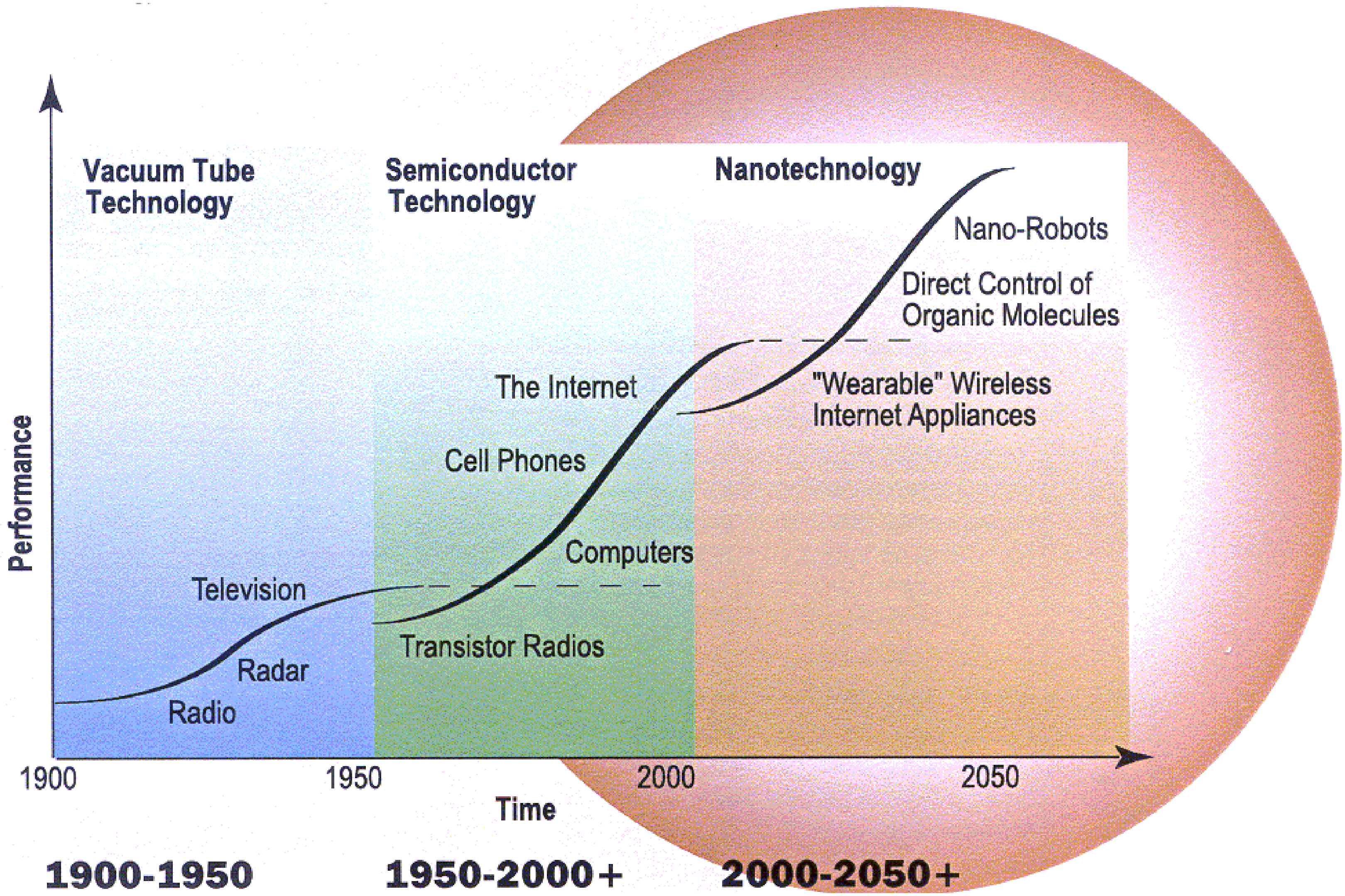
❖ Top-down approach start with a suitable starting material. The functionality is then "Scultp" from the starting material to form Nano building blocks.
(ex. "ball-milling", the formation of nanostructure building blocks through controlled, mechanical attrition of the bulk starting material)

❖ The nano building blocks thus formed are subsequenty Assembled into a new bulk material.

