

Nanochemistry Review

- ✓ Nano definitions
- ✓ Nanomaterials classification:
- ✓ Why nanochemistry
- ✓ Size dependent properties
- ✓ Preparation methodologies
- ✓ Identification techniques

Nano terms definitions

Nano: Greek words which means dwarf (small man).

Nano :In standard international units (SIU) is prefix denotes a fraction of 10^{-9} a given unit like nanometer, nanogram, nanolitter ,.....etc, for instance $1\text{nm} = 10^{-9}\text{ m}$.

Nanochemistry Confinement of chemical reactions on nanometer length scale to produce chemical products that are of nanometer dimensions (1to100nm) or Preparation and organization of nanoparticles.

Nanoscience is the actual “science” or basic study of systems and materials at the nanoscale (1-100nm).

Nanostructured Materials : any material that has a feature or properties of interest in at least one dimension that is nanoscale (under 100 nm

Nanotechnology is the “integration of multiple disciplines, technologies, materials, and processes to enable the creation, assembly, measurement or manipulation of things at the nano and molecular level

Nanotechnology is the application of Nanoscience to a broad set of emerging manufacturing technologies, which control and manipulate material at the level of atoms and molecules. Also can be defined as: research and technology development at the atomic, molecular or macromolecular levels, in the length scale of approximately 1 – 100 nanometer range or creating and using structures, devices and systems that have novel properties and functions because of their small and/or intermediate size, or ability to control or manipulate on the atomic scale.

Size dependent properties (unique properties)

The following are just a few examples:

- 1-melting point and other phase transition temperatures ;
 - 2-colour and other optical properties of nanomaterials
 - 3-Electrical conductivity
 - 4- Chemical properties: such as; activity, ionization potential and electron affinity
 - 5-magnetic properties: when gold and platinum become magnetic
 - 6- Mechanical properties of nanomaterials :CNT'S are 100 times stronger than steel .
- As an example: The differences between nanogold and bulk gold

Nanogold	Bulk gold
1-its melting points depends on size it decreases with decreasing on size 400-1150 C	1-fixed melting point 1150C
2-can be magnetized	2-Non magnetic
3-chemically active so it can used as Catalyst	3-chemically inert
4-can take any colors depending on its sizes (yellow-red-blue-violet)	4-it is well known yellow color
5-less conductivity	5-more electrically conductive

Other examples:

- Copper which is an opaque substance become transparent.
- Platinum which is an inert material become catalyst.
- Aluminum which is a stable material turns combustible.
- Silicon insulators become conductors.

The reasons for such differences

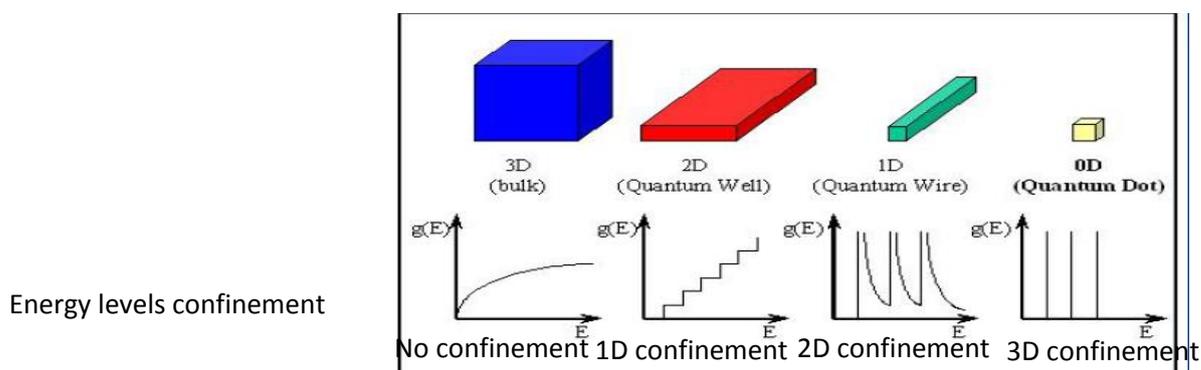
Some known properties of nanomaterials are related to different origins:

- 1-Quantum effect (spatial confinement) that make the energy gabs more affected by sizes of particles.
- 2-Surface area to volume ratio which became very far from bulk materials and led to make the particles more active (large fraction of surface atoms large surface energy and).
- 3-Particles have more freedom .
- 4-The effect of electromagnetic waves are more than the Gravity forces.

Nanomaterial clasification

1-According to dimention:

- 1-(0D) zero dimensions all three dimensions are at nanoscale or there is no micro-dimension like quantum dots (ZnO,PbS),nanogold,...
- 2-(1D) one dimensions (only one dimension is micro like length)such as carbon nanotubesw,Ni wires,....
- 3-(2D) two dimensions (two micro dimensions) like nano films (Ag,Au,...)
- 4-(3D) three dimensions (all dimensions are micro-size) like composite and clusters (polymers with nanoparticles) polystyrene with nano MgO.

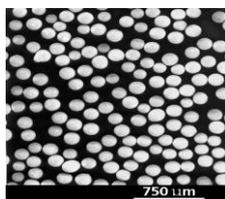


2-According to shape:

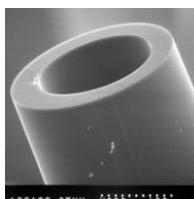
- 1-Nanoparticles or nanospheres: like quantum dots (ZnO,PbS),nanogold
- 2-Nanotubes or nanowires or nanorods: like carbon nanotubesw,Ni wires
- 3-Nanoscale thin films or ultra-thin films: like nano films (Ag,Au,...)
- 4-Nanocomposites: a material comprised of many nanoscale inclusions (such as nanoparticles)
- 5-Nanostructured materials: a material that exhibits a unique structure that can be measured at the nanoscale

3-According to composition:

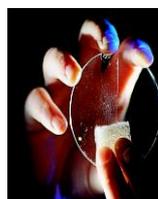
- 1-Carbon Based Materials(hollow spheres, ellipsoids, or tubes. Spherical and ellipsoidal , Carbon Nanotubes/Fullerenes).
- 2-Metal Based Materials(quantum dots, nanogold, nanosilver and metal oxides, such as titanium dioxide).
- 3-Dendrimers (nanosized polymers built from branched units) like polyimidomethyimethaacylate (PMMA).
- 4-Composites(combine nanoparticles with other nanoparticles or with larger, bulk-type materials, polystyrene with nano MgO).
- 5- Inorganic-Organic Hybrid Nanoparticles (Polyhedral Silsesquioxanes).
- 6-Nano-Intermediates like metal alkoxides (titanium isopropoxide).



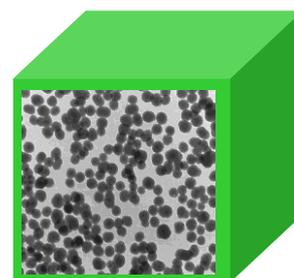
Nanoparticles



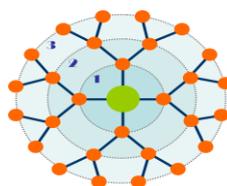
nanotubes



ultrathin film



nanocomposite



Dendrimer

Preparation Methodologies

There two main approaches:

A-Top-Down approach

1-Grinding/Milling

2-Nanolithography

Conventional Mask

Scanning E-Beam,I-Beam

Soft Nanoprinting

spherical

3-Laser ablation

B-Bottom-up approach

1-Gaseous phase methods

- CVD chemical vapor deposition and MOCVD
- IGC inert gas condensation
- MBE molecular beam epitaxy and MOVPE metal oxide vapor phase epitaxy
- ALD atomic layer deposition
- Flame pyrolysis (Combustion)
- Thermolysis
- Ion Implantatio

2-liquid phase methods

- MSA molecular self-assembly
- Supramolecular chemistry
- CBD chemical bath deposition
- Sol-gel process

- Single crystal growth
- Electrodeposition/electroplating
- Anodizing
- Molten salt electrolysis
- Hydrothermal
- Polyol
- Colloidal
- Water - oil microemulsions

3-solid phase methods

4-biological methods

Nanostructure Identification

- X-Ray diffraction (XRD)
- Electron Microscopy
 - Scanning Electron Microscope(SEM)
 - Transmission Electron Microscope(TEM)
- Scanning Probe Microscope(SPM)
 - Atomic Force Microscope(AFM)
 - Scanning Tunneling Microscope(STM)

Characteristic Information

Topography (SEM,AFM)

The surface features of an object or "how it looks", its texture.

Morphology(SEM,TEM,AFM)

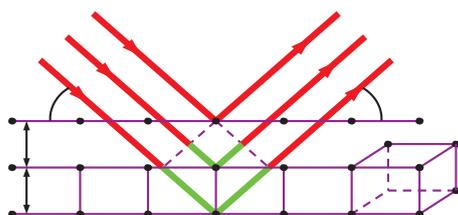
The shape and size of the particles making up the object.

Composition(XRD,XRF,AAS)

The elements and compounds that the object is composed of and the relative amounts of them;

Crystallographic Information(XRD,SEM,AFM)

How the atoms are arranged in the object.

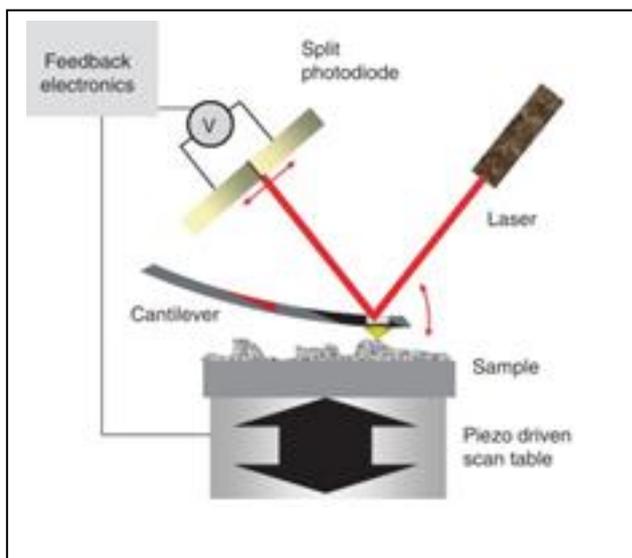
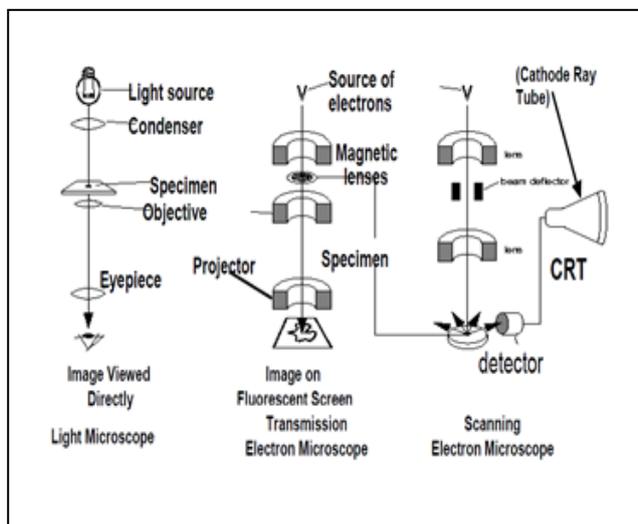
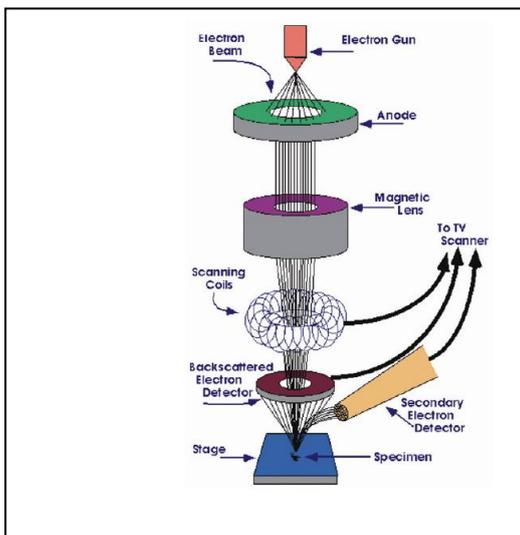


$$\lambda = 2d \sin\theta$$

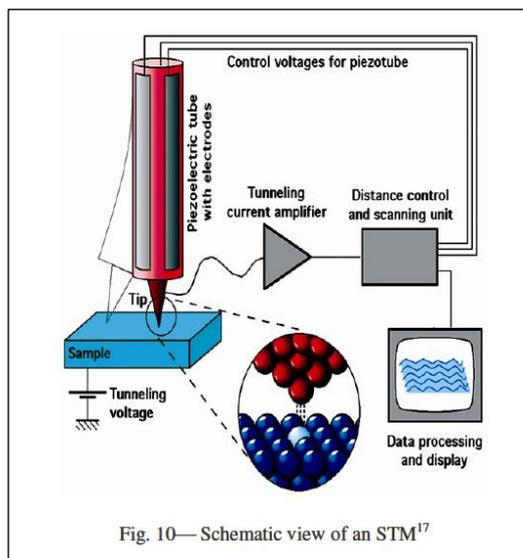
$$t = \frac{K * \lambda}{B * \cos\theta_B}$$

XRD principles

Comparison of OM,TEM and SEM



AFM

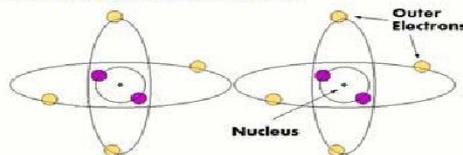


STM

Carbon Nanomaterials (Carbon Allotropes)

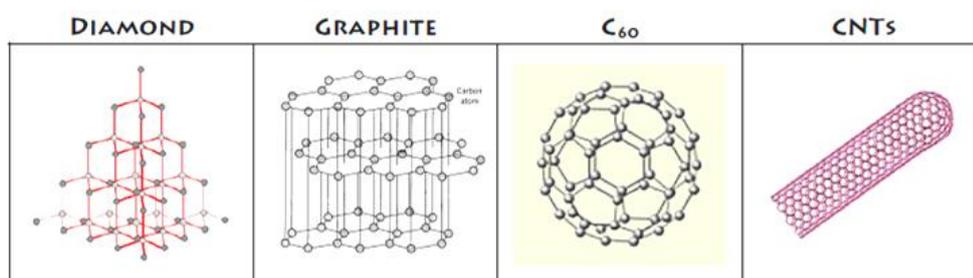
Carbon as element is non metal of group(IVA) with atomic number of 6 and atomic weight of 12, the electronic configuration ; $1S^2S^22P^2$

Carbon Atoms



Carbon has mainly 5 forms called Allotropes ((**different forms** of the same element where the atoms are arranged differently.)):

Diamond ,Graphite,Graphene (2D),Fullerenes (ball molecules),and Carbon nanotubes (rolled graphene sheet)

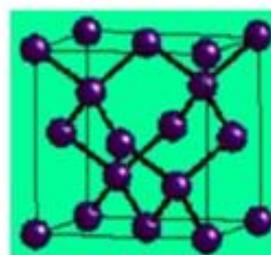


1- Diamond

Carbon atoms with orbitals of sp^3 hybridization, Has a rigid structure
 It does not conduct electricity because it doesn't have any free electrons.
 It is insoluble in water.

It is used in jewellery because it is transparent and lustrous.