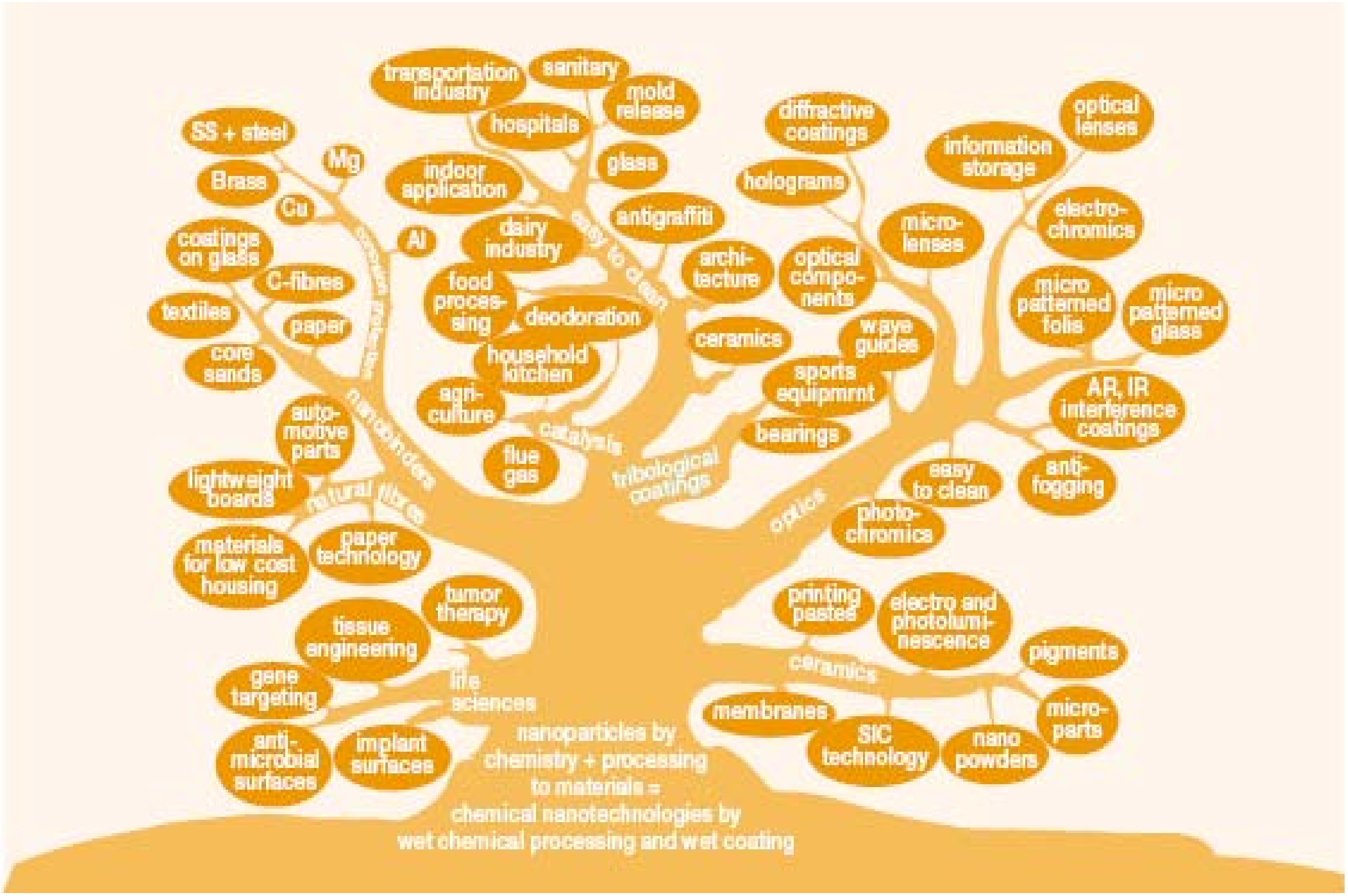
Synthesis of metal nanoparticles



Schematic procedure of cluster synthesis



NANOTECHNOLOGY
Technology of the 21st century

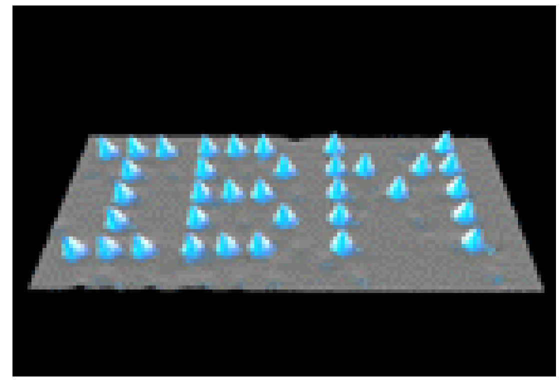


Potential application areas for Nanotechnology

There’s plenty of room at the bottom

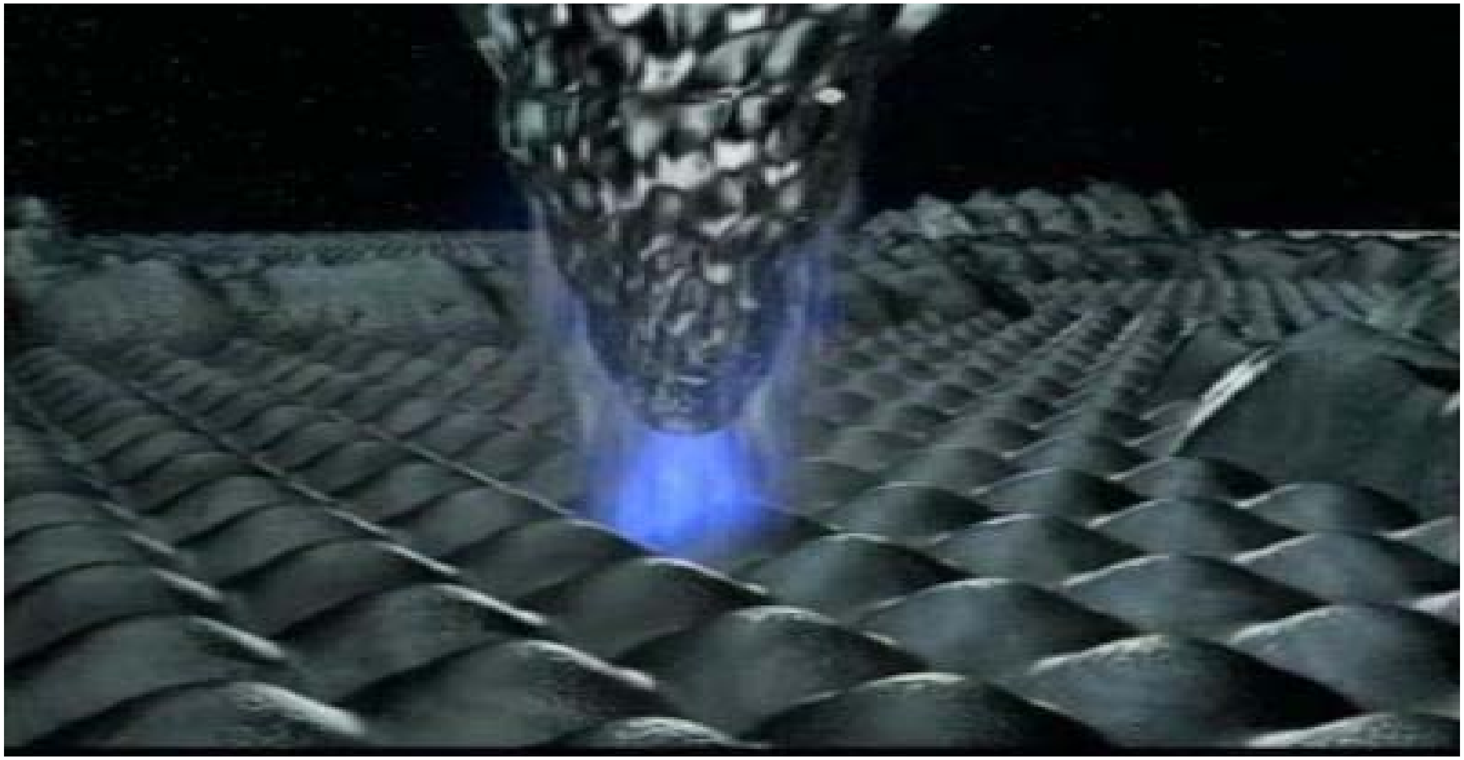
Nobel Prize for Physics – 1965
Field of interest - Quantum electodynamics

Autobiography : ”Surely you’re joking, Mr. Feynman”



Richard Phillips Feynman (1918-1988)

Proposed the concept of Nanotechnology in 1959
“The principles of physics, as far as I can see, do not speak against the possibility of moving things atom by atom. It is not an attempt to violate any laws; it is something, in principle, that can be done; but in practice, it hasn’t been done because we are too big.”
“…………. In near future we can arrange atoms the way we want; the very atoms, all the way down !”
He even speculated on how to write information at atomic levels and how to construct atomic-sized machines.



The invention of a very high definition microscope called a scanning tunnelling Microscope by Russell D. Young, in 1971, has revolutionized the field of Nanotechnology.
This microscope is an instrument like a blindfolded person feels the surface and scan atom by atom.
In this way it is possible to create an image of any particular surface on atomic scale. Not long after this invention it will be possible to manipulate atoms in this Way.

What then are the nanomaterials today and tomorrow ?

Three categories of nanotechnology :

1. **Incremental nanotechnology :**

   Nanoceramic powers : Constitute almost 90 % of the total market
   Nano sized ZnO particles : Sunscreen
   Iron nanoparticles : treatment of ground water contaminted with trichloroethylene
   Aluminium nanoparticles : Greater “bang for buck” – as solid rocket propellant
   Polymer nanocomposites : Increase hardness
   Reduce permeability of the polymer
   Automotive panels
   Step assists I vans

2. **Evolutionary nanotechnology :**

   Nanoscale sensors : Exploit the large surface area of nanotubes
   Semiconductor nanostructures such as quantum dots
   Silica based nanomaterials
   Molecular imprinted polymers
   Silica plat forms
   Envisoned for collection, concentration and detection of chemical weapons and other related compounds in security ad defense applications.

Fullerene – creation of a 60 carbon atom molecule
Bucky ball as termed by Smally in 1985

Carbon nanotubes : Highly conductive nanowires
Semiconductors
30 times stronger than steel at 1/6 th density
Thermal conductivity is 50 % higher than that of the diamond

Uses : Selected electronics
Key components in fuel cells
electrical transmission lines

"Carbon nanotubes are by no means the sole materials focus of evolutionary Nanotechnology."

Energy sector : High efficiency solar energy conversion
Advanced fuel cells
Batteries

Medicine : Diagnosis
Treatment
Different approaches to pharmaceuticals

Diamonds :
Natural diamond – Earth's mantle
Synthetic diamonds – treatment of graphite at high temp. and pressures

Material of choice :
Hard
Excellent transport properties
Transparent
Inert

Nanodiamonds :
Discovered by Lewis in 1987

Sources :
Meteorites
Detonation soots

Impurities : Hydrogen, Nitrogen and Oxygen
Composition : 87 – 90 % Carbon, 0.5 – 1 % Hydrogen, 1.6 – 2.5 % Nitrogen
6 -10 % oxygen
Functional groups : O-H, C-H, C=O, C=C and C-O-C
"A diamond becomes more stable than graphite below 3-10 nm"

Radical nanotechnology :

Next generation military uniforms being developed by MIT's Institute of soldiering nanotechnology.

Defend against chemical and biological weapons
Provide ballistic protection
Monitor health
Administer medical aid
Provide communication capabilities

"THE DOUBLE EDGED SWORD OF NANOMATERIALS "

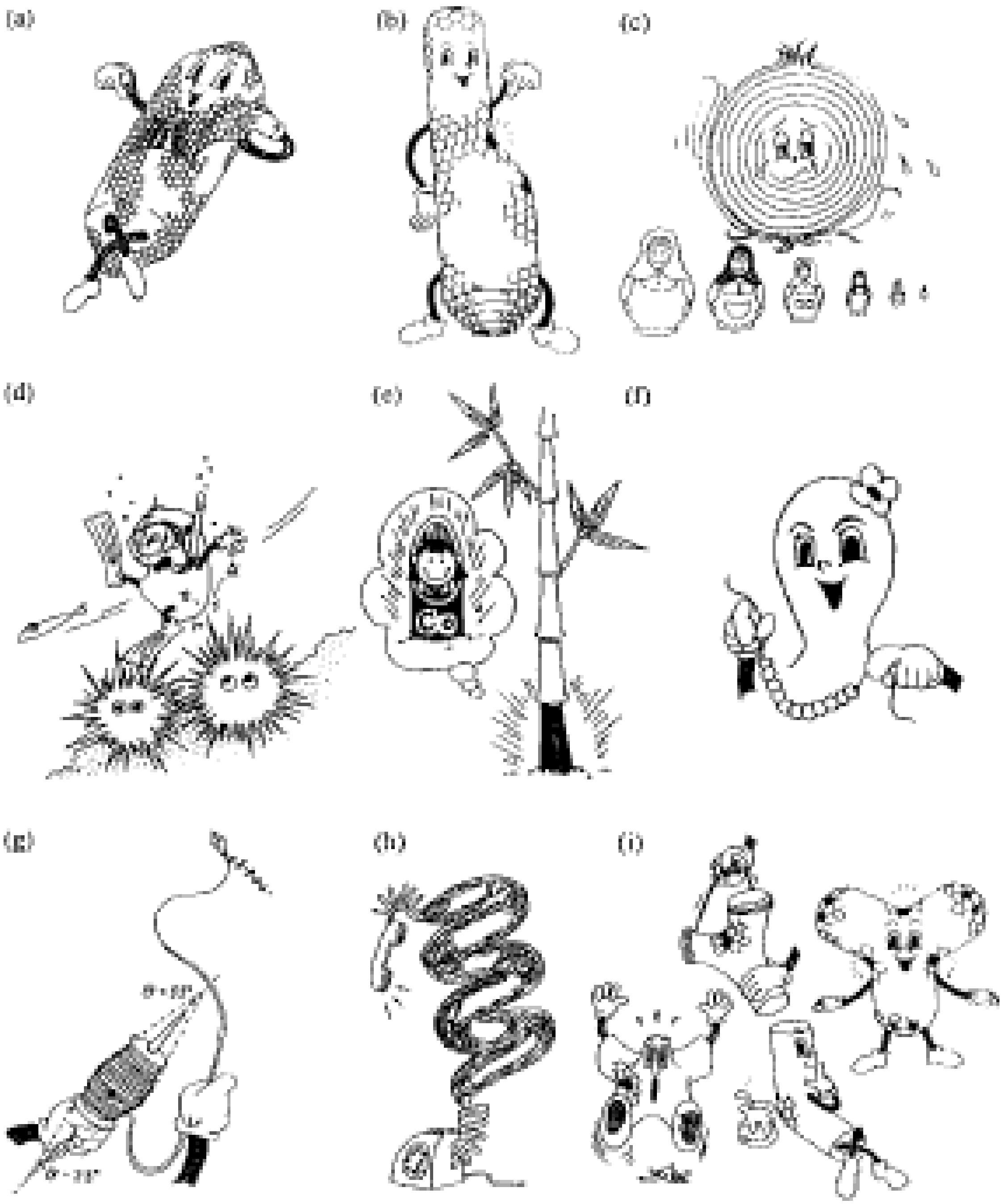
Greatly enhanced properties – very small size
very large surface area

Challenges in the environmental, health and safety (EHS) realm :

Mobility of nanoparticles
Unrestricted access to the human body

Table 1 shows 4 types of combustion-derived NP that cause a range of pathologies in humans or animals.

Nanoparticle type	Origin	Adverse health effects	
		animals	humans
Diesel exhaust particles	Combustion of diesel oil	Inflammation , fibrosis, cancer, adjuvant effects	Inflammation, cancer?
Welding fume	High temperature welding	Inflammation	Metal fume fever, fibrosis, cancer?, bronchitis
Fly-ash	Combustion of coal	Inflammation	?
NP Carbon black	Combustion of heavy fuel oil	Inflammation, lung cancer	?



Simple representation of Nanocarbons with PECULIAR Morphologies

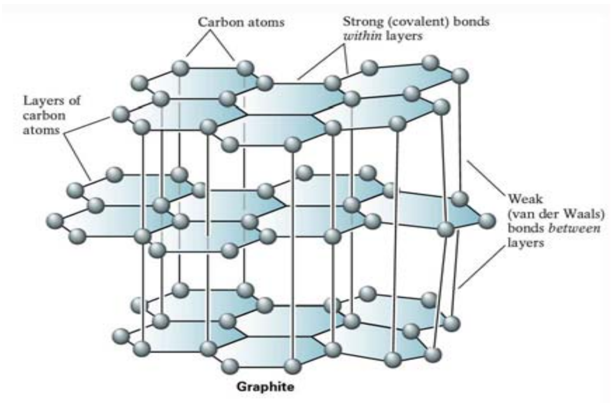
Shekar Subramoney, Advanced Materials, 10, 1998, 1157

Graphite

More 2D like; *sp*^{2} Orbitals

Strong bonds within layers and weak bond between layers

Good conductor of electricity

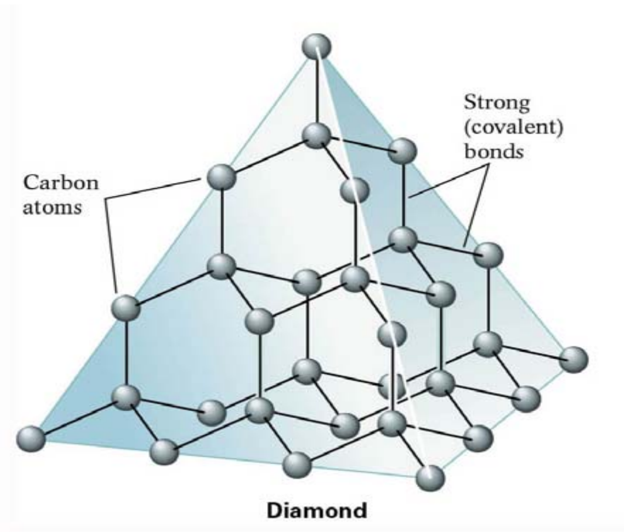


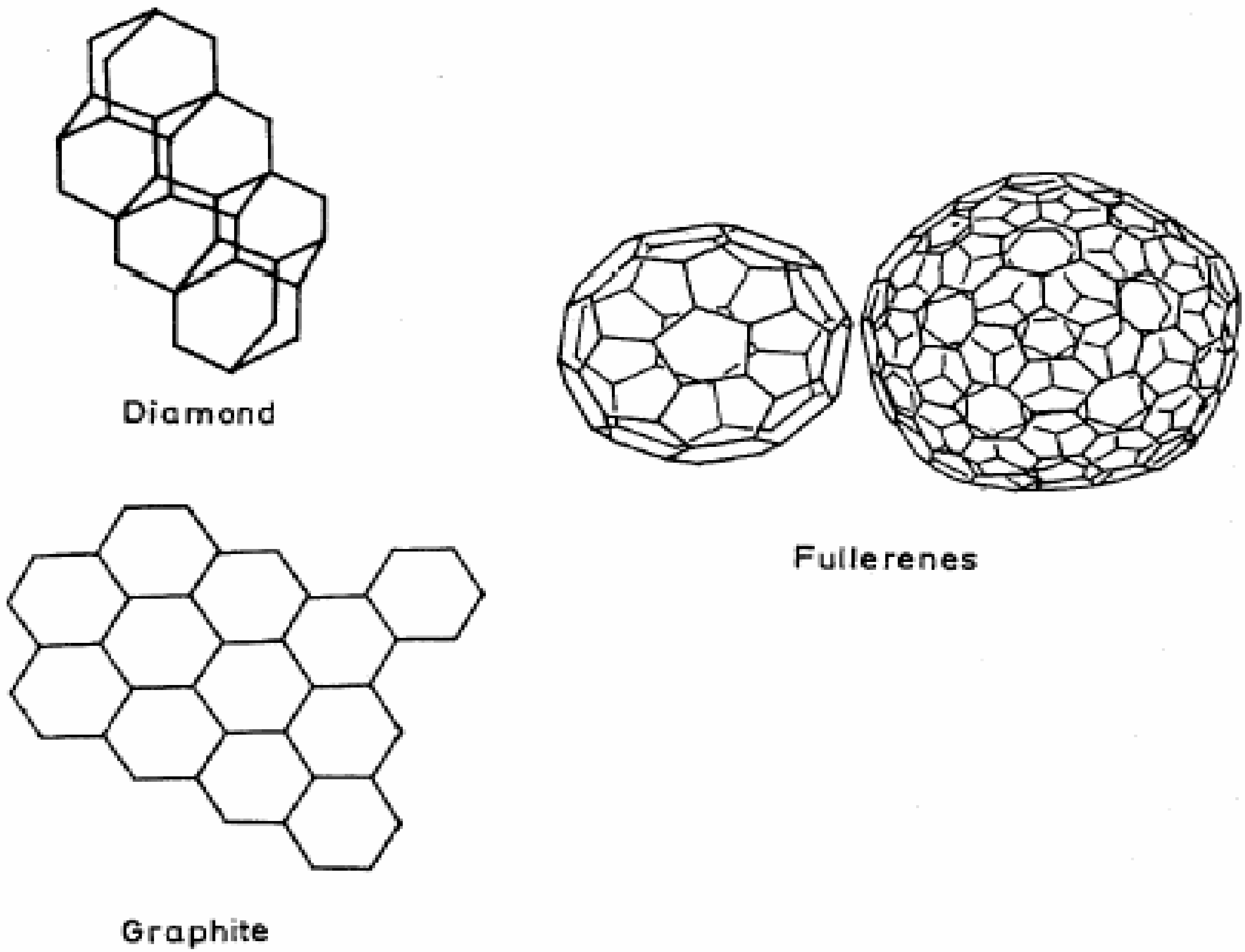
Diamond

More 3D like behavior; sp^3 orbital

Strong covalent bonding in 3 dimensions

Bad electrical conductor

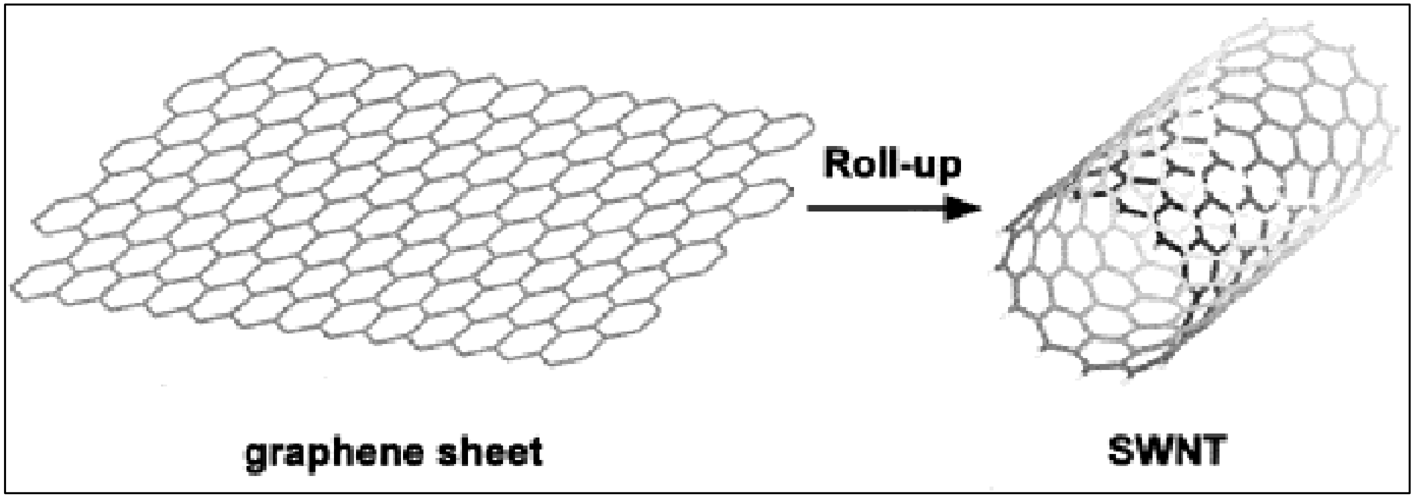




A Schematic representation of the structures of graphite, diamond and fullerenes

What are Nanotubes ?