Has a very high melting point because of the strong covalent bonds



2- Graphite

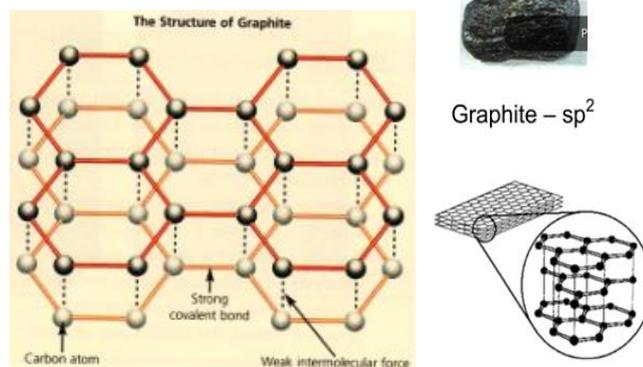
Carbon atoms with orbitals of sp^2 hybridization, Has a layered structure

It is insoluble in water, It is black which is why it is used in pencils

It conducts electricity because it has free electrons between two layers

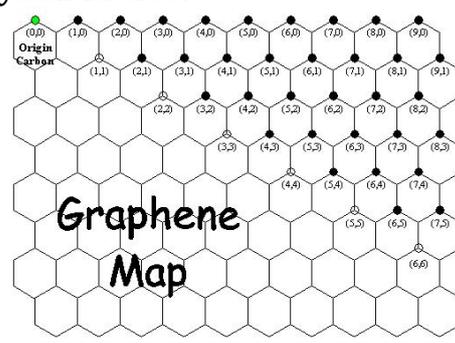
It has a high melting point because of the strong covalent bonds

The layers can slide over each other because of weak intermolecular forces between the layers



3- Graphene

Is one-atom-thick planar sheets of sp^2 -bonded carbon atoms that are densely packed in a honeycomb crystal lattice.

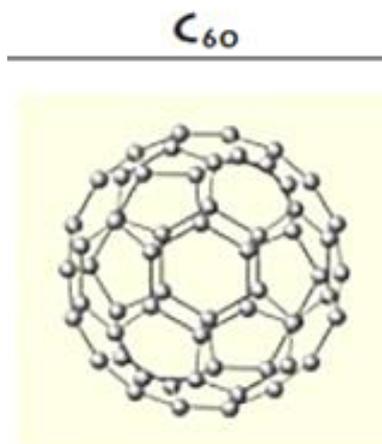


4-Fullerenes

Consists of fixed numbers of carbon atoms(60,180,...) arranged in a sphere. They are sometimes called “Bucky balls”.

It is a black solid,It makes a red solution when it is dissolved in petrol

Buckminster fullerenes or Buckyballs are otherwise known as C₆₀ - for the 60 carbon atoms which make up the soccerball shape, arranged as 12 pentagons and 20 hexagons



5-Carbon Nanotubes(CNT)

CNT can be described as a sheet of graphite rolled into a cylinder or made by joining fullerenes together. Are fullerene-related structures which consist of graphene cylinders closed at either end with caps containing pentagonal rings.

They are hexagons curled into a tube.

They conduct electricity

They are very strong (100times than ss).

There two types of CNT's :

MWCNT - Multi-Walled Carbon Nanotubes

SWCNT - Single-Walled Carbon Nanotubes

The thermal similarity of the different types of nanotubes and

The electrical differences between the different types of nanotubes

	DIAMOND	GRAPHITE	C_{60}	CNTs
Color	Colorless ¹	Steel black to grey ¹	Black solid / Magenta in solution	black
Density (g/cm ³)	3.515 ^{2,5}	1.9-2.3 ⁵	1.69 ⁵	1.33-1.4 ⁸
Specific Gravity	3.52 ³	2.2 ⁴	1.7-1.9 ⁷	2
Hardness (Moh's Scale)	10 ¹	1-2 ¹	1-2	1-2
Melting Point (°C)	3550 ⁵	3652 – 3697 ⁵	>800 (sublimes) ⁶	Similar to graphite
Boiling Point (°C)	4827 ⁵	4200 ⁵	n/a	n/a
Electrical Conductivity	Insulator ¹	Conductor ¹	Semi-conductor ⁶	Conductor to semi-conductor ¹
Hybridization	sp ³ - tetrahedral ¹	sp ² - trigonal planar ¹	sp ² - trigonal planar	sp ² - trigonal planar ¹
Crystal Shape and/or Structure	Cubic ¹	Tabular ¹	Truncated icosahedron ¹	Cylindrical ¹

The chemistry carbon nanotubes

SWNT diameter: 0.4 to 3 nm

MWNT diameter: ~1.4 to 100 nm

Length: up to several millimeters at best, usually a few microns

Single-walled carbon nanotubes (SWCNTs)

The structure of a SWNT can be conceptualized by wrapping a one-atom-thick layer of graphite called graphene into a seamless cylinder. The way the graphene sheet is wrapped is represented by a pair of indices (n,m). The integers n and m denote the number of unit vectors along two directions in the honeycomb crystal lattice of graphene.

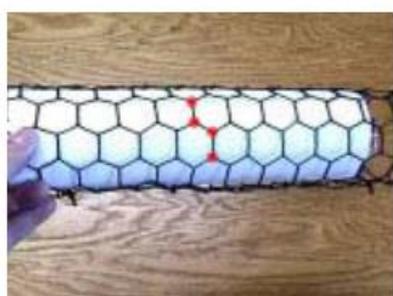
If $m = 0$, the nanotubes are called zigzag nanotubes, and if $n = m$, the nanotubes are called armchair nanotubes. Otherwise, they are called chiral. The diameter of an ideal nanotube can be calculated from its (n,m) indices as follows

$$d = \frac{a}{\pi} \sqrt{(n^2 + nm + m^2)}.$$

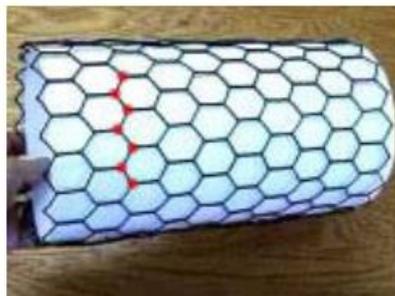
where $a = 0.246$ nm.

are most properties of SWNTs change significantly with the (n,m) values, and this dependence is non-monotonic.

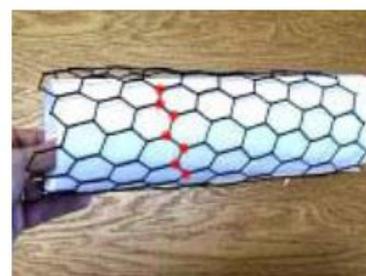
In particular, their band gap can vary from zero to about 2 eV and their electrical conductivity can show metallic or semiconducting behavior. Nanotubes are formed by rolling up a graphene sheet into a cylinder and capping each end with half of a fullerene molecule.



Armchair (n,n)

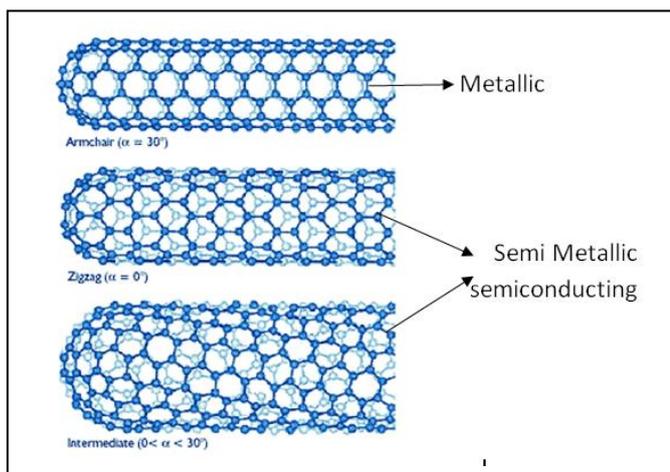
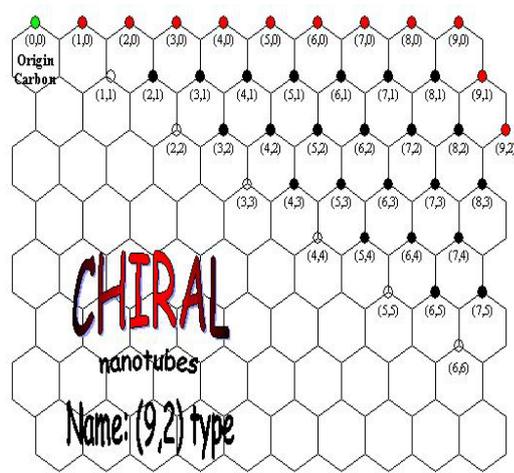
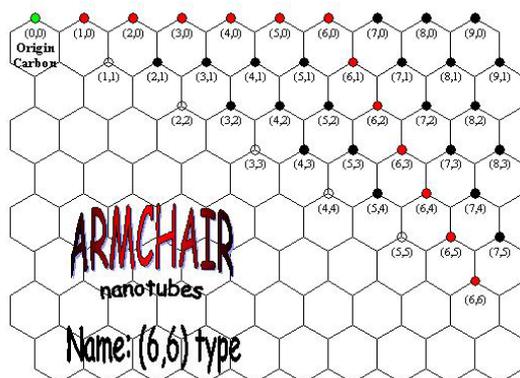
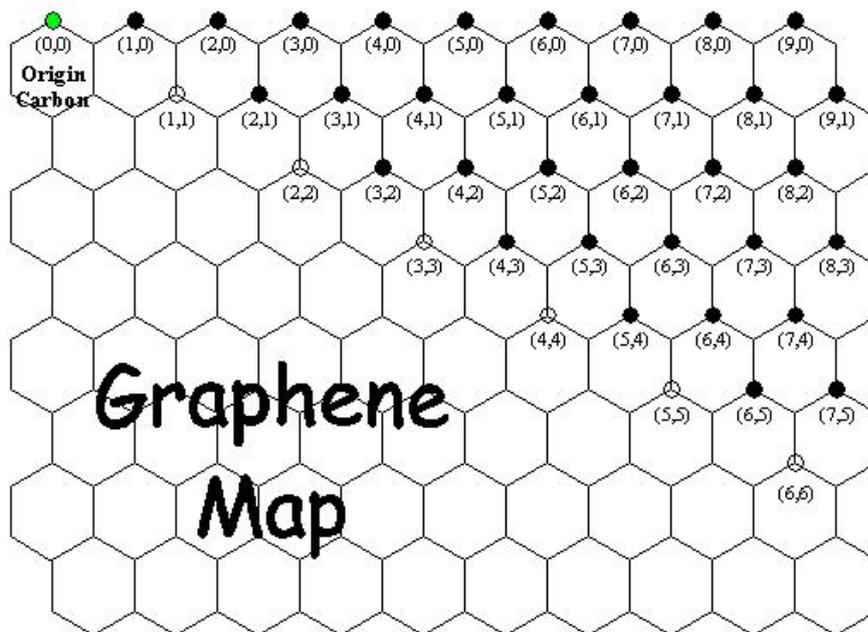


Zigzag (n,0)



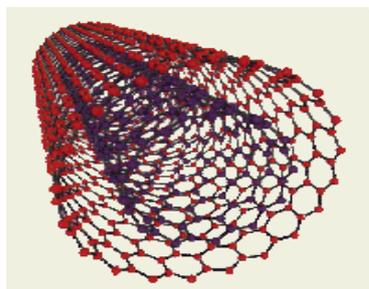
Chiral (n,m)

The way to find out how the carbon atoms are arranged in a molecule can be done by joining the vector coordinates of the atoms. By this way it can be identified whether if the carbon atoms are arranged in a zig-zag, armchair or in a helical shape.



multi-walled carbon nanotubes (MWCNTs)

Multi-walled nanotubes (MWNT) consist of multiple rolled layers (concentric tubes) of graphite.



There are two models that can be used to describe the structures of multi-walled nanotubes.

- 1- The Russian Doll model, sheets of graphite are arranged in concentric cylinders, e.g., a (0,8) single-walled nanotube (SWNT) within a larger (0,17) single-walled nanotube.
- 2- The Parchment model, a single sheet of graphite is rolled in around itself, resembling a scroll of parchment or a rolled newspaper.

The interlayer distance in multi-walled nanotubes is close to the distance between graphene layers in graphite, approximately 3.4 Å.

Double-walled carbon nanotubes (DWNT) form a special class of nanotubes because their morphology and properties are similar to those of SWNT but their resistance to chemicals is significantly improved. This is especially important when fictionalization is required (this means grafting of chemical functions at the surface of the nanotubes) to add new properties to the CNT. In the case of SWNT, covalent fictionalization will break some C=C double bonds, leaving "holes" in the structure on the nanotube and, thus, modifying both its mechanical and electrical properties. In the case of DWNT, only the outer wall is modified.

The main differences between SWCNT & MWCNT :

SWCNT	MWCNT
1-single layer of grapheme	1-multiple layer of graphene
2-requierd catalyts for synthesis	2- no need for catalyts
3-bulk synthesis is difficult	3-bulk synthesis is easy
4-purity is poor	4-purity is high
5-easy to be characterized	5-has very complex structure
6-can be twisted easily	6-difficult to twist

Chemical functionalization of Carbon nanotube

Because of their hydrophobic nature, carbon nanotubes tend to agglomerate hindering their dispersion in solvents or viscous polymer melts. Unsurprisingly, the resulting aggregates reduce the mechanical performance of the final composite. Effort has been directed at modifying the surface of the carbon nanotube to reduce the hydrophobicity and improve interfacial adhesion to a bulk polymer through chemical attachment. The carbon nanotube chemistry involves three main approaches, where reactions target:

- 1- surface groups generated through acid-induced oxidation of the carbon nanotube surface;
- 2- direct addition to the carbon nanotube sidewalls;
- 3- groups attached to polycyclic aromatic hydrocarbons that are immobilised to the carbon nanotube surface through Van der Waals forces.

Nanotubes

Special properties of CNTs

- 1-Difference in chemical reactivity for end caps and side wall
- 2-High axial mechanical strength
- 3-Special electrical properties: Metallic, Semi conducting

Synthesis techniques:

There are mainly three Techniques to prepare CNTs they differ in:

- Type of prepared nanotubes (SWNT / MWNT / Aligned)
- using or not Catalyst
- the Yield of the process
- the Purity of the final products

these techniques are;

1-Chemical vapor deposition(CVD)

Which produces both SWNTs / MWNTs

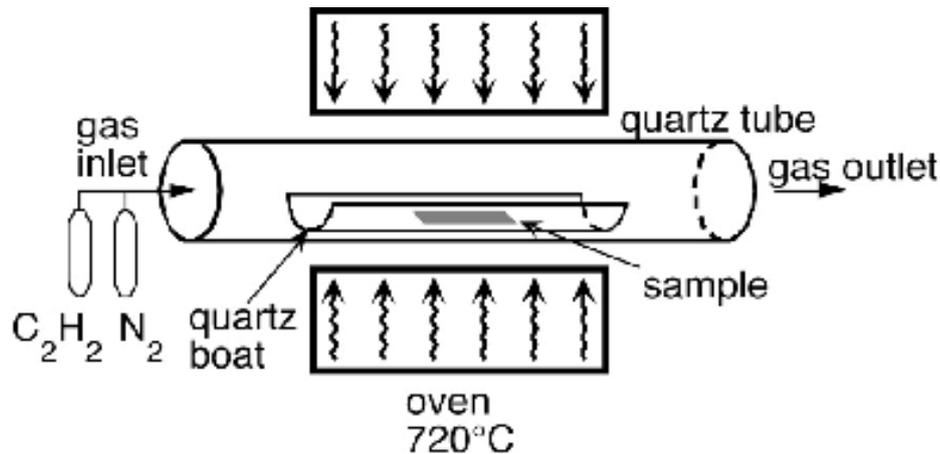
The nanotubes are Aligned

Can be deposited on Patterned substrates

The reaction take place from Gas phase deposition

In This method Large scale is possible

It is Relatively cheap



Need to Deposit CNTsa few particles of Iron (most common) or Ni to act as catalyst.

Apply a hot environment of carbon containing gas (typically CH₄ nor C₂H₂)

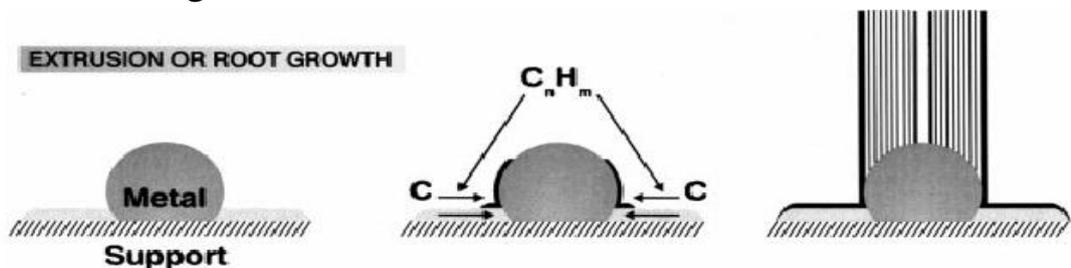
The particle catalyzes the decomposition of the gas and carbon dissolves in the particle.