- Discovered by Iijima (1991)
- Rolled up sheet of graphene
- Capped at the ends with half a fullerene



Single Walled Nanotube (SWNT)

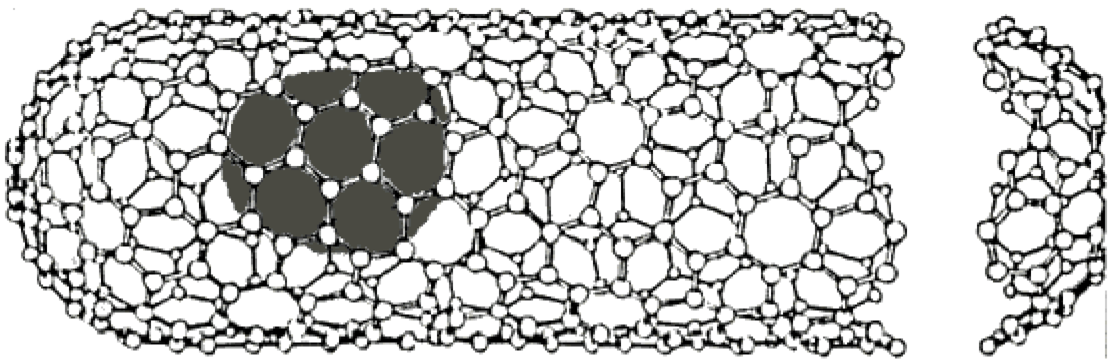
- Single atomic layer wall
- Diameter of 1 – 5 nm

Multi Walled Nanotube (MWNT)

- Concentric tubes ~50 in number
- Inner diameters : 1.5 – 15 nm
- Outer diameters : 2.5 – 30 nm

Carbon Nano test tube

The nano sized tubular carbon – Rolled hexagonal graphene sheets with fullerene caps at both ends

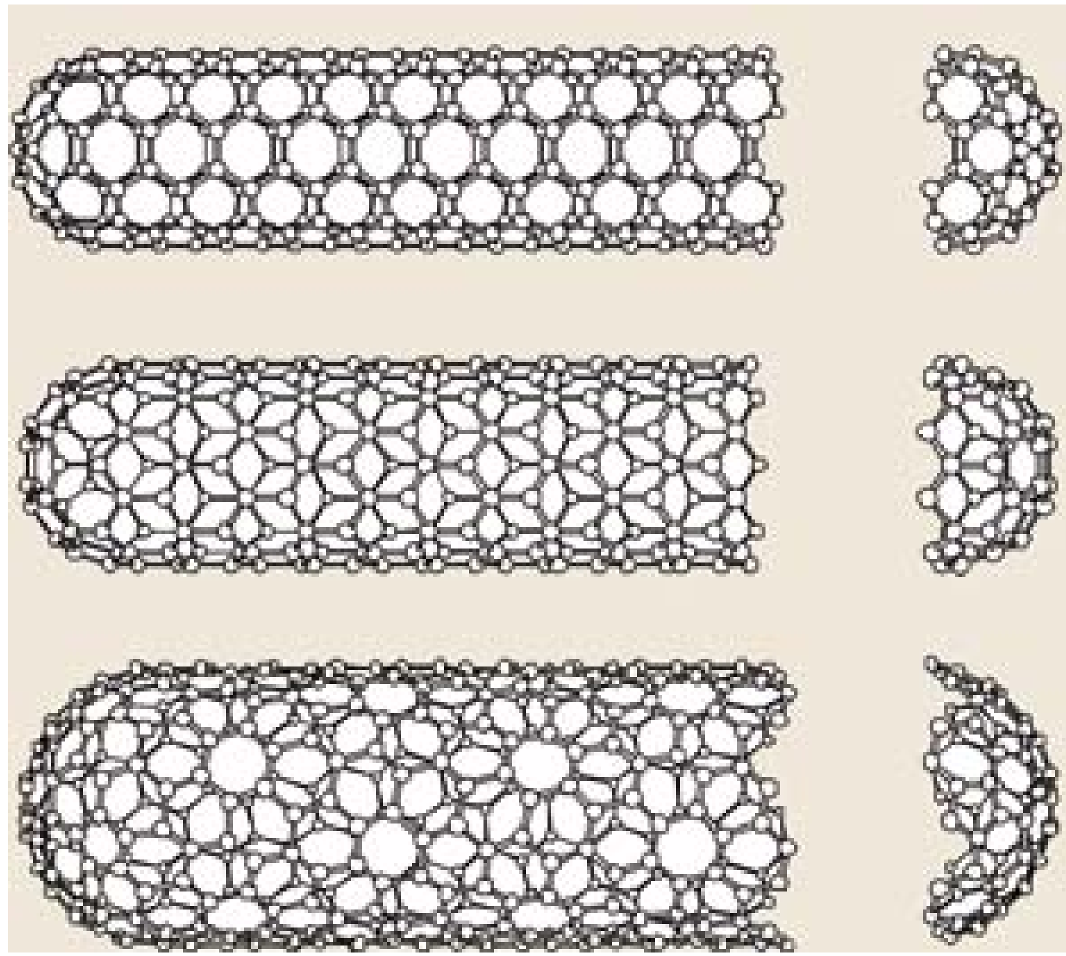


Hollow carbon tube - As a nano-scale test tube for doing chemistry
As a mold for making nano rods of other materials
Storage material
Magnetic and Electronic applications

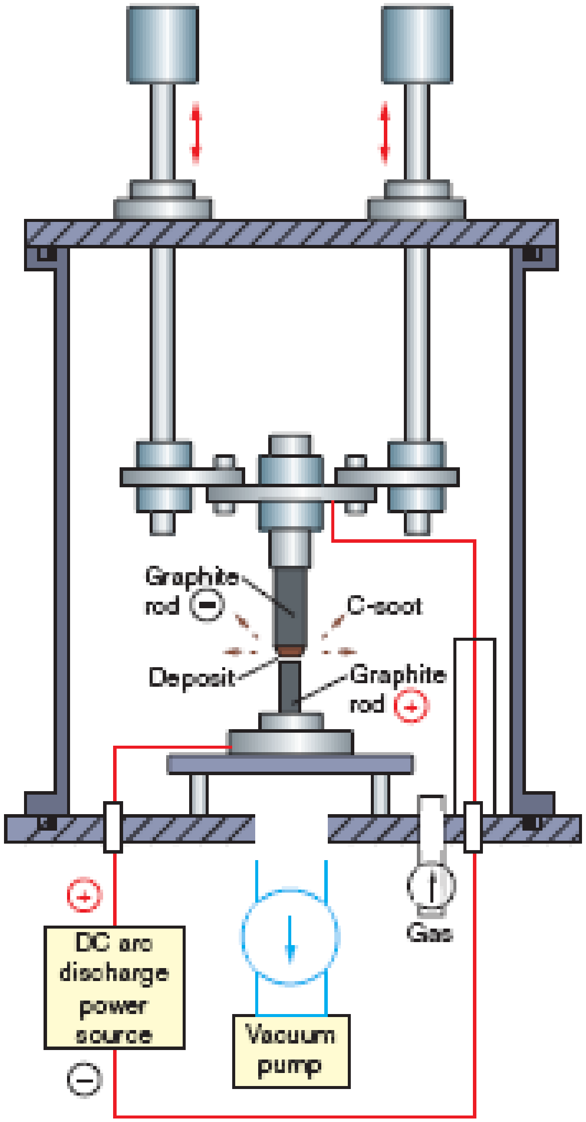
Difficult task - Handling because of size

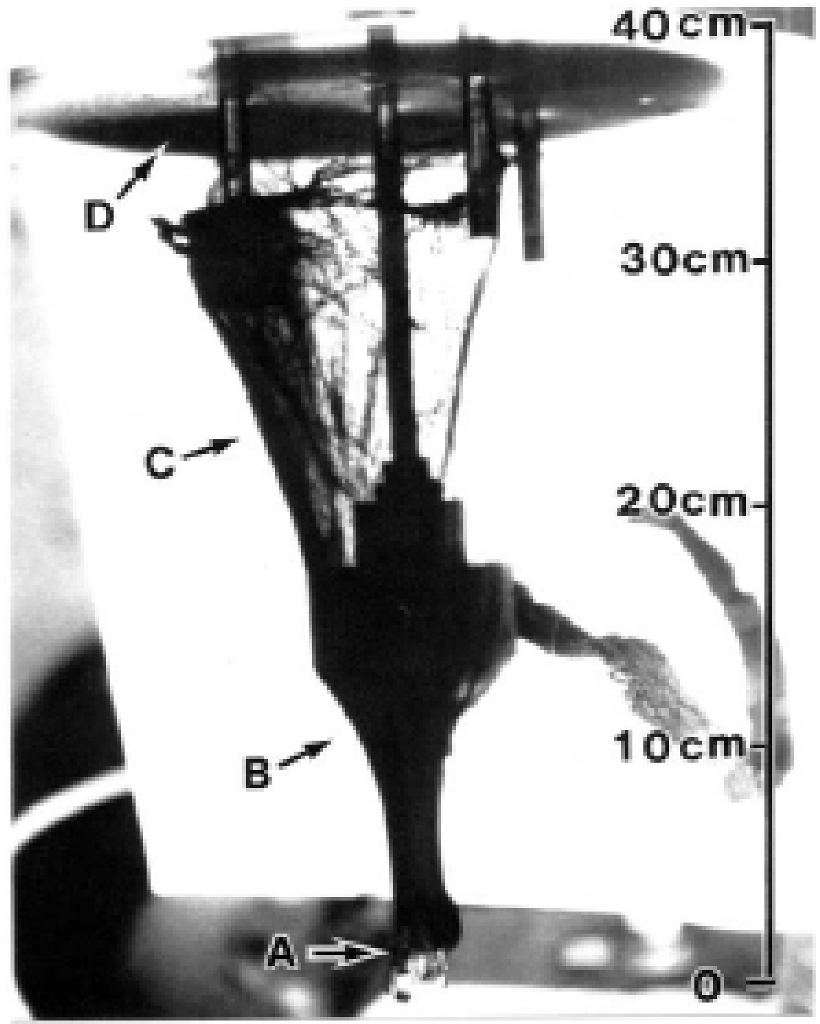
Different Types of SWNTs

- armchair (n,n)
- zigzag (n,0)
- chiral (2n,n)