When the particle is supersaturated with carbon, it extrudes the excess carbon in the form of a tube.

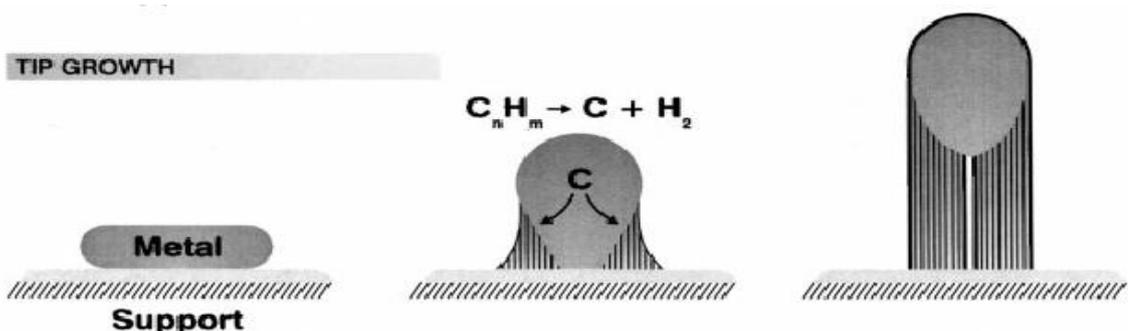
Growth mechanism

There are two mechanisms :

First :Extrusion growth

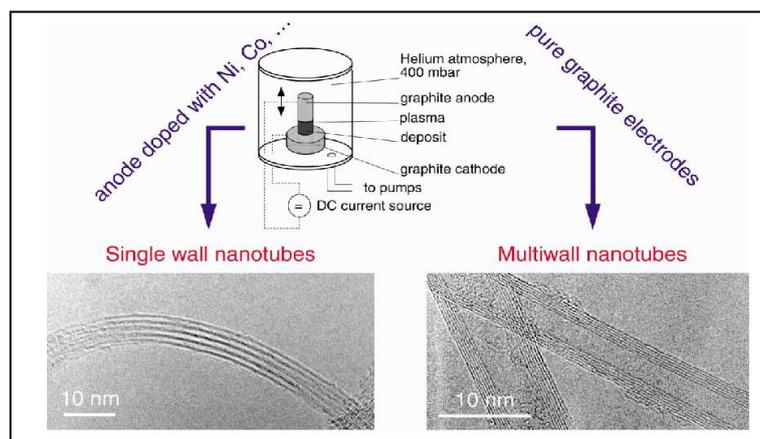


Second: Tip growth



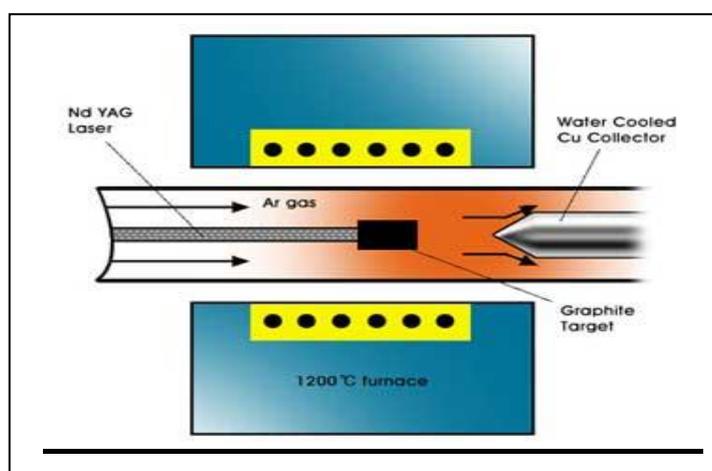
2-Arc discharge

- MWNTs and SWNTs
- Batch process
- Relatively cheap
- Many side-products



3-Laser ablation

- Catalyst / no catalyst
- MWNTs / SWNTs
- Yield <70%
- Use of very strong laser
- Expensive (energy costs)
- Commonly applied



Purification techniques

The Prepared CNTs always need to be purified ,and the way depends on the kinds of impurities ;

1-Removal of catalyst:

- A-Acidic treatment (+ sonication)
- B-Thermal oxidation
- C-Magnetic separation (Fe)

2- Removal of small fullerenes

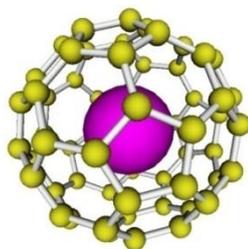
- A-Micro filtration
- B-Extraction with CS₂

3- Removal of other carbonaceous impurities

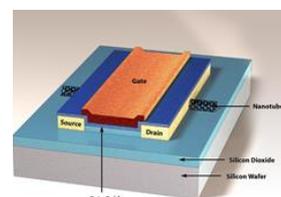
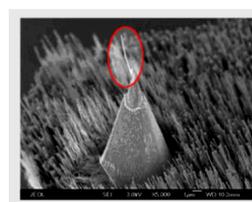
- A-Thermal oxidation
- B-Selective functionalization of nanotubes
- C-Annealing

Applications of nanocarbons

1-They can be used to cage other molecules inside them They will be useful for drugs. For example a major new HIV treatment uses “Bucky balls” to deliver a material which disrupts the way the virus works.

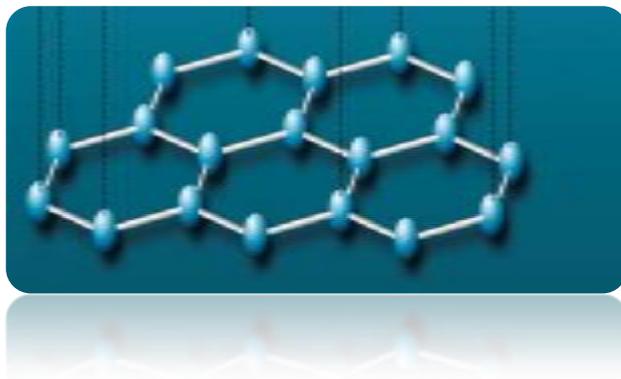


- 2- They conduct electricity and are very strong.
- 3-They are used to reinforce polymers
- 4- Make semiconductors in modern computers
- 5-develop new, more efficient catalysts
- 6-AFM Tip
- 7-Molecular electronics (Transistor)
- 8-FED devices (Displays)
- 9-Energy storage:Li-intercalation,Hydrogenstorage,Super capacitors
- 10-sensors
- 11-Field Emission (LED, etc)
- 12-Conductive plastics
- 13-Conductive adhesives & Connectors
- 14-Thermal materials (conduct or insulate)
- 15-Structural composites (Boeing 787,buildings,etc)
- 16-Catalytic & biomedical supports
- 17-Controlled Drug Delivery/release
- 18-Artificial muscles
- 19-Supercapacitors
- 20-Batteries
- 21-Nano lithography
- 22-Nano balance
- 23-Nano tweezers
- 24-Magnetic nanotube
- 25-Nanogear
- Nanotube actuator
- 27-Hydrogen Storage



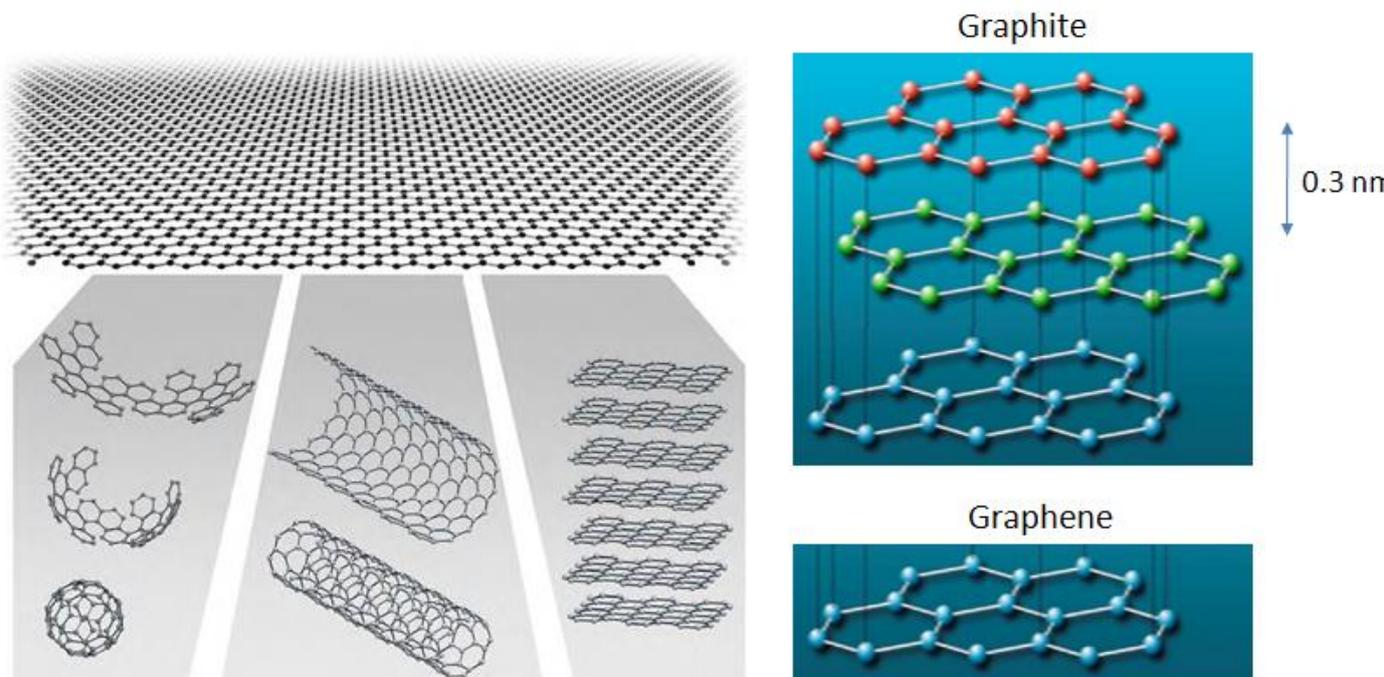
The Chemistry of Graphene

Graphene is an allotrope of carbon, whose structure is one-atom-thick planar sheets of sp²-bonded carbon atoms that are densely packed in a honeycomb crystal lattice.



Graphene is a flat monolayer of carbon atoms tightly packed into a two-dimensional (2D) honeycomb lattice, and is Mother of all Graphitic Forms;

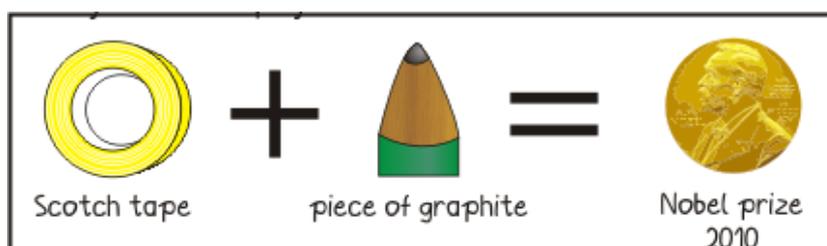
- 1- Is a basic building block for graphitic materials of all other dimensionalities.
- 2- It can be wrapped up into 0D fullerenes,
- 3- rolled into 1D nanotubes or stacked into 3D graphite



Graphene is a 2D building material for carbon materials of all other dimensionalities. It can be wrapped up into 0D **buckyballs**, rolled into 1D **nanotubes** or stacked into 3D **graphite**.

The carbon-carbon bond length in graphene is about 0.142 nanometers

Graphene sheets stack to form graphite with an interplanar spacing of 0.335 nm, which means that a stack of three million sheets would be only one millimeter thick. The Nobel Prize in Physics for 2010 was awarded to Andre Geim and Konstantin Novoselov "for groundbreaking experiments regarding the two-dimensional material graphene"



Unusual properties

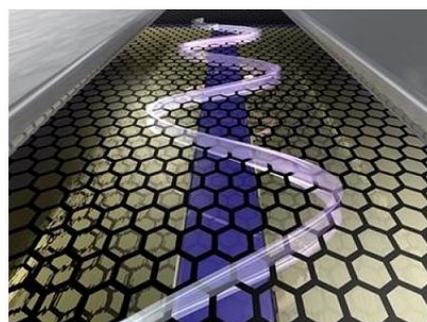
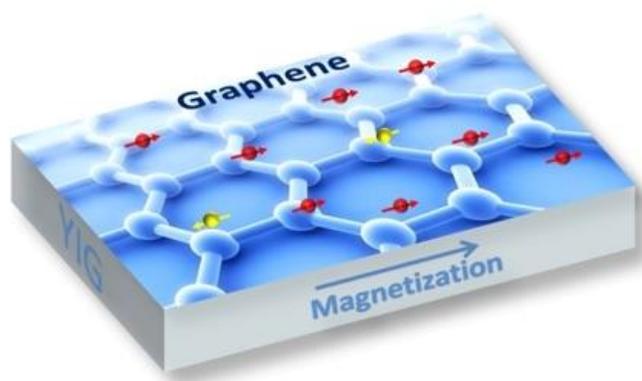
1-transparency like glass, Absorbs 2.3% white light

- Optical electronics absorb <10% white light
- Highly conductive
- Strong and flexible

2-ballistic transport of charges and electrons, the speeds at which electrons flow through a material at room temperature) were ten times faster than previous theoretical limits which offers a New Capability in Graphene

3-harder than steels

4-huge surface area (3000m²/g)



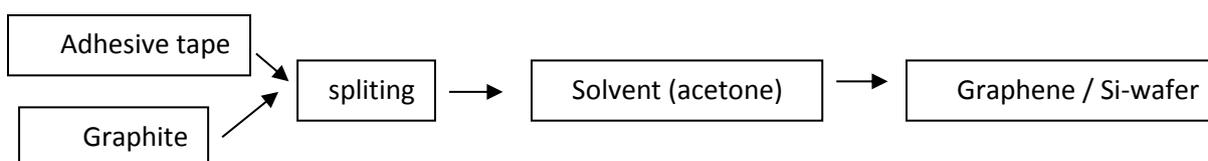
Graphene planes become even well separated in intercalated graphite compounds. The measured electronic properties of the obtained flakes and showed their unique properties.

It is now well known that tiny fragments of graphene sheets are produced whenever graphite is abraded, **such as when drawing a line with a pencil.**

Graphene preparation methods

1-Drawing method (Micromechanical Cleavage)

Graphene can be obtained by micro-mechanical alleviation of graphite. using adhesive tape(Scotch Tape) to repeatedly split graphite crystals into increasingly thinner pieces. The tape with attached optically transparent flakes was dissolved in acetone, and, after a few further steps, the flakes including monolayers were sedimented on a substrate like silicon wafer.



free-standing atomic planes were often "presumed not to exist" because they are thermodynamically unstable on a nanometer scale and, if unsupported, have a tendency **to scroll and buckle**.

2-Epitaxial growth

Another method of obtaining graphene is ;

to heat silicon carbide (SiC) to high temperatures (>1100 °C) to reduce it to graphene. This process produces epitaxial graphene with dimensions dependent upon ;
-the size of the SiC substrate (wafer).

-The phase of the SiC used for graphene formation, silicon- or carbon-terminated, highly influences the thickness, mobility and carrier density of the graphene. found that graphene monolayers grown on SiC and Ir are weakly coupled to these substrates and the graphene–substrate interaction can be passivated further.

3-Graphite oxide reduction

Graphite oxide (GO) which can be prepared from graphite flakes by different ways such as Hummer , the exfoliation of GO can be achieved by rapid heating and yields highly dispersed carbon powder with a few percent of graphene flakes



Reduction of graphite oxide monolayer films e.g. by

- hydrazine,
- annealing in argon/hydrogen

4- Growth from metal-carbon melts

The general idea in this process is;

to dissolve carbon atoms inside a transition metal melt at a certain temperature, and then allow the dissolved carbon to precipitate out at lower temperatures as single layer graphene. Keeping the melt in contact with carbon source at a given temperature will give rise to dissolution and saturation of carbon atoms in the melt based on the binary phase diagram of metal-carbon. Upon lowering the temperature, solubility of the carbon in the molten metal will decrease and the excess amount of carbon will precipitate on top of the melt. The floating layer can be either skimmed or allowed to freeze for removal afterwards.

5-Pyrolysis of sodium ethoxide

Gram-quantities of graphene, can be produced by the reduction of ethanol by sodium metal, followed by pyrolysis of the ethoxide product, and washing with water to remove sodium salts



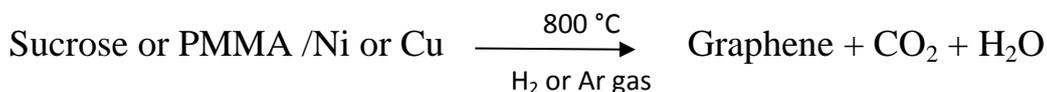
6-From nanotubes

multi-walled carbon nanotubes can be converted to graphene by;

- by action of potassium permanganate(KMnO₄) and sulfuric acid (H₂SO₄).
- In another method graphene nanoribbons are produced by plasma etching of nanotubes partly embedded in a polymer film.

7-From sugar

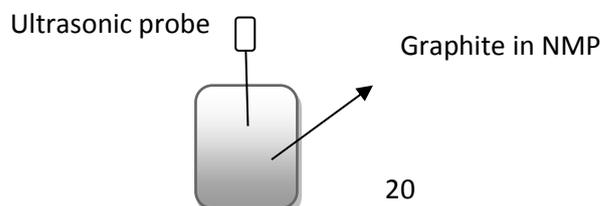
Sucrose among other substances such as Plexiglas (PMMA) have been turned into graphene via application to a copper or nickel substrate and being subjected to 800 °C under low pressure with exposure to argon and hydrogen gas. The process can be completed in ten minutes and is scalable for industrial production.



8-From graphite by sonication

It consists in dispersing graphite in a proper liquid medium that is then sonicated. Non exfoliated graphite is eventually separated from graphene by centrifugation.

This method was first proposed by Hernandez who obtained graphene concentration up to 0.01 mg/ml in N-methylpyrrolidone (NMP).



9-Dry ice method

a simple method for producing high yields of graphene by burning magnesium metal in dry ice — a common experiment, but one where the products have not been fully characterized until now. The team has shown that graphene was formed in few-layer nanosheets up to 10 atoms thick.

Applications of graphene

- OLED Technologies
- Body Armour
- Lightweight Aircraft/vehicles
- Photovoltaics
- Superconductor/battery
- Filtration



Chemistry of Quantum Dots (Artificial Atoms)

A special Class of zero dimension (0D) nanocrystals semiconductors with a sizes ranging between 1-10nm (10-50 atoms) on the order of the compound's Exciton Bohr Radius and with an easily tunable bandgap, at these small sizes materials behave

differently and have a range of useful electrical and optical properties that diverge in character from those of bulk material, giving unprecedented tenability and enabling never before seen applications to science and technology, in general QD composed of element from periodic table groups 2 and 6 , groups 3 and 5 and groups 4 and 6.

group IIB :Zn,Cd,Hg group IIA: B,Al,Ga,In,Tl group IV: C,Si,Ge,Sn,Sb
group VIA ; O,S,Se,Te, group VA: N,P,As,Sb,Bi group VIA ; O,S,Se,Te,

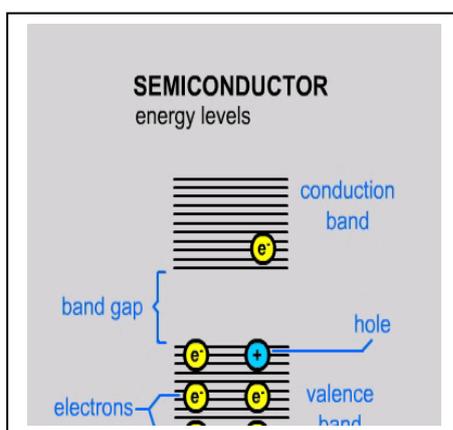
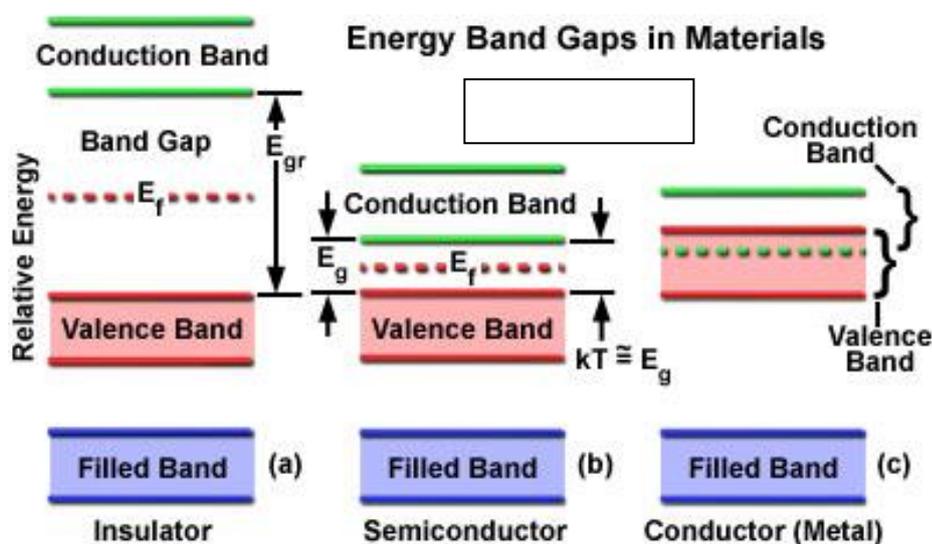
semiconductors critical parts of many different kinds of electrical circuits and optical applications such as; the Light Emitting Diode (LED),personal computer, and others.By changing size, shape, and composition, quantum dots can change their absorptive and emissive properties dramatically.

The average distance between an electron and a hole in a exciton is called the Excited Bohr Radius.When the size of the semiconductor falls below the Bohr Radius, the semiconductor is called a quantum dot.

Bands and Band gaps; In bulk, energy levels are very close together, so close that they are described as continuous, meaning there is almost no energy difference between them. It is also established that some energy levels are simply off limits to electrons; this region of forbidden electron energies is called the bandgap, and it is different for each bulk material. Electrons occupying energy levels below the bandgap are described as being in the valence band. Electrons occupying energy levels above the bandgap are described as being in the conduction band.

The bandgap separates the valence band from the more energetic conduction band, making it difficult for electrons to jump to the conduction band. In a regular semiconductor crystal, the bandgap is fixed owing to continuous energy states.

In a quantum dot crystal, the bandgap is size dependent and can be altered to produce a range of energies between the valence and conduction band.



Electrons and Holes; The only way for an electron in the valence band to jump to the conduction band is to acquire enough energy to cross the band gap, and most electrons in bulk simply do not have enough energy to do so. Applying a stimulus such as heat, voltage, or photon flux can induce some electrons to jump the forbidden gap to the conduction band. The valence location they vacate is referred to as a hole since it leaves a temporary "hole" in the valence band electron structure.

A sufficiently strong stimulus will cause a **valence band** electron to take residence in the **conduction band**, causing the creation of a **positively charged hole** in the valence band.

The raised electron and the hole taken as a pair are called an **exciton**.

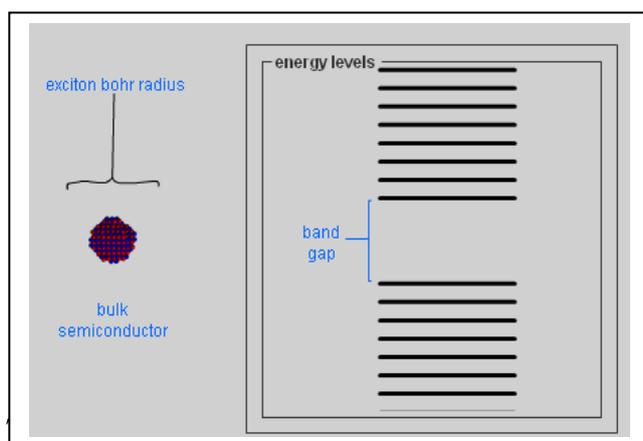
There is a minimum energy of radiation that the semiconductor bulk can absorb towards raising electrons into the conduction band, corresponding to the energy of the band gap the bandgap energy of bulk semiconductor material of a given composition is fixed.

As the electron falls back down across the bandgap, electromagnetic radiation with a wavelength corresponding to the energy it loses in the transition is emitted. Because the bandgap of the bulk is fixed, this transition results in fixed emission frequencies.

Quantum dots offer the unnatural ability to tune the bandgap and hence the emission wavelength. The electrons have a range of energies.

Excitons have an average physical separation between the electron and hole, referred to as the Exciton Bohr Radius this physical distance is different for each material. In bulk, the dimensions of the semiconductor crystal are much larger than the Exciton Bohr Radius, allowing the exciton to extend to its natural limit. However, if the size of a semiconductor crystal becomes small enough that it approaches the size of the material's Exciton Bohr Radius, then the electron energy levels can no longer be treated as continuous - they must be treated as discrete (quantum confinement).

The bandgap in a quantum dot will always be energetically larger; therefore, we refer to the radiation from quantum dots to be "blue shifted" reflecting the fact that electrons must fall a greater distance in terms of energy and thus produce radiation of a shorter, and therefore "bluer" wavelength.



Semiconductor	Exciton Bohr Diameter	Band gap Energy
CuCl	13 Å	3.4 eV
ZnSe	84 Å	2.58 eV
CdS	56 Å	2.53 eV
CdSe	106 Å	1.74 eV
CdTe	150 Å	1.50 eV
GaAs	280 Å	1.43 eV
Si	37 Å (longitudinal) 90 Å (transverse)	1.11 eV
Ge	50 Å (longitudinal) 200 Å (transverse)	0.67 eV
PbS	400 Å	0.41 eV

making it difficult for electrons to jump to the conduction band. In a regular semiconductor crystal, the bandgap is fixed owing to continuous energy states. In a quantum dot crystal, the bandgap is size dependent and can be altered to produce a range of energies between the valence and conduction band. Quantum mechanics dictates that the bandgap of a quantum dot will always be larger in magnitude.

The band gap (the minimum energy necessary to excite an electron from the valence level to the conduction level) of semiconductor nanocrystals (quantum dots) is given by

$$E_{g,QD} = E_{g,bulk} + \frac{\hbar^2 \pi^2}{2\mu r^2}$$

where the second term describes the energy levels of a particle of mass μ in a spherically symmetric potential box. Above equation explains qualitatively well the quantum size effects in quantum dots: the increase of inter band energy separation with the decrease of quantum dot size.

CONDUCTION BAND

This band contains the energy levels that are above the bandgap and higher. Because the bandgap is always much larger than the distance between energy levels, not many electrons can jump the bandgap and cross into the conduction band from the valence band.

CONTINUOUS

The set of physical conditions where energy levels are separated by such a small amount of energy that for some processes, they may be treated as if they were not separated by any energy amount at all., the bandgap of a material may be treated as fixed and unchangeable.

DISCRETE

The set of physical conditions where energy levels are separated by enough energy that the addition or subtraction of one atom or electron to the crystal will measurably change the energy of the bandgap.

ENERGY LEVEL

The result is that in any crystal, electrons will start filling the lowest energy levels first, and continue to fill levels with higher energies until no more electrons remain without energy levels.

EXCITON

An exciton is the term used to describe the electron-hole pair created when an electron leaves the valence band and enters the conduction band. Excitons have a natural physical separation between the electron and the hole that varies from substance to substance; this average distance is called the Exciton Bohr Radius.

In a large semiconductor crystal, the Exciton Bohr Radius is small compared to the crystal, and the exciton is free to wander throughout the crystal. In a quantum dot, the Exciton Bohr Radius is on the order of the physical dimension of the dot or smaller, and the exciton is confined. This second set of conditions is called quantum confinement, which is synonymous with having discrete, rather than continuous energy levels.

EXCITON BOHR RADIUS

This is the natural physical separation in a crystal between an electron in the conduction band and the hole it leaves behind in the valence band. The size of this radius controls how large a crystal must be before its energy bands can be treated as continuous. Therefore, the Exciton Bohr Radius can rightly be said to define whether a crystal can be called a semiconductor quantum dot, or simply a bulk semiconductor.

QUANTUM CONFINEMENT

The set of conditions under which a crystal is on the order of or smaller than the Exciton Bohr Radius of its constituent compound. Under quantum confinement, energy levels may be treated as discrete. By definition, quantum dots are in a state of quantum confinement.

SEMICONDUCTOR

A material with electrical properties resembling those partially of insulators and partially of conductors. The application of external stimuli such as heat or voltage can radically alter the conductivity of a semiconductor. Semiconductors, especially Silicon and Germanium, are the cornerstone of the modern electronics industry.

VALENCE BAND

This band contains all the electrons from the one with the lowest energy, to the one with energy just on the lower edge of the bandgap. Since electrons tend to occupy energy states with the lowest energy possible, the valence band's energy levels are usually almost completely full.

Application of QD:

quantum dot formulations is so important for future applications and can create opportunities in a range of global markets including:

1. Displays
2. Life Sciences
3. Thermoelectrics
4. Photonics & Telecommunications
5. Security Inks
6. Solar Cells & Photovoltaics
7. Biology : biosensors, imaging
8. Light emitting diodes: LEDs
9. Quantum computation
10. Flat-panel displays
11. Memory element
12. Photodetectors
13. Lasers

Preparation Of Quantum Dots

There are three main ways to confine excitons in semiconductors:

Lithography

Colloidal synthesis

Epitaxy

- Patterned Growth -Self-Organized Growth

Example for colloidal method:

Preparation of CdSe Quantum Dots ;

- in a 25 mL round bottom flask add approximately 13 mg of CdO. Clamp the flask above the heating mantle.
- Using a 1 mL syringe, add 0.6 mL oleic acid to the flask.
- Then add 10 mL octadecene heat the flask to 225 °C While waiting for the reaction mixture to heat up, prepare ten test tubes.
- A 0.038 M selenium stock solution has been prepared for by dissolving elemental selenium in octadecene and trioctylphosphine. As soon as the temperature of the reaction mixture reaches 225 °C Using a syringe transfer 1 mL of the room temperature selenium stock solution to the 225 °C cadmium solution. Because the size of the nanoparticles depends on reaction time, start timing when the selenium solution is added.

The chemistry of Dendrimers

Organic nanopolymers

The name came from Greek word “dendron” which means “tree”, they are defined as highly branched spherical macromolecules, with highly degree of surface functionality. They called as the polymers of 21st century; dendritic polymers are highly branched polymer structures, with complex secondary architectures and well-defined spatial location of functional groups. the structure of these materials has a great impact on their physical and chemical properties. As a result of their unique behavior dendrimers are suitable for a wide range of biomedical and industrial applications. Much like proteins and natural products, dendrimers are near monodisperse with predictable molecular weights and nano-scale dimensions.