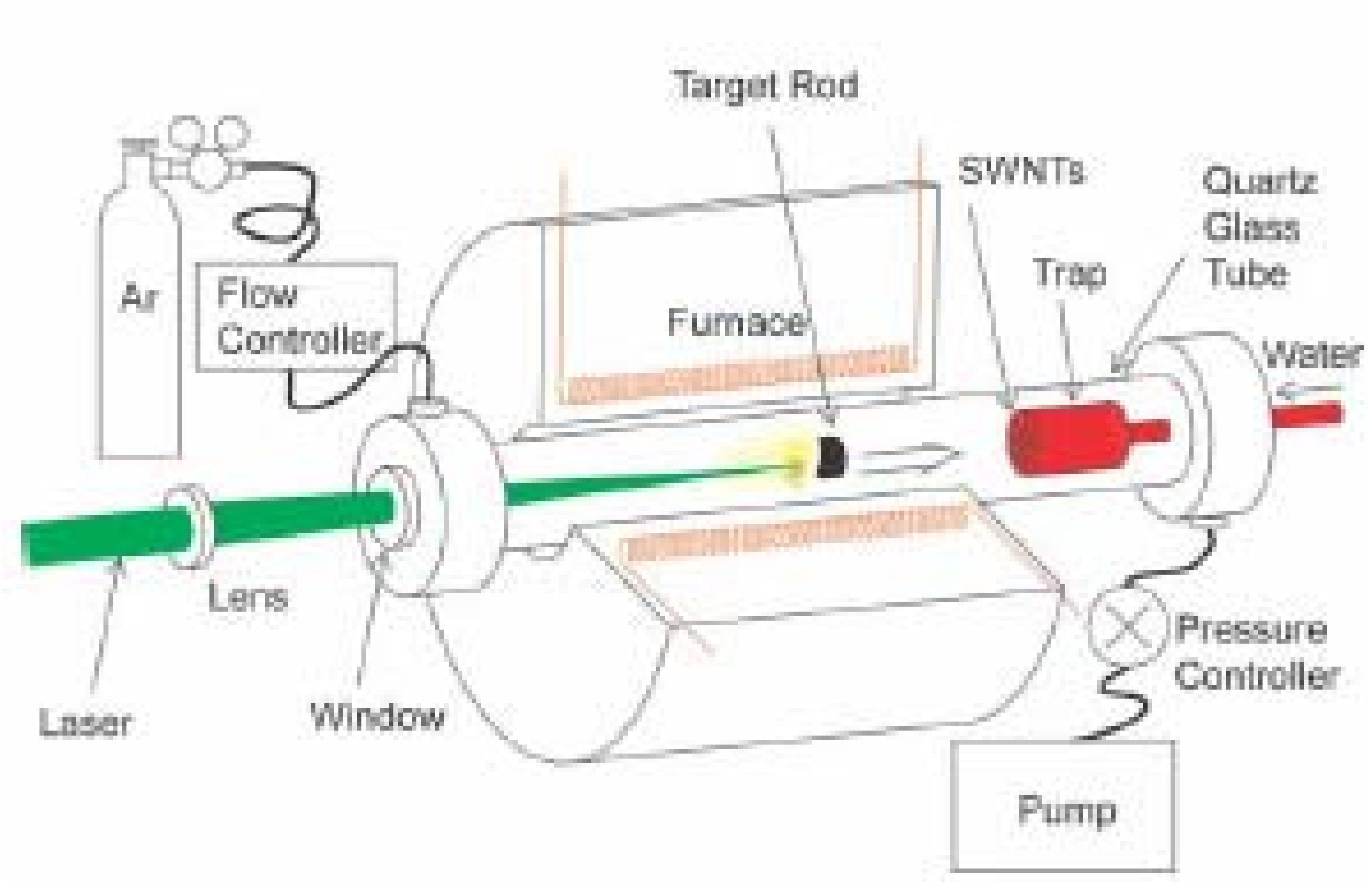
Arc Discharge





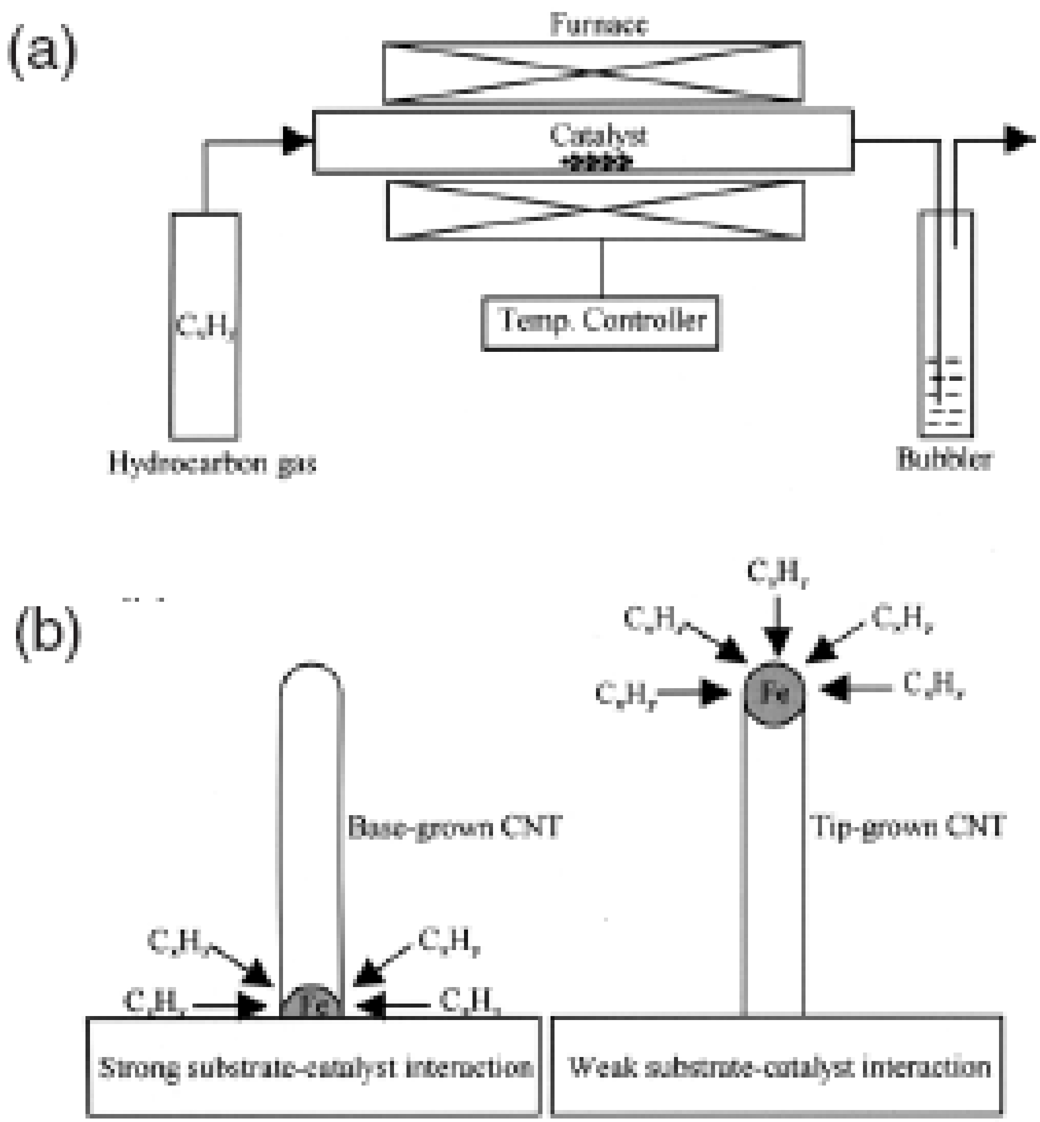
Yoshinori Ando et al., Materials today, 2004, 22

Laser Furnace Method



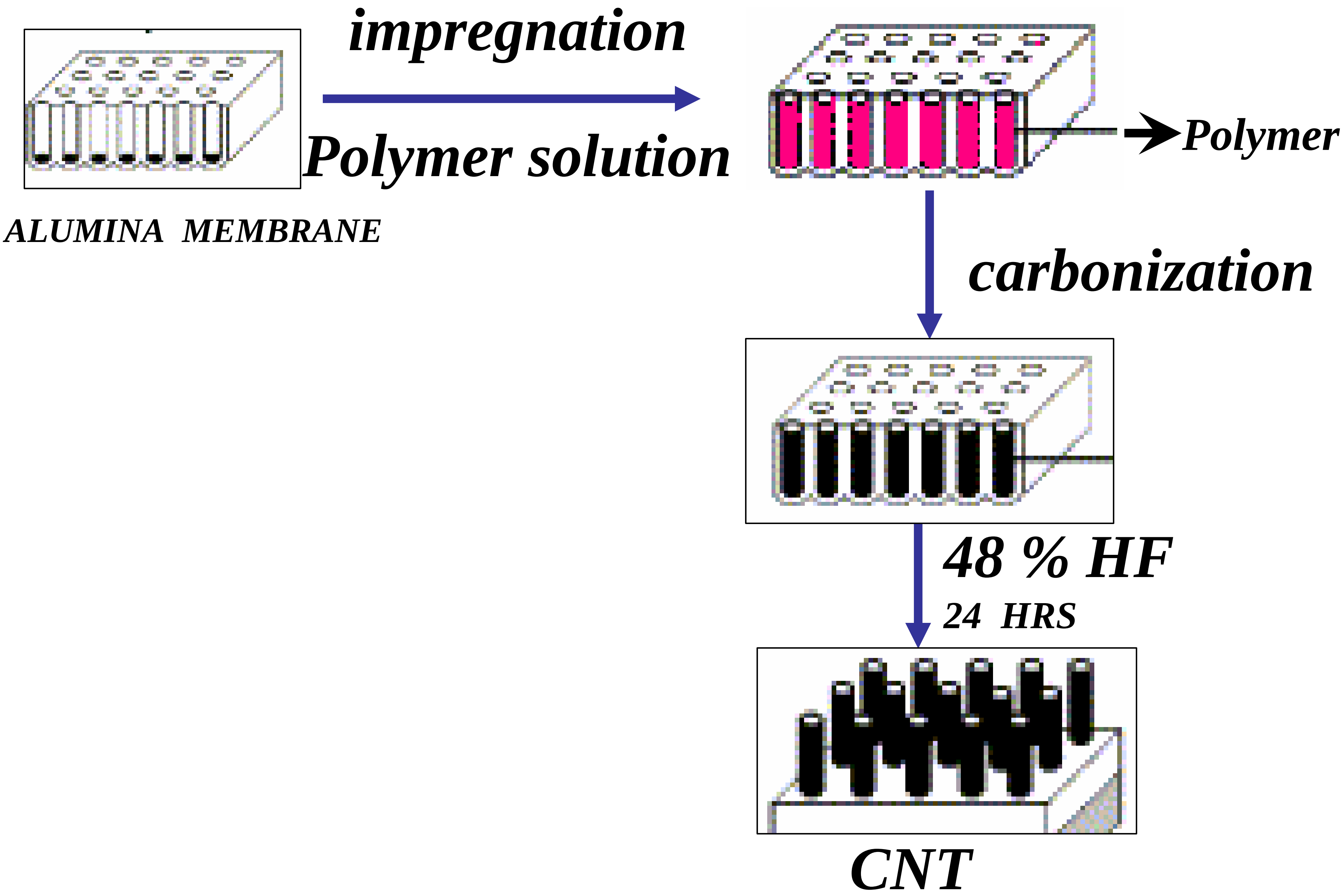
Yoshinori Ando et al., Materials today, 2004, 22