The similarity and differences between dendrimers & proteins are explained as follow;

Similarities

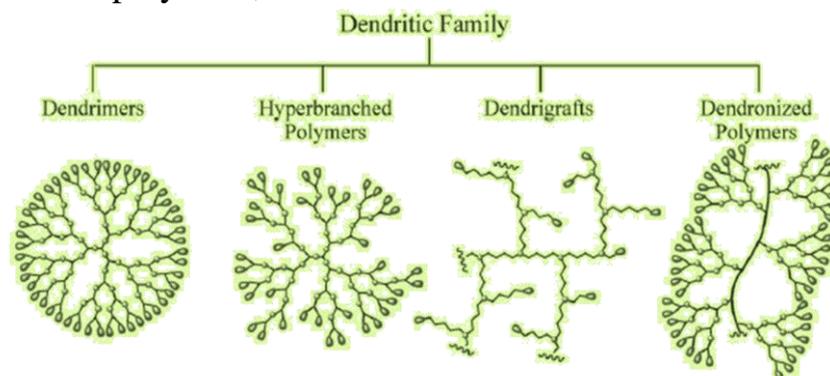
- ✓ Size
- ✓ Weight
- ✓ Well defined chemical structure (known bonding structure)
- ✓ 3 dimensional position of each atom is difficult to determine - yet a consistent specific 3 dimensional structure exists
- ✓ Difficult to perform chemical analysis
- ✓ Easy for cell to uptake

Main Difference

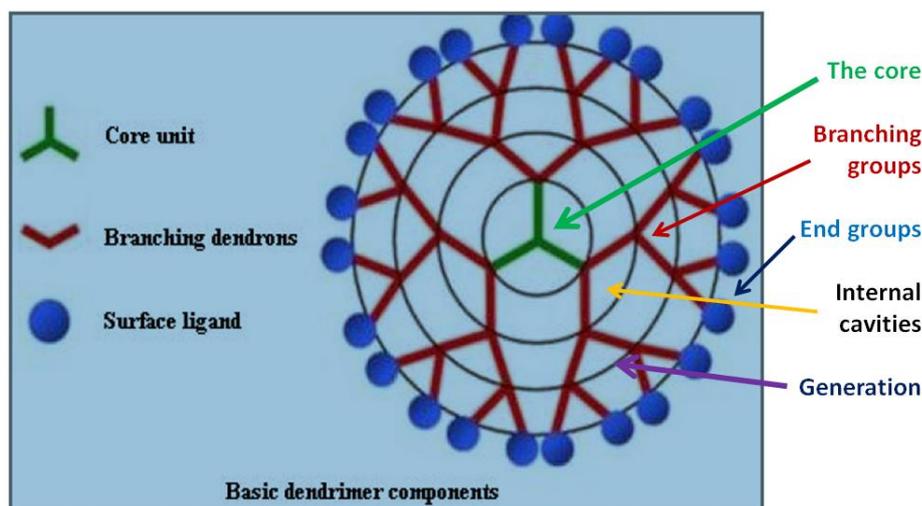
- ☒ Proteins are polymers made from 20 different monomers, while dendrimers are polymers made from two monomers.

There are four types of dendritic polymers;

- 1- Dendrimers
- 2- Hyperbranched
- 3- Dendrigrraft
- 4- Dendronized



The structure of Dendrimers



The unique properties of dendrimers are attributed to;

- Their globular structure, resulting from internal structures
- All bonds emerge radially from a central core,
- A large number of end-groups are present at its surface.
- Dendrimers can be seen as nano-particles with the ability of core encapsulation .
- In contrast to linear polymers, these macromolecules do not entangle, have unusual viscosity behaviors, such as low solution viscosity.
- Functional groups can be either protected or exposed.

The more familiar examples for dendrimers are ;

Tomalia-type poly(amidoamine) (PAMAM)
 Frechet-type poly(benzylether)
 Newkome's arborol dendrimers
 phosphorus-containing dendrimers
 poly(2,2-bis(hydroxymethyl)propionic acid

Insulin	G3
Cytochrome C	G4
Hemoglobin	G5
Transthyretin	G6
Histone	G7

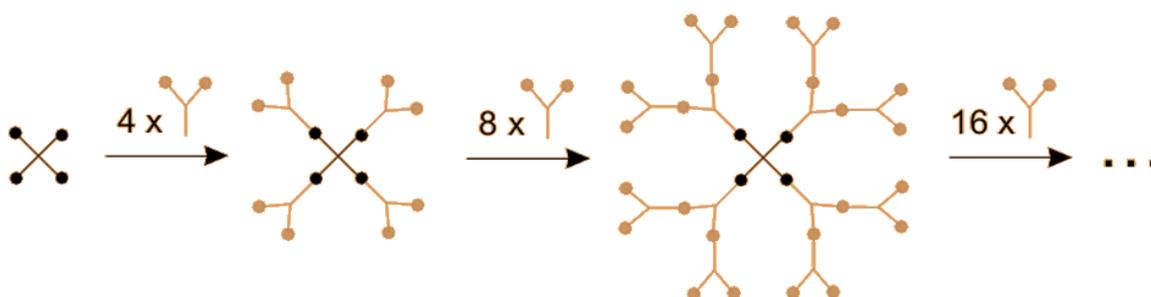
P(bis-MPA) dendrimer

Synthesis of dendrimers;

There are two main methods to synthesize dendrimers;

First - the Divergent method;

dendrimer grows outwards from a multifunctional core molecule. The core molecule reacts with monomer molecules containing one reactive and two dormant groups giving the first generation dendrimer

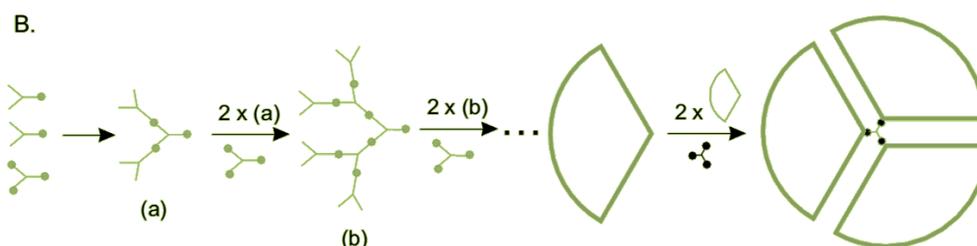


Each complete addition of branch group followed by end group called generation (nG), and adding only branch group called half generation (n.5G); the importance of dendrimers are increased with increasing their generation until reaching generation 10, after that the size of dendrimers became in microscales losing their novel properties. Dendrimers of lower generations (0, 1, and 2) have highly asymmetric shape and possess more open structures as compared to higher generation dendrimers. As the chains growing from the core molecule become longer and more branched (in 4 and higher generations) dendrimers adopt a globular structure. Dendrimers become densely packed as they extend out to the periphery, which forms a closed membrane-like structure. When a critical branched state is reached dendrimers cannot grow because of a lack of space. This is called the 'starburst effect'. For PAMAM dendrimer synthesis it is observed after tenth generation. The rate of reaction drops suddenly and further reactions of the end groups cannot occur. The tenth generation PAMAM contains 6141 monomer units and has a diameter of about 124 Å.

Generation	Ammonia core		EDA core	
	molecular mass	number of terminal groups	molecular mass	number of terminal groups
0	359	3	516	4
1	1043	6	1428	8
2	2411	12	3252	16
3	5147	24	6900	32
4	10619	48	14196	64
5	21563	96	28788	128
6	43451	192	57972	256
7	87227	384	116340	512
8	174779	768	233076	1024
9	349883	1536	466548	2048
10	700091	3072	933492	4096

The convergent methods;

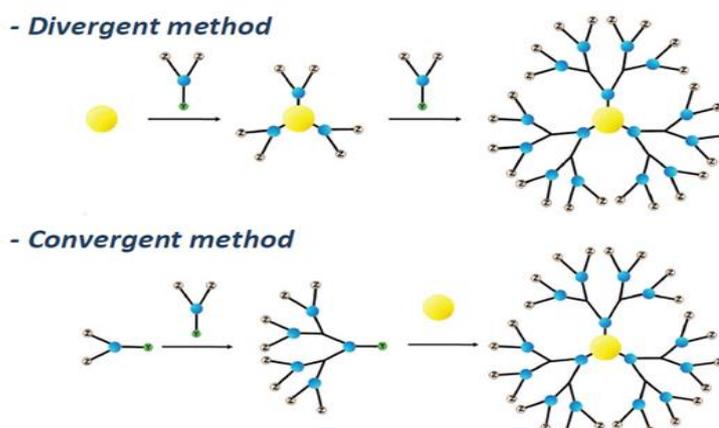
The dendrimer is constructed stepwise, starting from the end groups and progressing inwards. When the growing branched polymeric arms, called dendrons, are large enough, they are attached to a multifunctional core molecule



The Divergent vs The convergent

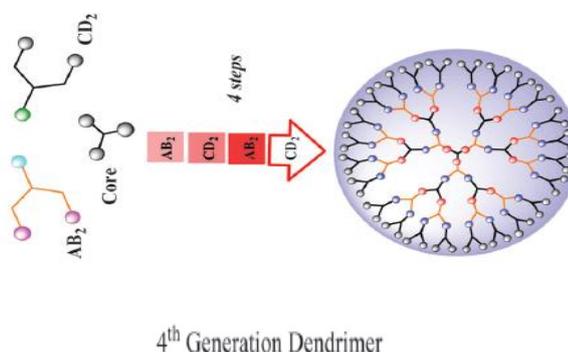
- dendrimer grows outwards from a multifunctional core molecule
- divergent approach is successful for the production of large quantities of dendrimers
- Problems occur from side reactions and incomplete reactions of the end groups
- difficulties in the purification of the final product.

- In the convergent approach, the dendrimer is constructed stepwise, starting from the end groups and progressing inwards
- does not allow the formation of high generations because steric problems
- It is relatively easy to purify the desired product



Click Chemistry

There is one more approach to synthesize dendrimers called ((Click Chemistry))
 The synthetic procedure for obtaining dendrimers can be accelerated by utilizing two different kinds of monomers, instead of only a single AB_x -type monomer. In this approach monomers of AB_2 -functionality are coupled to monomers with CD_2 -functionality. Here, A can selectively react with D and B can only react with C. Due to this, no protection/ de-protection steps are required in the procedure and a dendrimer having a layered structure composed of two alternating repeat units is obtained.



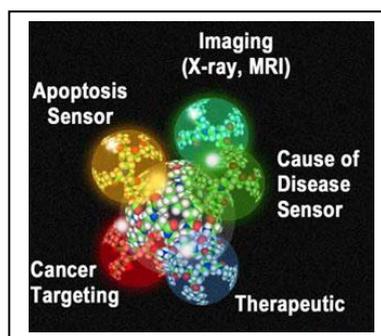
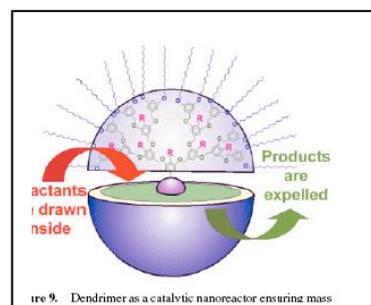
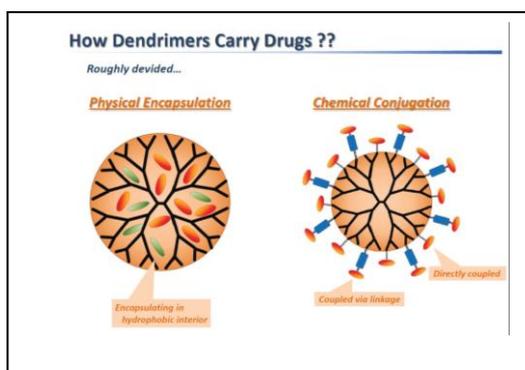
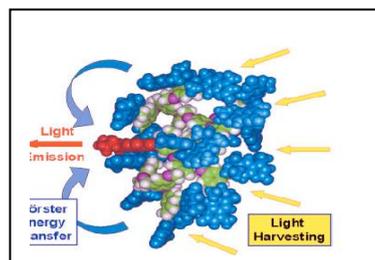
Surface-Engineered Dendrimers

Common functional groups of dendrimers surfaces are
 Hydroxyl (OH) (can be converted to active intermediates)
 Carboxyl (COOH),
 primary amine (NH₂),
 Thiol (SH)

Due to presence of multiple surface sites on the dendrimer surface, moieties of various functionalities can be simultaneously attached to the surface through covalent or non-covalent bonding to make dendrimers multifunctional.

Applications of Dendrimers

- 1-Light Harvesting
- 2-Organic Light Emitting Diodes
- 3-Catalysis
- 4-biological applications
 - Drug Delivery
 - antiviral
 - scaffold for tissue repair



The rules of nanomaterials in Photovoltaic Solar Cell

Photovoltaic cell

Silicon solar cell

Cells convert light energy directly into electrical energy called Photovoltaic Solar Cell. These cells are made up of semiconductors materials such as silicon.

Silicon atom has 14 electrons arranged in three general electron shells.

- The first two shells closest to the nucleus are full.
- The outer shell has four electrons and is only half-full.
- However, silicon will and can share electrons with its neighbors. In the case of crystalline silicon, there are other silicon atoms that will provide electrons for sharing. pure crystalline silicon is a poor conductor as there are no extra electrons free to move

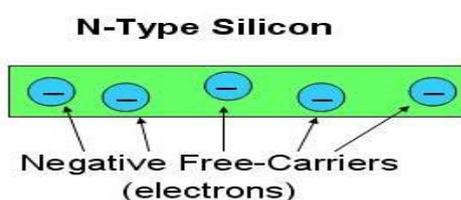
about. Because of this a solar cell is constructed with silicon mixed with impurities; this is **called doping the silicon**.

N-doped Si (negative)

phosphorus atoms could be mixed with the silicon. Phosphorus has five electrons in its outer shell. It still bonds with the silicon atoms but now there is an **extra electron**.

When energy is added to the crystal, this extra electron can break free of bond and this leaves a hole. Throughout the lattice, so a series of extra electrons moving freely of their bonds; these electrons are **called free carriers**.

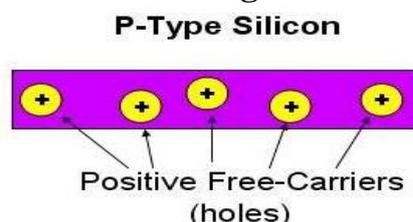
When silicon is doped with phosphorus, it is called an **N-type crystal** as it has extra electrons (N for negative). Part of a common photovoltaic cell is created as an N-type crystal.



P-doped Si(positive);

Boron can be used as positive doped materials because it has three valence electrons, consequently, has more holes available for the free electrons created when the N-type silicon is energized. A hole can be thought of as an absence of an electron or a positive charge. The holes can appear to move just like free electrons.

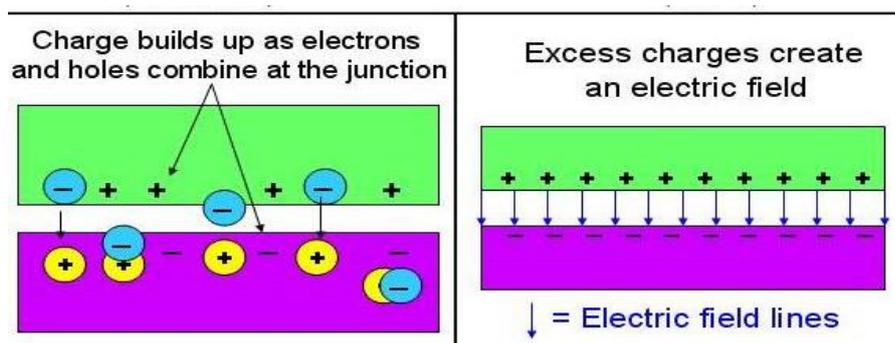
Both electrons and holes can be called **charge carriers**.



The common photovoltaic cell has a N-type silicon put together with a P-type. When placed atop each other the free electrons in the N-type move into the holes available in the P-type. This occurs immediately when the two types of silicon are first brought together, but only close to the contact surface of each type.

The N-type silicon becomes positively charged at its surface and the P-type silicon becomes negatively charged at its surface due to this migration of electrons. This creates an electric field when both types are in contact.

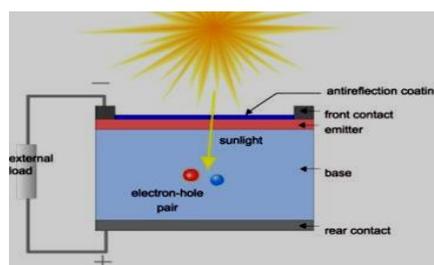
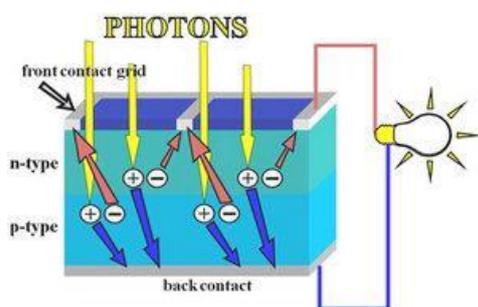
When the two types of silicon are sandwiched, there is a creation of a **p-n junction**, the name of the interface between both types of silicon. This p-n junction acts as a diode permitting electric current to flow in one direction only. At this junction, there are virtually no mobile charge carriers. However, the electric field pulls electrons and holes in opposing directions. Electrons are forced to flow from the P-type silicon to the N-type.



Sunlight is composed of photons when a photon of the correct energy strikes the solar cell, it can knock out electrons from outer valence bands and energize these electrons into the conduction band. This leaves a hole in the valence band, excess heat is often produced and this represents energy unavailable to be converted into electricity. If these electron-hole pairs are created in the correct location in the solar cell (near the p-n junction), the electrons will be attracted to the positive n-type silicon and the holes will be attracted to the negative p-type silicon. Some photons do not carry enough energy to create the electron-hole pair, about 2/3 of the photons from the sun cannot be utilized by a silicon solar cell.

The base (boron-doped, P-type silicon) makes up a thicker part (500microns) of the solar cell .The emitter phosphorus-doped, N-type silicon with thickness around 1 micron or less the total cell thickness can be up to 500 microns.

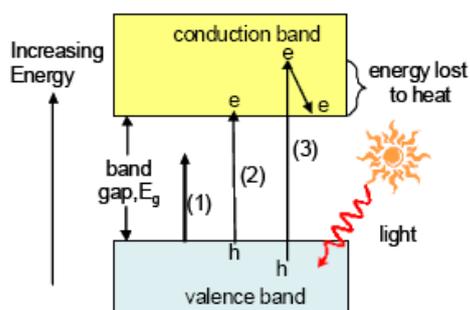
To construct the crystalline silicon cell, the boron-doped, P-type silicon is layered to a conductive back contact. The back contact is aluminum or some alloy. An antireflection coating is used to limit the reflection of sunlight on the top of the emitter. As photons hit the silicon layers, some of these photons create **electron-hole pairs**. These freed electrons and hole **drift and some recombine** and are useless for electricity generation. Some do reach the p-n junction; electrons are attracted to the emitter (N-type, phosphorus-doped) region and holes are attracted to the base. The electrons attracted to the emitter can reach the fingers and from there to the bus. If the circuit is complete (external load or complete pathway), these energized electrons can give up part of its extra energy as electrical power and return to recombine with the extra holes via the rear contact.



- Each cell produces **0.5 Volts** with a power output of approximately **0.05 Watts**.
- Solar cells are added together into a unit called a **module or panel**.
- Modules are linked together in units called **arrays**.

These basic silicon-based crystalline solar cells have an efficiency of about **15%**. Over 50% of the photons that hit the silicon solar cell **cannot be utilized for energy** because :

- 1-they either don't have enough energy to create electron-hole pairs or are too energetic and create energy along with electron-hole pairs.
- 2-Even if electron-holes are created, they often recombine before they can be split into useable current.
- 3-Some of the sunlight is reflected from the front and because of this isn't absorbed into the silicon.
- 4- Additionally, there are resistive effects in the silicon and the circuit that can lead to efficiencies.



- (1) the photon does not have enough energy to create electron (e) – hole (h) pairs.
- (2), the light has just enough energy to create e-h pairs.
- (3) the photon has energy in excess of the band gap, E_g , and this excess energy is wasted as heat and not converted to electrical energy.

Analyze of solar cell

One way to analyze a solar cell is with a **current-voltage graph**. A resistance is placed in a simple circuit and the **voltage** and **current** is measured. The resistance is then changed and new voltage and current readings are obtained. using resistances varying from **0 Ohms to 2200 Ohms**. It is electrical power that is important for a solar cell. Power is the product of voltage and current. Additionally because the photons are striking an area, we can calculate the power per area of solar cell. This quantity is called **the power density**.

Example:

A solar cell of 8 cm long and 5.5 cm wide with a peak power of 0.011 watt. determine the electrical energy conversion efficiency at this point for this solar cell. If the **insolation value** ((the incoming solar energy that strikes the ground at a particular city)) for Baghdad City, was 25 mW/cm²?

1-caculate the Peak power density:

$$\text{Peak power density} = 0.011 / 8 * 5.5 = 0.00025 \text{ W/cm}^2$$

$$=0.25\text{mw/cm}^2$$

2-Electrical Energy Conversion Efficiency= Peak power density/ insolation value*100
 EECE%= $0.25 \text{ mW/cm}^2 / 25 \text{ mW/cm}^2 * 100 = 1\%$.

Evaluation (validation) of DSSC:

$$I = V/R$$

By recording the voltage across different values of known resistances the current can be calculated or measured

Calculation of fill factor (ff):

$$ff = I_m \times V_m / I_{sc} \times V_{oc}$$

Calculation of conversion efficiency (η):

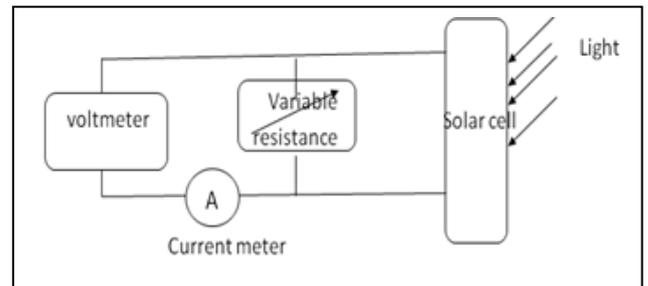
$$\eta \% = \text{output power} / \text{input power} \times 100$$

$$= P_m (\text{mw/cm}^2) / \text{light}$$

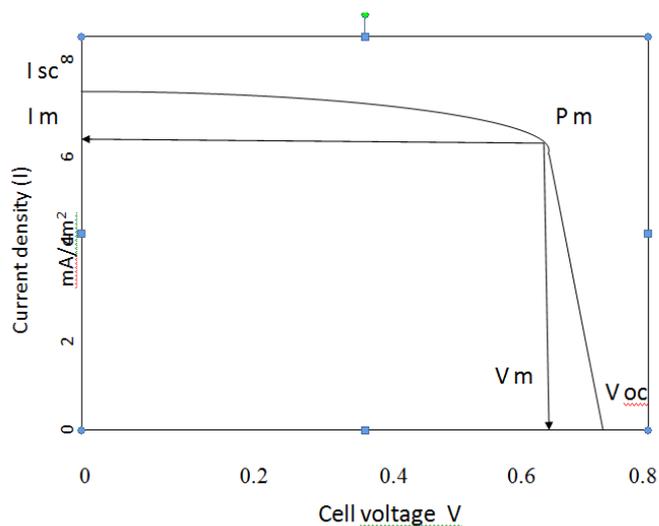
$$\text{intensity}(\text{mw/cm}^2) \times 100$$

$$= I_{sc} (\text{mA/cm}^2) \times V_{oc}(\text{V}) \times ff / \text{light}$$

$$\text{intensity}(\text{mw/cm}^2) \times 100$$



$$\eta = \frac{J_{sc} V_{oc} FF}{P_{in}}$$



Dye	λ abs (nm), ϵ ($M^{-1}cm^{-1}$)	J_{sc} ($mA\ cm^{-2}$)	Voc	FF	η (%)
JK-206	391 (19800), 527 (18000)	19.63	0.74	0.72	10.39
JK-207	368 (38700), 530 (16800)	13.83	0.69	0.66	6.32
N-719	380 (13100), 520 (1300)	18.79	0.75	0.7	9.8

Factors affecting solar systems

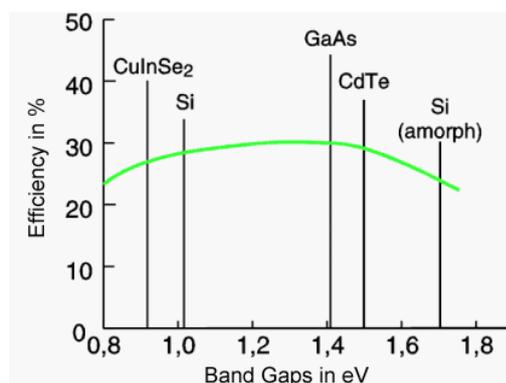
Solar panels are often sold listing their capacity in watt-peak. A solar panels power in watt-peak represents its *peak output* under standardized test conditions (**25C' temperature, 1.5 air mass, 1 kW/m² intensity**).

The following factors influence the performance of a solar panel:

- 1-Temperature:** the efficiency of a solar cell *decreases* with increasing temperature. higher temperature increases the conductivity of the semiconductor. reducing the magnitude of the electric field at the junction which lowers the voltage across the cell
- 2-The sun's intensity:** There a map called insolation map. It displays the average amount of kilowatt-hours received per day .It represents the *average amount of daily hours of sunshine*.
- 3-Shading:** if small part of the solar panel to be shaded by a tree or building, it reduce the panel's ability to produce power.
- 4-Tilt angle:** tilting solar panels with an angle equal to the latitude of location on Earth.
- 5-Tilt direction:** point solar panels towards the sun.
- 6-Soiling:** accumulating dust and other debris (bird droppings, pollen, sand etc.) reduces the transparency of the glass cover.
- 7-Series resistance:** When tying solar cells together, it is important to keep series resistance of the circuit to a minimum. Since the material in a solar cell acts as a resistor to current flow, it is often advisable to limit the amount of serially connected solar cells.

The efficiency & Band gabs

Each semiconducting material has its own properties which make it more or less suitable for use in a solar cell. One of these properties is the so-called band gap, certain materials will be able to extract more energy from it than others. The below diagram displays the relation between band gap and maximum efficiency.



the actual efficiency of a material depends on more factors than band gap alone like the reflective properties of the material and crystal matrix defects both play an important role in the conversion between light and power. To overcome all these limitations, solar cells can be constructed using multiple materials. Such a so-called multiple junction solar cell is basically a stack of several materials, which combined absorb a larger portion of the solar radiation spectrum.

Types of Solar Cells

1-silicon-based solar cell

high-grade silicon used for commercial solar cells essentially comes in three types:

I-Monocrystalline silicon Such cells are relatively efficient (18%), yet also expensive due to the manufacturing process.

II-Polycrystalline silicon are cheaper than monocrystalline but they are less efficiencies (15%).

III-Amorphous silicon: Amorphous silicon is less effective (10%) at light conversion. However, since only a very thin layer of the material is needed, panels based on amorphous silicon can be cheaper per watt than regular solar panels.

2-Concentrator solar cells:

A higher light intensity will be focused on the solar cells by the use of mirror and lens systems. This system tracks the sun, always using direct radiation. For example, in the picture below, lenses concentrate solar energy on the array to produce an equivalent of 250 suns.

3-non silicon solar cell

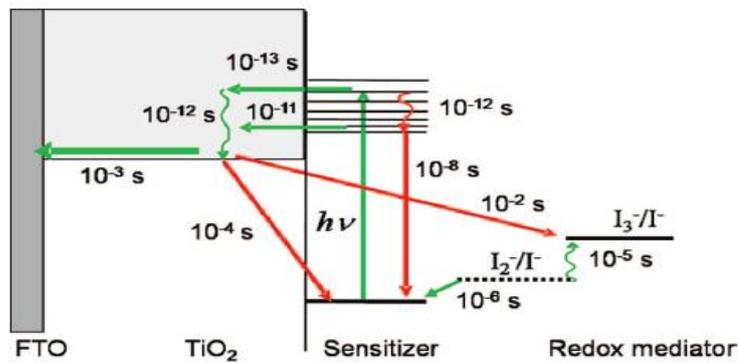
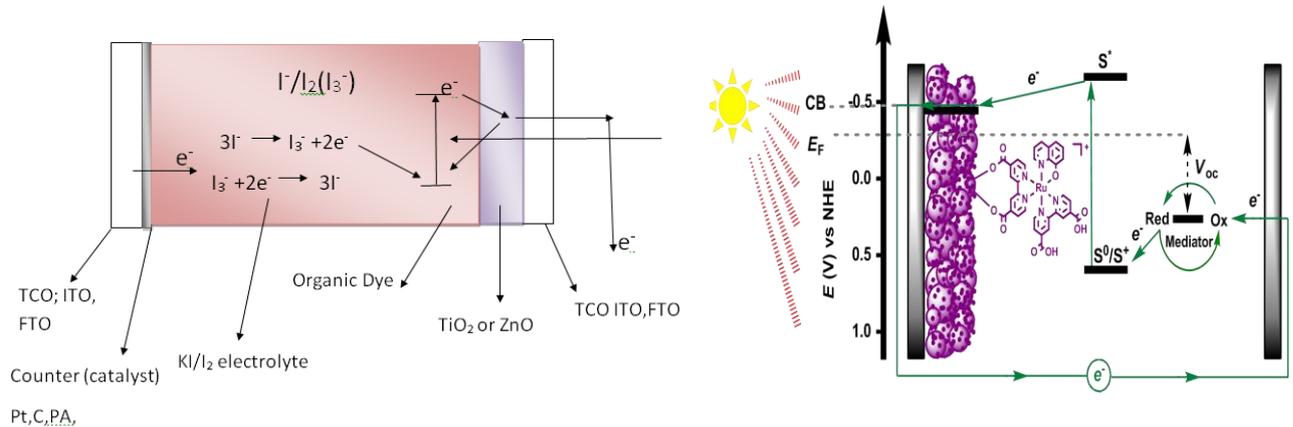
Other materials offering far higher conversion efficiencies are available. Commonly used materials are:

Gallium Arsenide, Germanium, Copper-Indium Gallium Selenide (CIGS) and Cadmium Telluride.

These materials can yield conversion efficiencies of up to 40%, but are hard to acquire and thus very expensive.

4- Nanomaterials-based Solar Cells

I- The Grätzel cell dye-sensitized solar cell



The elements of DSSC:

1- semiconducting electrode

n-type TiO₂, n-type ZnO, and p-type NiO

2-transparent conductive oxide (TCO):

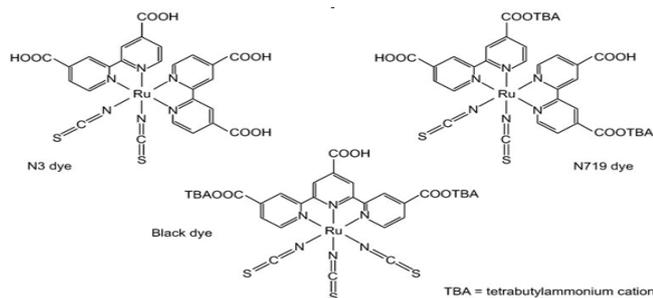
ITO: Indium doped tin oxide/glass or flexible polymer

FTO: fluorinated tin oxide/glass or flexible polymer

3-Photosensitive Dye: Light harvesting and electronic transition

a-natural dyes (anthocyanin):blackberries, raspberries, pomegranate seeds, green citrus leaves

b-synthetic dyes:



4-Electrolyte (Redox mediator):

I^-/I_3^- or Co^{II}/Co^{III} complexes

5-Counter electrode:

Graphite, Pt, or conductive polymer

The Grätzel cell converts sunlight into electrical current as follows.

- Light is absorbed by the dye and an electron is excited to a higher energy level in the dye.



- This excited electron is rapidly injected into the semiconductor layer such as titanium dioxide, Zinc oxide, or Nickel oxide nanoparticles and travels to one of the solar cell electrodes by hopping from particle to-particle.



- The positively charged dye undergoes an electrochemical reaction with I^- in the electrolyte to form I_3^- which shuttles the “the hole” to the counter electrode where it is reduced back to I^- to repeat the cycle.