Chemical Vapour Deposition

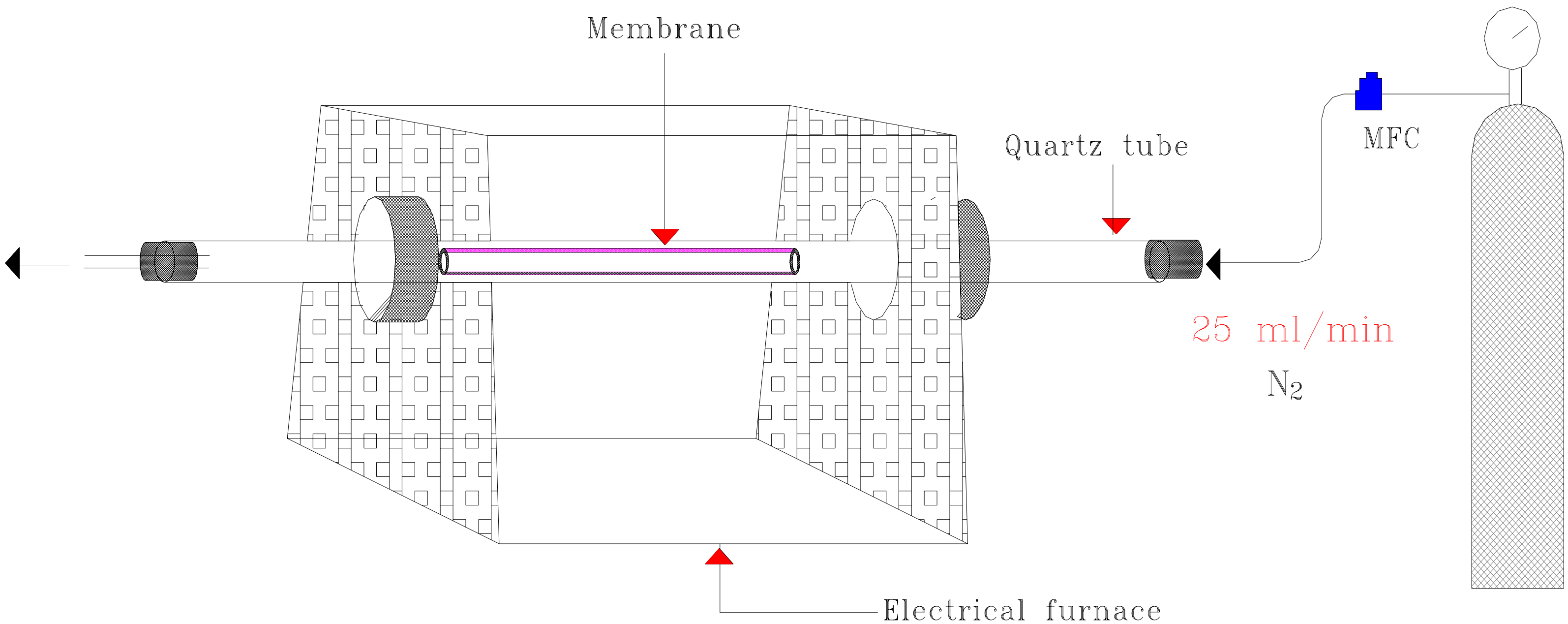


Yoshinori Ando et al., Materials today, 2004, 22

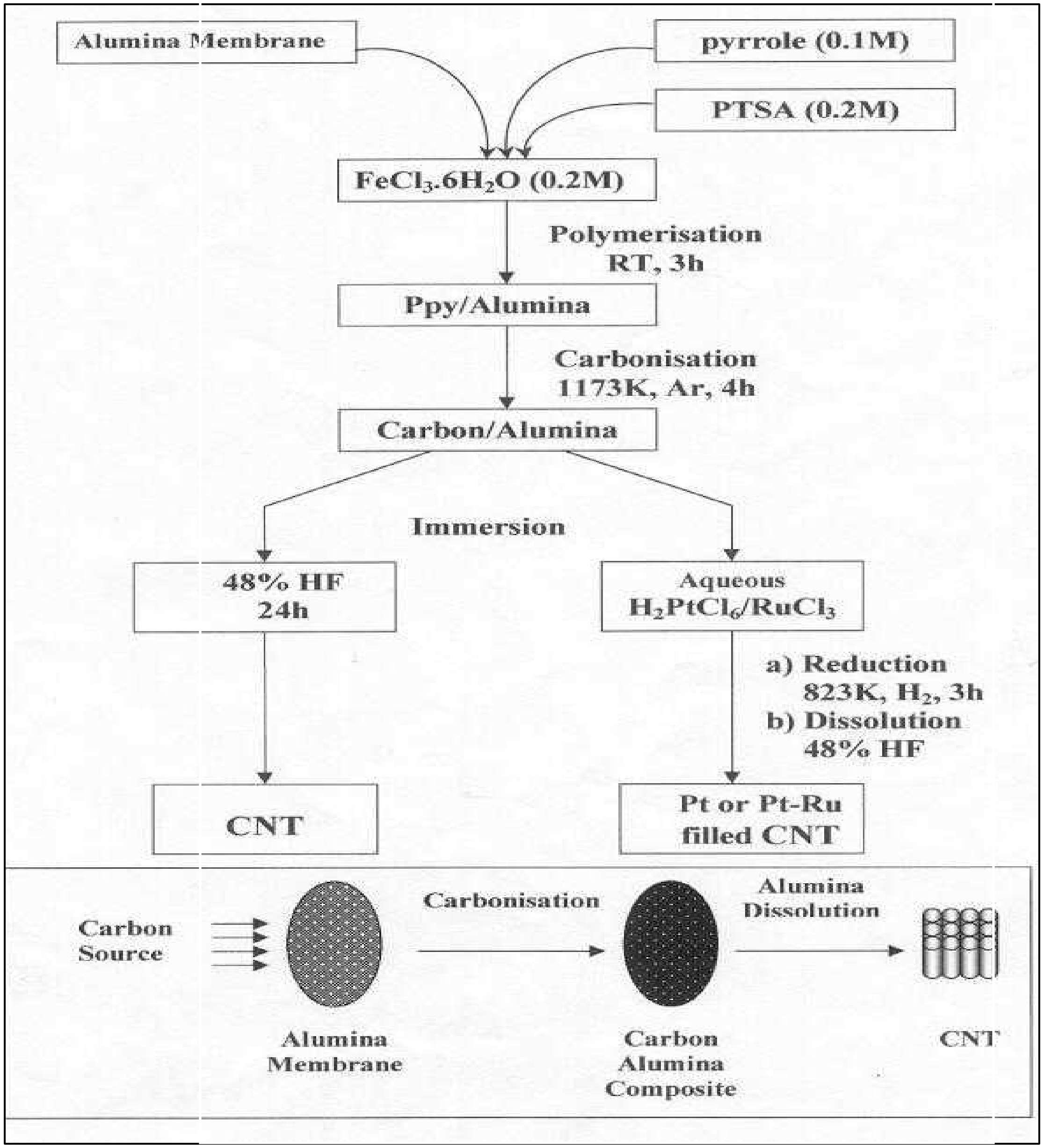
Schematic Diagram



Carbonization apparatus



Synthesis of loaded (metal(s)) carbon nanotubes



Physical Properties of Carbon Nanotubes

Going to Extremes

PROPERTY	SINGLE-WALLED NANOTUBES	BY COMPARISON
Density	1.33 to 1.40 grams per cubic centimeter	Aluminum has a density of 2.7 g/cm^3
Tensile Strength	45 billion pascals	High-strength steel alloys break at about 2 billion Pa
Resilience	Can be bent at large angles and restraightened without damage	Metals and carbon fibers fracture at grain boundaries
Current Carrying Capacity	Estimated at 1 billion amps per square centimeter	Copper wires burn out at about 1 million A/cm^2

Slide Generated by Dr. E. J. Siochi,
NASA Langley Research Center

Biomimicking Lotus Leaf Microstructures

- Dream of human beings – Creation of clothes that clean themselves
- Self cleaning clothes
- Two main concepts – Design surfaces that can break down, decompose dust
  Produce surfaces with repellent properties
- Common route – Treat target surface with self cleaning coatings
- Self cleaning coatings – Hydrophilic and hydrophobic
- Hydrophilic coatings – Window glass
  Cement
  Textiles
  Paints
  Self cleaning clothes