The semiconductor nanoparticles are at the heart of this device because they provide the large surface area for dye adsorption. Light traveling through the nanoparticle film passes through the dye layer many times, which increases the probability of absorption. The surface area provided by the nanoparticle film is typically 1000 times that of the flat electrode area and a solar cell made using nanoparticles gives approximately 1000 times the current from a solar cell made from a thin layer of titanium dioxide covered with a monolayer of dye.

The advantages of DSSC:

- 1- Ease of fabrication
- 2- Can be fabricated as flexible
- 3- Low cost

4- Highly transparent

II-The Nanowire Dye Sensitized Solar Cell:

III-Carbon nanotubes in photovoltaics:

IV- Quantum Dot Sensitized Solar Cell

WHAT DO NANOSTRUCTURED MATERIALS HAVE TO OFFER?

photovoltaics based on nanotechnology as any approach that makes use of materials and structures that have dimensions approximately in the 1-100 nm length scale. Nanostructured materials such as nanoparticles and nanowires have three unique advantages that make them useful in photovoltaic designs:

First, ensembles of nanometer size objects have very large surface areas per unit volume or per unit mass. This enables one to pack very large interfacial areas between into small volumes.

Second, quantum confinement effects encountered in nanometer size materials impart them with unique optical and physical properties that are much different than the properties of the bulk material. nanoparticles provide the ability to tune the optical properties of the solar cell. nanoparticles provide the ability to tune the optical properties of the solar cell.

Third, photovoltaic devices based on nanomaterials have the potential to be inexpensive because nanoparticles and nanowires can be manufactured using solution synthesis and large area substrates can be coated from colloidal solutions using well developed coating and printing techniques.

Electrical Solar system:

Any electrical solar system should contains the following parts:

- 1-The solar panels array :group of solar panels(modules) identified by its wattages, voltages, amperages.
- 2-Batteries: lead-acids or alkaline sealed batteries identified by their voltages(12or 24 vdc) and amperages.h (60,80,100,.....300Ah).
- 3-Charge controller: an electronic component prevent excessive batteries charging and reverse flow back to the solar cells.
- 4-voltage inverter :to inverts the batteries voltage (12 or 24 vdc) to the desired ac voltage (220vac) also it should have the proper power capacities.
- 5-The house load :like lamps,freezer,television,.....etc.
- 6-wiring between solar panels themselves and the charge controller and the batteries

Solar system calculations:

System to offer 2000w house for 2 hours

Baghdad Insolation time 5h

1-Wattages requested= $2000\text{w} \times 2\text{h} = 4000\text{w.h}$

2-quantities of solar panels:

Total required wattages of the solar cells= $4000\text{w.h}/5\text{h}$
 $=800\text{w}$

If we have (100w-12vdc) solar panels: the quantity will be $=800\text{w}/100\text{w}$
 $=8$ solar panels

3- quantities of batteries:

Amperages.h required = Wattages requested/solar panel voltage
 $=4000\text{w.h}/12\text{v}$
 $=334$ A.h

If we have (12vdc,100A.h batteries) the quantity will be $=334/100$
 $=4$ batteries

For preventing deep discharging (less than 70%) of batteries multiply by factor 3

The quantity will be= 12 batteries

Smart materials

Materials that can significantly change their mechanical, thermal, optical, or electromagnetic properties, in a predictable or controllable manner in response to their environment.

Materials that show tailored new properties, useful for smart device applications.

Phase transitions in materials induce new properties

Smart materials may be of ;

- Micron-scaled materials-the properties change as a function of size and size depends on external effects (the 'squeezed butterfly')
 - Nano-scaled materials-the properties depend on size and agglomeration and size and agglomeration might depend on external effects (ferrofluids)
- smart materials have special functions allowing them to adequately respond to any interior and/or external stimuli in their environments. Here are a few major smart materials listed in the following table;

material	environmental change	effect
Piezoelectric materials	Voltage	Shape
Dielectric elastomers	Voltage	Strain
Polymers and conductive polymers: pH and temperature-responsive	pH and Temperature	Swell and resistance
Shape memory alloys or shape polymers	Temperature and stress	Shape
Electrochromic (liquid crystals) thermochr.,	Voltage, Temperature	Color
Photochromic (sunglasses)	Light	Opacity
Ferrofluids	Magnetic field	Magnetization

Piezoelectric: Undergo mechanical change when subjected to electric charge/voltage and vice versa (direct and converse effects).

Electrostrictive: Same as piezoelectric but proportional to the square of the field.

Magnetostrictive: Undergo mechanical strain when subjected to a magnetic field and vice versa (direct and converse effects) i.e. Terfenol-D.

Magnetorheological fluid: Change from fluid to viscous solid when subjected to a magnetic field.

Electrorheological fluid: Change from fluid to viscous solid when subjected to an electrical field.

Shape Memory Alloys (SMA): Undergo shape changes due to phase transformations when subjected to a thermal field. It deforms to its martensitic condition, and regains its original shape to its austenite condition when heated i.e. Nitinol.

Shape Memory Polymers (SMP): Same as SMA but with polymers instead of Alloys
 Combining two or more materials in an attempt to utilize synergistically the best properties of their individual constituents is the ultimate objective of any smart composite material. Their advantages and adaptability to the above design requirements have led to a profusion of new products.

Advantages of smart and nano materials

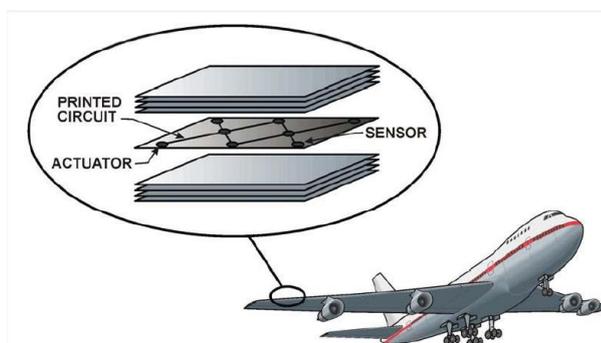
Using smart and nano materials in systems could have the following advantages:

1. Optimizing the response of complex systems. This is done by establishing early warning systems, enhancing the range of survivability conditions and/or providing adaptive response to cope with unforeseen conditions and situations.
2. Enhancements otherwise not possible; such as minimizing the distortion of the responses, increasing the precision as well as providing better control of the system. This could lead to improving the design and performance of new geometries for special applications.
3. Improving the functionality of the system by a proper preventive maintenance and performance optimization.

4. Significant impact on manufacturing and processing techniques.
5. Improving the health monitoring of the system and better control of its active, adaptive or smart functions.

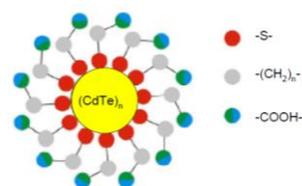
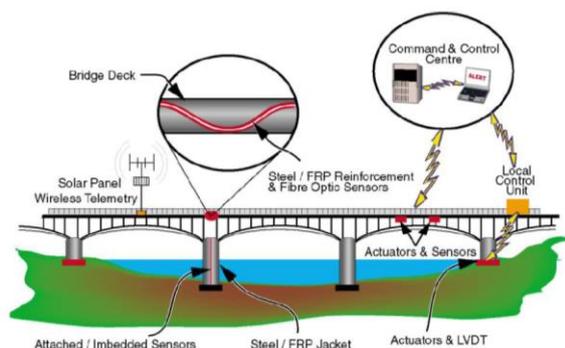
Applications of smart and nano materials in systems

- 1-Made-up smart nano composite: Since the objective is to increase the capabilities or/and improve the basic functions or characteristics of the final product such as ;its strength, stiffness, flexibility, these materials are formed at their nano scale level.
- 2-Structural health monitoring (SHM) and assessment of structural components
- 3- Composites are used more and more in the aerospace industries due to their light weight, better stiffness and corrosion properties

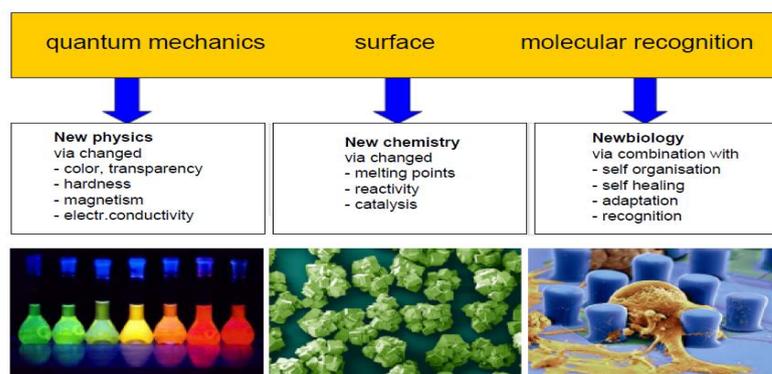
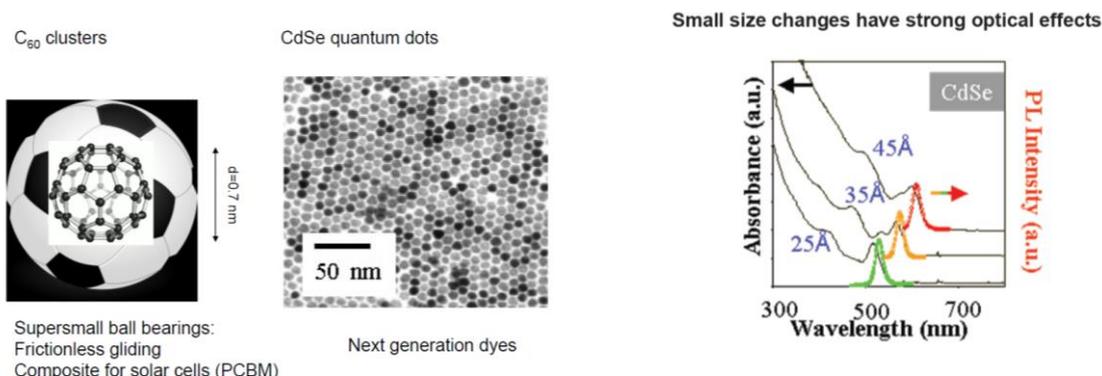


Embedding of smart nanomaterials in composite structure using printed circuit technology.

- 4-Reduction of structural vibration
- 5- Multiple thin sheets
- 6-Electroactive polymers: for many electromechanical actuator, transducer and active vibration damping applications
- 7- For civil engineering applications such as the smart bridge the first step of achieving a smart structure



CdTe nanoparticles with stabilizing shell



Wet nanochemistry Nanofluids

Nanofluids are a relatively new class of fluids which consist of a base fluid with nano-sized particles (1–100 nm) suspended within them.

Preparation of Nanofluids

- A-The one-step method simultaneously makes and disperse the nanoparticles directly into a base fluid prevent oxidation of pure metal particles (non commercial).
- B-The two-step method produced the nanoparticles and dispersed them into a base fluid .

Advantages of nanofluids

Cooling becomes one of the top technical challenges facing high-tech industries such as microelectronics, transportation, manufacturing, and metrology.

- 1-unique transport properties, different from conventional suspensions:
- 2-do not settle under gravity,
- 3-do not block flow,
- 4-High specific surface area and therefore more heat transfer surface between particles and fluids.
- 5-High dispersion stability with predominant Brownian motion of particles.
- 6-Reduced pumping power as compared to pure liquid to achieve equivalent heat transfer intensification.

7-Adjustable properties, including thermal conductivity and surface wettability, by varying particle concentrations to suit different applications.

Applications of nanofluids

1-Transportation (Engine cooling/vehicle thermal management)

2-Electronics cooling

3-Defens & Space

4-Nuclear systems cooling

5-Heat exchanger

6-Biomedicine

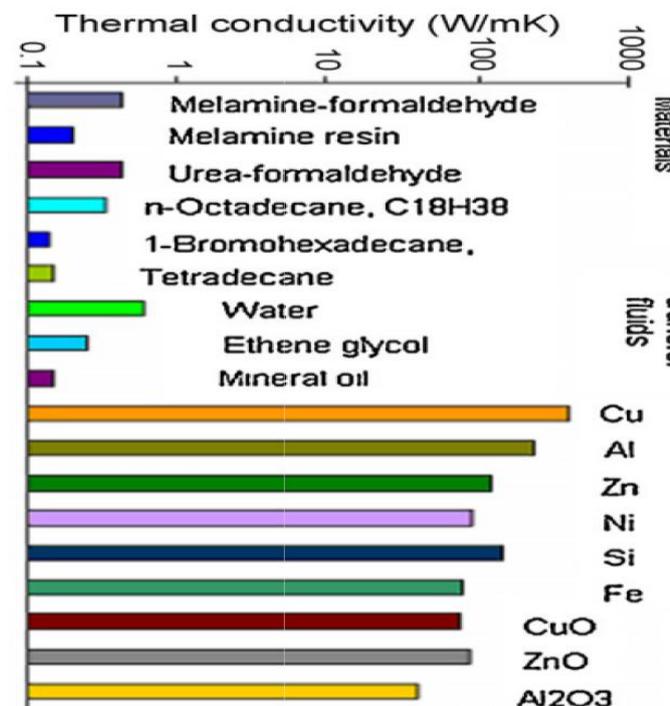
7-Other applications (heat pipes, fuel cell, Solar water heating, chillers, domestic refrigerator, Diesel combustion, Drilling,

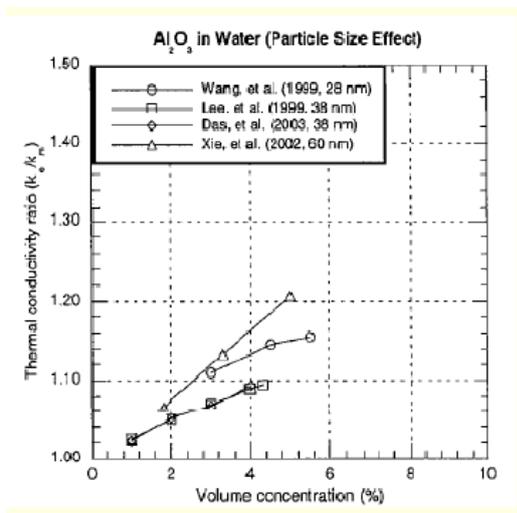
Lubrications, Thermal storage,...)

- Energy conversion and energy storage system
- Electronics cooling techniques
- Thermal management of fuel cell energy systems
- Nuclear reactor coolants
- Combustion engine coolants
- Super conducting magnets
- Biological systems and biomedicine

The thermal conductivity of nanofluid is increases with decreasing particle size and increasing the vol% of nanomaterials in the same fluid.

Base fluid	Particle material	Particle size	Volume fraction (vol.%)
Water	$\gamma\text{Al}_2\text{O}_3$ TiO_2	13 nm 27 nm	1-3 1-3
Water	CuO	<100 nm	0.9
Water	$\gamma\text{Al}_2\text{O}_3$	26-56 nm	0.6, 1, 1.6
Water	Al_2O_3	20 nm	0.2-3.0
Water	CuO	50-60 nm	0.2-3.0
Water	$\gamma\text{Al}_2\text{O}_3$	20 nm	0.2, 0.5, 1, 1.5, 2, 2.5
Water	Al_2O_3	20 nm	0-1%
Water	Al_2O_3	10 nm	0.5-1.8%
Water	ZrO_2	46 nm 60 nm	0.9-3.6 0.2-0.9
Water	Cu	<100 nm	0.3, 0.5, 0.8, 1, 1.2, 1.5, 2
Water	Cu	26 nm	0.5, 1, 1.5, 2
Acetone	Cu	80-100 nm	0.0-4.0 g/l
Water	Cu	26 nm	0.5, 1, 1.5, 2
Water	CNT	<100 nm	1.1, 2.2, 4.4
Oil	Graphite	20-40 nm	0.7-1.0
Water	MWCNT	100 nm	0.1-1.0 wt%
Ethylene glycol	TiO_2 CNT	-	-





Important Historical Events in Nanoscience

Early examples

Early examples of nanostructured materials were based on craftsmen's empirical understanding and manipulation of materials. Use of high heat was one common step in their processes to produce these materials with novel properties.