- Self cleaning clothes - Titania nanoparticles
- Potential hazards with titania nanoparticle films

- Surfaces with extreme water repellent properties are known in Nature
- Super hydrophobic nature of lotus leaves – lotus leaf effect or self cleaning effect

Youyang Liu, J. Mater. Chem., 17 (2007) 1071

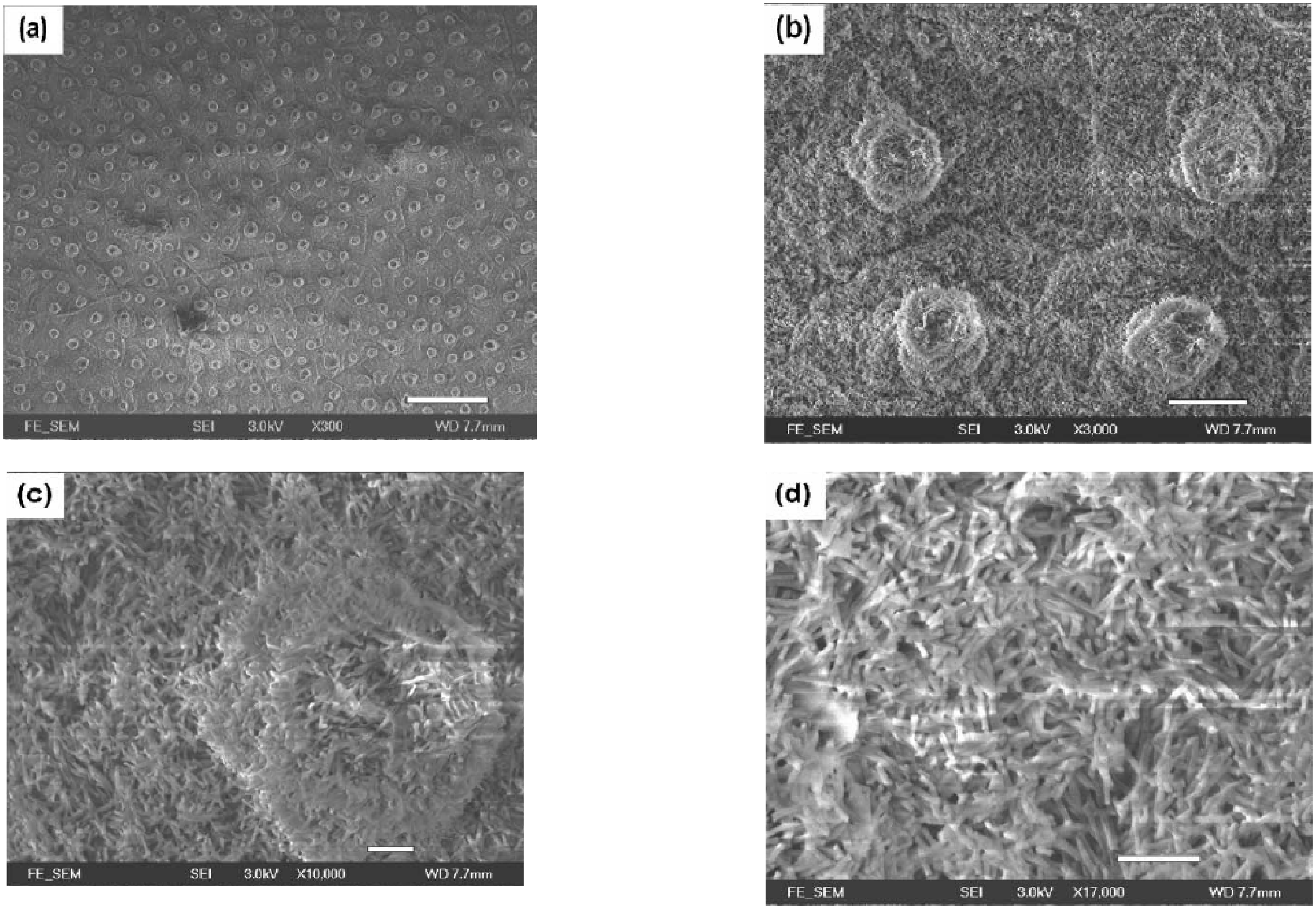
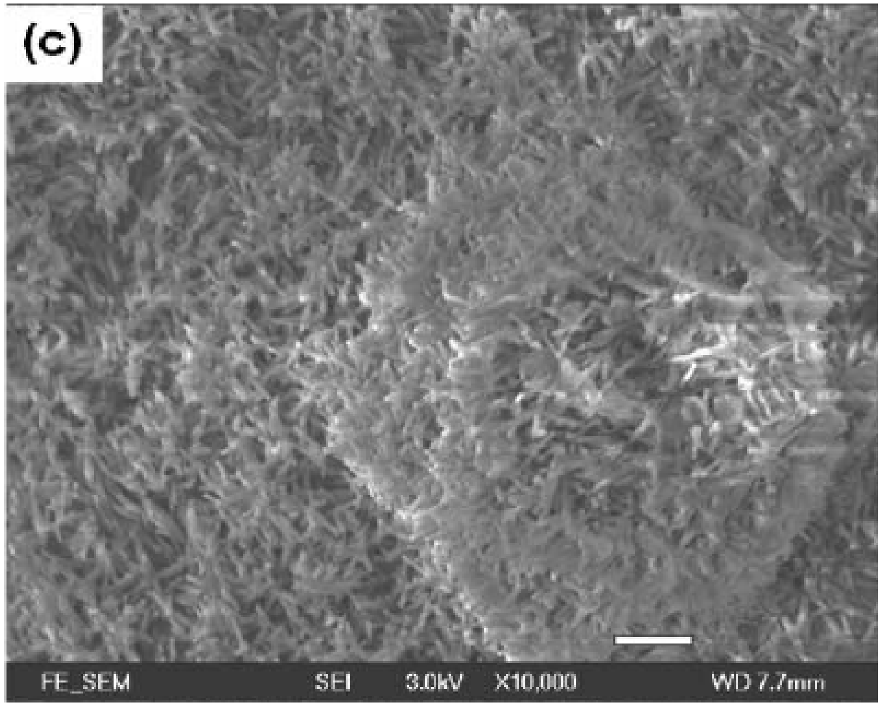


Fig. 10. (a) top view of a lotus leaf (bar = 50 mm). (b) Magnified section of the lotus leaf from (a) (bar = 5 mm). (c) Magnified view of a papilla from (b) (bar = 1 mm). (d) SEM image of the bottom surface of the lotus leaf from (a) (bar = 1 mm).

Morphology of Lotus leaves Vs Carbon nanotube clusters



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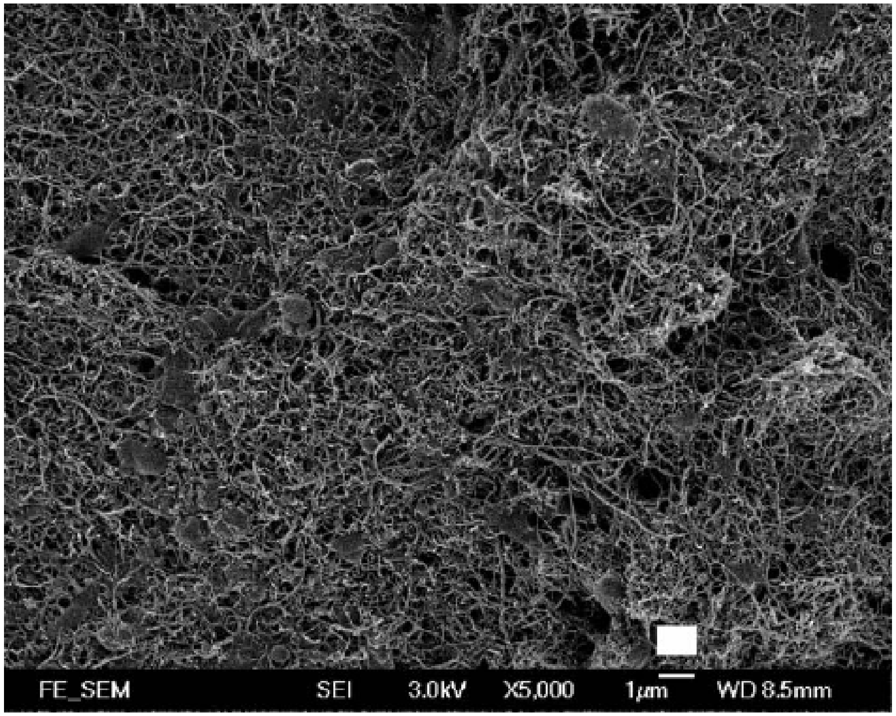
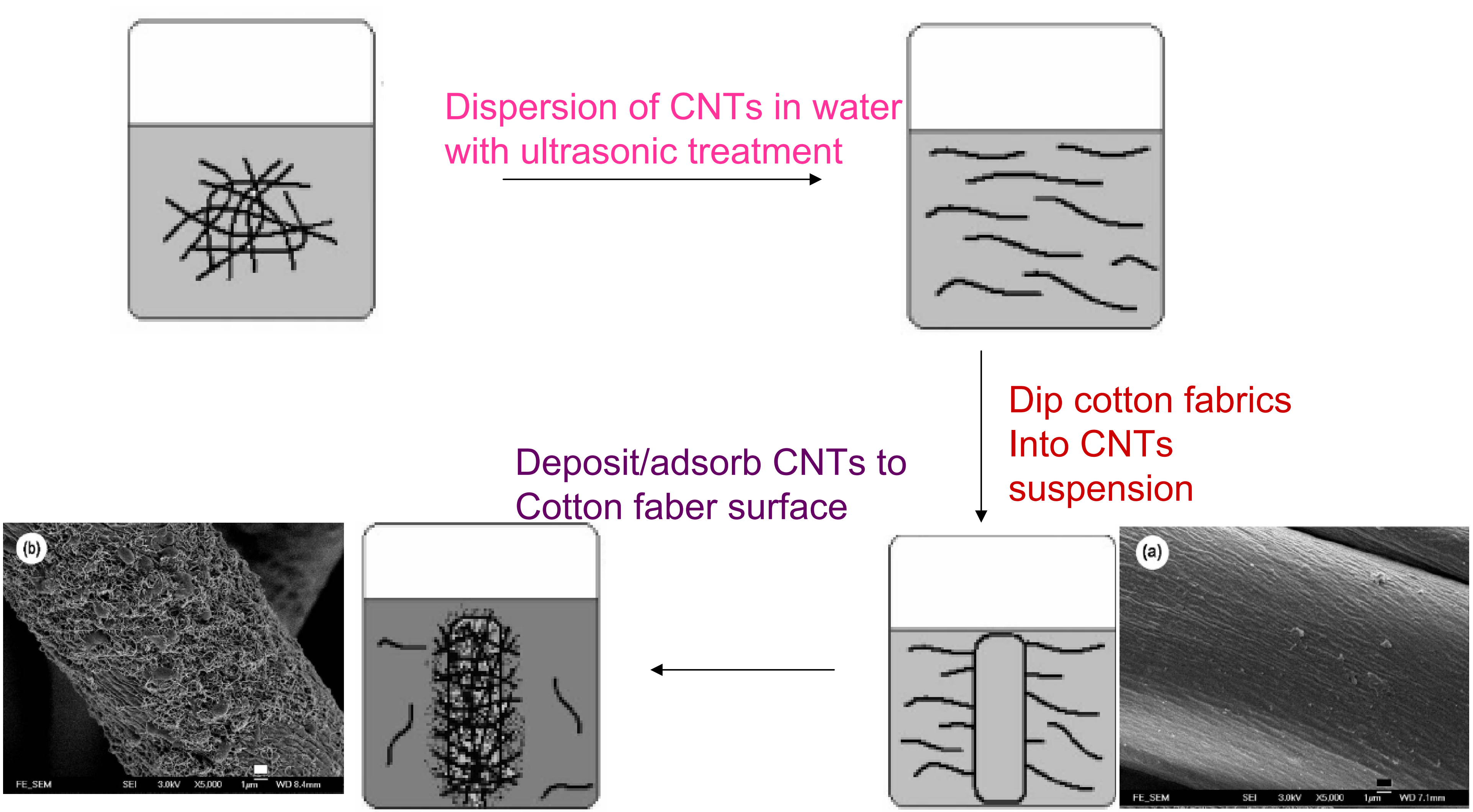


(2)

Fig. 11. (1) Magnified vew of Papilla of Lotus leaf, (2) SEM image of MWNTs deposited on silicon wafer (bar = 1 μm)

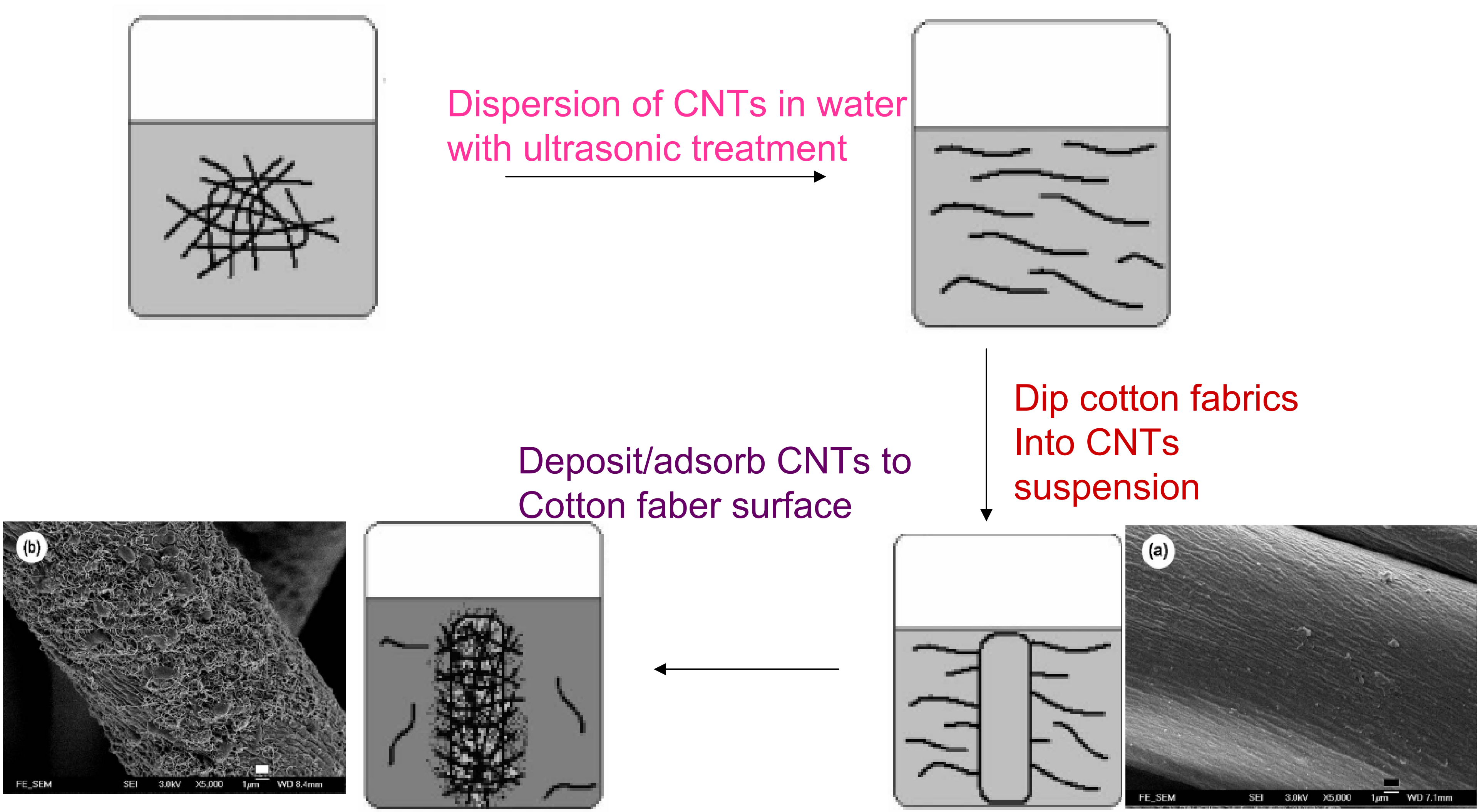
- Carbon Nanotubes are ideal candidates for the fabrication of artificial lotus leaves
- Carbon nanotube clusters with micro-nano binary structures form a good mimic of lotus leaves

Self cleaning coating – Lotus leaf effect



Scheme 1. Procedure for coating cotton fibres with carbon nanotubes

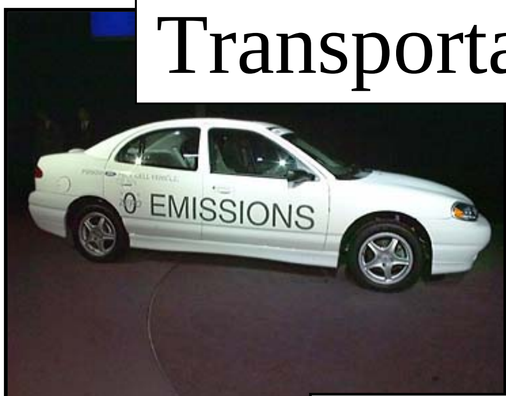
Self cleaning coating – Lotus leaf effect



Scheme 1. Procedure for coating cotton fibres with carbon nanotubes

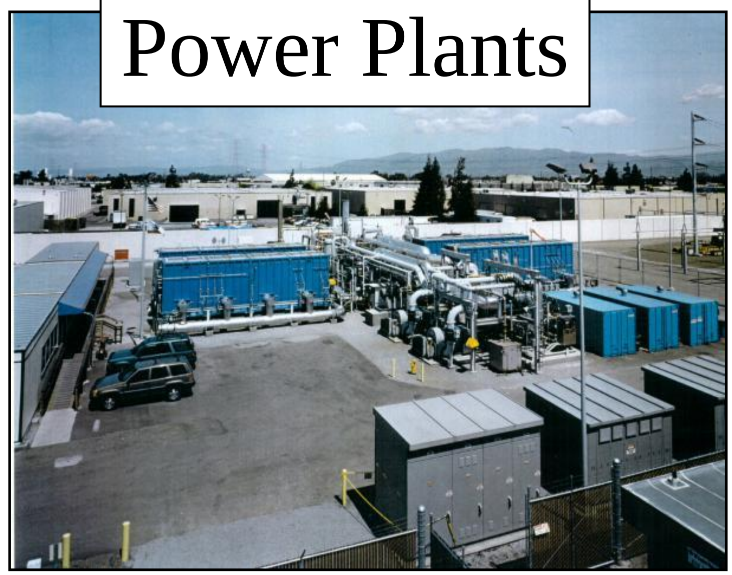
Fuel Cell Applications

Transportation



Residential

Industry &
Power Plants



- Current understanding of Nanoscience and technology is only the tip of a pyramid that has recently been uncovered from the sands of ignorance.

- Ready availability of ever more sophisticated characterization methods that allow us to visualize and probe materials at the nanoscale has accelerated the pace of activities in this field.

- Commercial nanotechnology is at a nascent stage. Efforts should be directed at learning how to build robust manufacturing processes.

- Chemicals and electronics are the two industries with the most to gain from nanotech R & D

The bottlenecks facing early stage nanotechnology commercialization :

- ❖ Large-scale production challenges
- ❖ High production cost
- ❖ The public's general reluctance to embrace innovative technology without real safety data or products
- ❖ A well-established micron-scale industry

References :

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