4th Century:

The Lycurgus Cup (Rome) is an example of dichroic glass; colloidal gold and silver in the glass allow it to look opaque green when lit from outside but translucent red when light shines through the inside.



9th-17th Centuries:

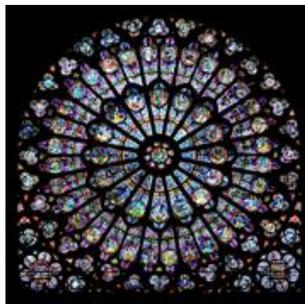
Glowing, glittering "luster" ceramic glazes used in the Islamic world, and later in Europe, contained silver or copper or other metallic nanoparticles.



*Polychrome lustreware bowl,
 9th C, Iraq, British Museum*

6th-15th Centuries:

Vibrant stained glass windows in European cathedrals owed their rich colors to nanoparticles of gold chloride and other metal oxides and chlorides; gold nanoparticles also acted as photocatalytic air purifiers.



*The South
rose window
of Notre
Dame
Cathedral,
ca 1250*

13th-18th Centuries:

“**Damascus**” **saber blades** contained carbon nanotubes and cementite nanowires—an ultrahigh-carbon steel formulation that gave them strength, resilience, the ability to hold a keen edge, and a visible moiré pattern in the steel that give the blades their name.



(**Left**) A Damascus saber (photo by Tina Fineberg for The New York Times). (**Right**) High-resolution transmission electron microscopy image of carbon nanotubes in a genuine Damascus sabre after dissolution in hydrochloric acid, showing remnants of cementite nanowires encapsulated by carbon nanotubes (scale bar, 5 nm)

1857 Michael Faraday discovers colloid gold

This suspension of gold nanoparticles in solution was totally transparent in some lighting, but in other lighting conditions could produce differently coloured solutions of ‘ruby, green, violet or blue.



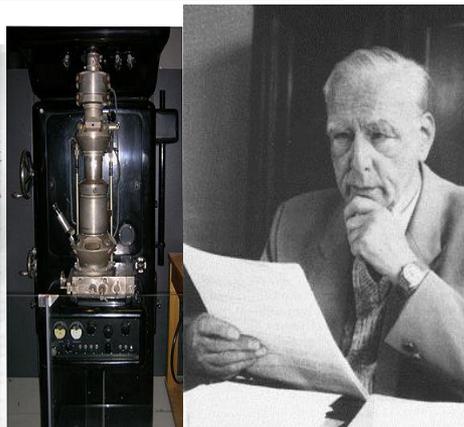
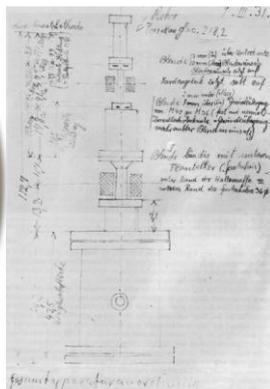
1905 Albert Einstein explains the existence of colloids

This theory was confirmed by the experiments of Jean-Baptiste Perrin, which contributed toward Perrin's 1926 Nobel prize.

1931 Max knoll & Ernst Ruska: invented Electron microscope



Ernst Ruska
(1906-1988)



1932 Langmuir discovers layers of atoms one molecule thick

Langmuir established the existence of monolayers (layers of atoms or molecules one atom thick). These monolayers have peculiar two-dimensional qualities, and led to the development of a totally transparent glass produced by forming a thin film of fluorine compound on the surface. He was awarded the Nobel prize in 1932 for this work on thin films.

1956 Arthur von Hippel at MIT introduced many concepts of—and coined the term—**“molecular engineering”** as applied to dielectrics, ferroelectrics, and piezoelectrics

1958 Jack Kilby of Texas Instruments originated the concept of, designed, and built the first integrated circuit, for which he received the Nobel Prize in 2000.



1959 Feynman suggests that there is ‘plenty of room’ to work at the nanoscale

Richard P. Feynman gave a ground-breaking speech ‘There’s plenty of room at the bottom’ where he discussed the possibility of controlling materials at the level of atoms and molecules – this was the first vision of the possibilities of science and technology at the nanoscale. He became a Nobel laureate in 1965.



1965 Intel co-founder Gordon Moore

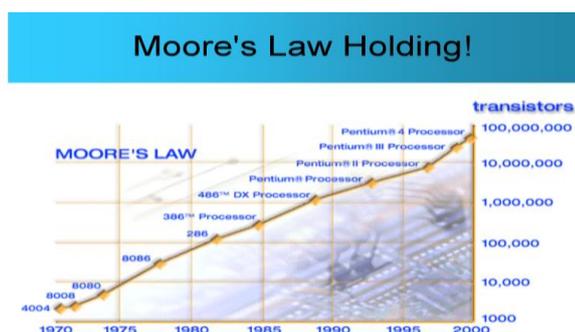
described in *Electronics* magazine several trends he foresaw in the field of electronics. One trend now known as “**Moore’s Law**,” described the density of transistors on an integrated chip (IC) doubling every 12 months (later amended to every 2 years). Moore also saw chip sizes and costs shrinking with their growing functionality—with a transformational effect on the ways people live and work. That the basic trend Moore envisioned has continued for 50 years is to a large extent due to the semiconductor industry’s increasing reliance on nanotechnology as ICs and transistors have approached atomic dimensions.

Moore’s Laws:

Gordon Moore, one of the founders of the Intel corporation, came up with two empirical laws to describe the amazing advances in integrated circuit electronics.

Moore’s first law says that the amount of space required to install a transistor on a chip shrinks by roughly half every 18 months.

Moore’s second law. the cost of building a chip manufacturing plant doubles with every other chip generation, or roughly every 36 months.

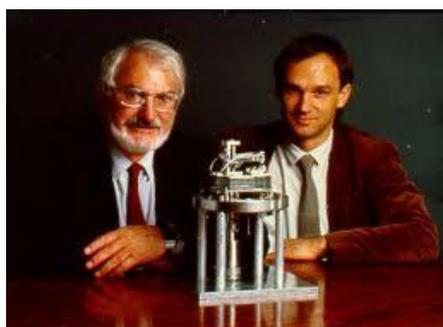


1974 Norio Taniguchi (University of Tokyo)The word ‘nanotechnology’ first used

The term ‘nanotechnology’ was coined in 1974 .He used the word to refer to ‘production technology to get the extra high accuracy and ultra fine dimensions, i.e. the preciseness and fineness on the order of 1 nm (nanometre).

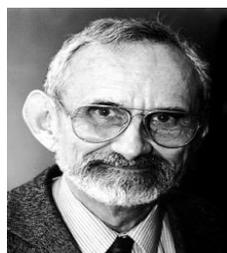
1981 IBM invent a machine which can move single atoms around

Gerd Binnig and Heinrich Rohrer invented the Scanning Tunneling Microscope (STM) at IBM. They were awarded the Nobel prize in 1986 for this work.**at the Zurich Research Lab in 1981**

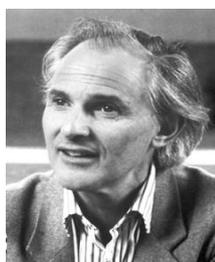


1985 A new form of carbon is discovered: C60

Richard Smalley, Robert Curl and Harold Kroto discovered C60 for which they were awarded the Nobel Prize in 1996. C60 is more commonly known as a buckyball as the 60 carbon atoms are arranged into a sphere made of 12 pentagons and 20 hexagons (exactly like a football).



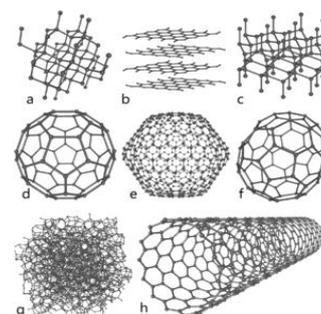
Robert F. Curl Jr



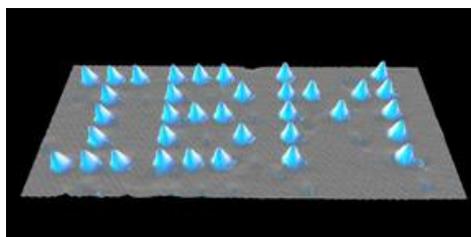
Sir Harold W. Kroto



Richard E. Smalley



1986 K.Eric Drexler: writing with a STM tool.

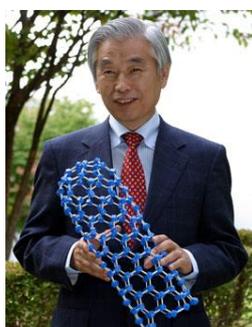


1990 IBM demonstrate ability to control the position of atoms IBM logo in atoms

IBM research scientist Don Eigler showed that the position of atoms could be controlled precisely. Using the STM he maneuvered 35 xenon atoms on a nickel surface so that they spelled out 'IBM'. This was achieved at high vacuum and in the supercooled temperature of liquid helium.

1991 Carbon nanotubes discovered

Sumino Iijima discovered a process to make 'graphitic carbon needles ranging from 4nm to 30nm in diameter and 1 micron in length.



1992 C.T. Kresge and colleagues at Mobil Oil discovered the **nanostructured catalytic materials MCM-41 and MCM-48**, now used heavily in refining crude oil as well as for drug delivery, water treatment, and other varied applications.

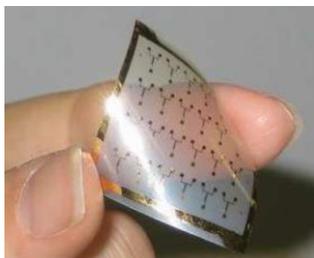
1993 **Professor Richard E. Smalley envisioned the *first nanotechnology center in the world.***

1993 First high-quality quantum dots prepared

Murray, Norris and Bawendi synthesise the first high quality quantum dots of nearly monodisperse CdS CdSe and CdTe quantum dots are very small particles with interesting optical properties.

1997 Lucent Technologies fabricated the ‘nanotransistor’

It was only 60nm wide and 1.2nm thick

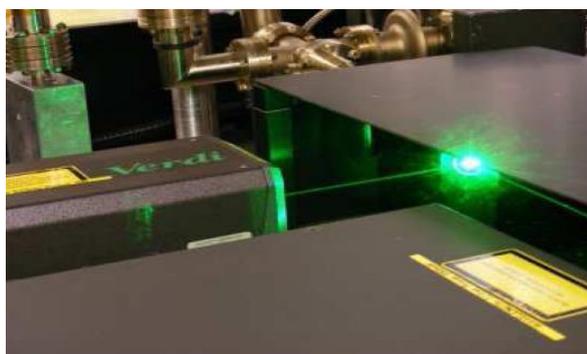


1999–early 2000’s:

Consumer products making use of nanotechnology began appearing in the marketplace, including lightweight nanotechnology-enabled automobile bumpers that resist denting and scratching, golf balls that fly straighter, tennis rackets that are stiffer (therefore, the ball rebounds faster), baseball bats with better flex and "kick," nano-silver antibacterial socks, clear sunscreens, wrinkle- and stain-resistant clothing, deep-penetrating therapeutic cosmetics, scratch-resistant glass coatings, faster-recharging batteries for cordless electric tools, and improved displays for televisions, cell phones, and digital cameras.



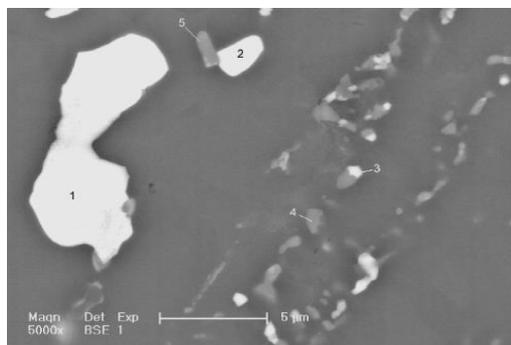
2000 Lucent Technologies with Oxford University created the first DNA motor **Eigler et al: Construction of quantum mirrors**



2001 Prototype fuel cell made using nanotubes

Nanohorns, irregularly shaped nanotubes, were developed as fuel cell for hydrogen-based fuel such as methanol. They group together creating a high surface area ideal for catalysts. NEC corporation announced that the latest generation weigh under 2 pounds, when fully fuelled, and power a laptop for 5 hours before needing refuelling.

2001 Florian Bambers: Soldering of nanotube with e-beam.



2002 Stain-repellent trousers reach the high street

Clothing embedded with nanoparticles that produce a stain-repellent coating has been developed. Nano-care™ khakis have the fabric fibres coated with nanowhiskers 10–100nm in length. This new stain-repellent fabric is available from a number of high street retailers and is available in trousers, shirts and ties.

2003 Prototype nano-solar cells produced

Prototype solar cells have been made by Nanosolar Inc. in California. They use conducting polymers and nano-based particles. These cells are also produced in flexible sheets, making them suitable for many applications.

2004 Intel launches the Pentium iv 'PRESCOFT' processor based on 90 nm technology.

2005 Erik Winfree and Paul Rothemund from the California Institute of Technology developed theories for **DNA-based computation** and “**algorithmic self-assembly**” in which computations are embedded in the process of nanocrystal growth.

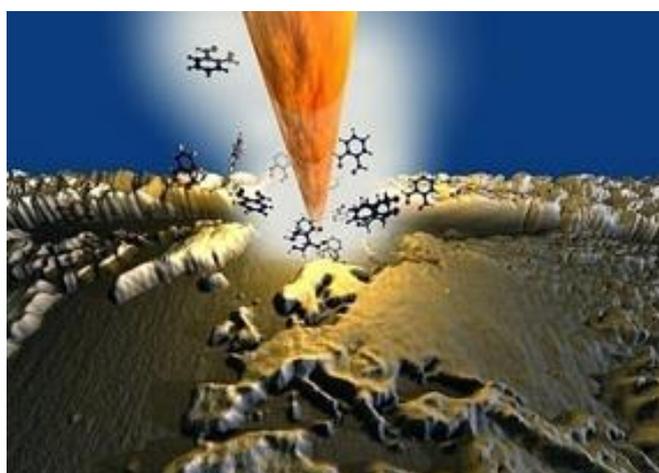
2006:James Tour and colleagues at Rice University built a **nanoscale car** made of oligo(phenylene ethynylene) with alkynyl axles and four spherical C60 fullerene (buckyball) wheels. In response to increases in temperature, the nanocar moved about on a gold surface as a result of the buckyball wheels turning, as in a conventional car. At temperatures above 300°C it moved around too fast for the chemists to keep track of it.

2007:Angela Belcher and colleagues at MIT built a **lithium-ion battery with a common type of virus** that is nonharmful to humans, using a low-cost and environmentally benign process. The batteries have the same energy capacity and power performance as state-of-the-art rechargeable batteries being considered to power plug-in hybrid cars, and they could also be used to power personal electronic devices. (Image at right.)

2009–2010:

Nadrian Seeman and colleagues at New York University created several **DNA-like robotic nanoscale assembly devices**. One is a process for creating 3D DNA structures using synthetic sequences of DNA crystals that can be programmed to self-assemble using “sticky ends” and placement in a set order and orientation. Nanoelectronics could benefit: the flexibility and density that 3D nanoscale components allow could enable assembly of parts that are smaller, more complex, and more closely spaced. Another Seeman creation (with colleagues at China’s Nanjing University) is a “DNA assembly line.” For this work, Seeman shared the Kavli Prize in Nanoscience in 2010.

2010 IBM used a silicon tip measuring only a few nanometers at its apex (similar to the tips used in atomic force microscopes) to chisel away material from a substrate to create a complete nanoscale 3D relief map of the world one-one-thousandth the size of a grain of salt—in 2 minutes and 23 seconds. This activity demonstrated a powerful patterning methodology for generating **nanoscale patterns and structures as small as 15 nanometers** at greatly reduced cost and complexity, opening up new prospects for fields such as electronics, optoelectronics, and medicine. (Image below.)



2013 Stanford researchers develop the first carbon nanotube computer.