Lecture-1

INTRODUCTION TO NANOMATERIALS

1. Introduction

Nanomaterials are cornerstones of nanoscience and nanotechnology. Nanostructure science and technology is a broad and interdisciplinary area of research and development activity that has been growing explosively worldwide in the past few years. It has the potential for revolutionizing the ways in which materials and products are created and the range and nature of functionalities that can be accessed. It is already having a significant commercial impact, which will assuredly increase in the future.

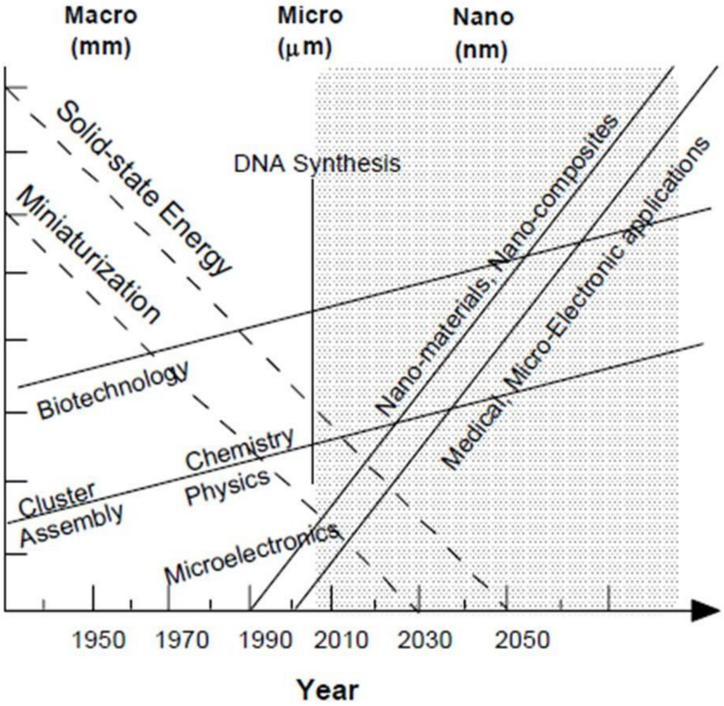


Fig. 1. Evolution of science and technology and the future

1.1. What are nanomaterials?

Nanoscale materials are defined as a set of substances where at least one dimension is less than approximately 100 nanometers. A nanometer is one millionth of a millimeter - approximately 100,000 times smaller than the diameter of a human hair. Nanomaterials are of interest because at this scale unique optical, magnetic, electrical, and other properties emerge. These emergent properties have the potential for great impacts in electronics, medicine, and other fields

.

Fig. 2. Nanomaterial (For example: Carbon nanotube)

1.2. Where are nanomaterials found?

Some nanomaterials occur naturally, but of particular interest are engineered nanomaterials (EN), which are designed for, and already being used in many commercial products and processes. They can be found in such things as sunscreens, cosmetics, sporting goods, stain-resistant clothing, tires, electronics, as well as many other everyday items, and are used in medicine for purposes of diagnosis, imaging and drug delivery.

Engineered nanomaterials are resources designed at the molecular (nanometre) level to take advantage of their small size and novel properties which are generally not seen in their conventional, bulk counterparts. The two main reasons why materials at the nano scale can have different properties are increased relative surface area and new quantum effects. Nanomaterials have a much greater surface area to volume ratio than their conventional forms, which can lead to greater chemical reactivity and affect their strength. Also at the nano scale, quantum effects can become much more important in determining the materials properties and characteristics, leading to novel optical, electrical and magnetic behaviours.

Nanomaterials are already in commercial use, with some having been available for several years or decades. The range of commercial products available today is very broad, including stain-resistant and wrinkle-free textiles, cosmetics, sunscreens, electronics, paints and varnishes. Nanocoatings and nanocomposites are finding uses in diverse consumer products, such as windows, sports equipment, bicycles and automobiles. There are novel UV-blocking coatings on glass bottles which protect beverages from damage by sunlight, and longer-lasting tennis balls using butyl-rubber/nano-clay composites. Nanoscale titanium dioxide, for instance, is finding applications in cosmetics, sun-block creams and self-cleaning windows, and nanoscale silica is being used as filler in a range of products, including cosmetics and dental fillings.

2. Advances in Nanomaterials

The history of nanomaterials began immediately after the big bang when Nanostructures were formed in the early meteorites. Nature later evolved many other Nanostructures like seashells, skeletons etc. Nanoscaled smoke particles were formed during the use of fire by early humans. The scientific story of nanomaterials however began much later. One of the first scientific report is the colloidal gold particles synthesised by Michael Faraday as early as 1857. Nanostructured catalysts have also been investigated for over 70 years. By the early 1940's, precipitated and fumed silica nanoparticles were being manufactured and sold in USA and Germany as substitutes for ultrafine carbon black for rubber reinforcements.

Nanosized amorphous silica particles have found large-scale applications in many every-day consumer products, ranging from non-diary coffee creamer to automobile tires, optical fibers and catalyst supports. In the 1960s and 1970's metallic nanopowders for magnetic recording tapes were developed. In 1976, for the first time, nanocrystals produced by the now popular inert- gas evaporation technique was published by Granqvist and Buhrman. Recently it has been found that the Maya blue paint is a nanostructured hybrid material. The origin of its color and its resistance to acids and biocorrosion are still not understood but studies of authentic samples from Jaina Island show that the material is made of needle-shaped palygorskite (clay) crystals that form a superlattice with a period of 1.4 nm, with intercalates of amorphous silicate substrate containing inclusions of metal (Mg) nanoparticles. The beautiful tone of the blue color is obtained only when both these nanoparticles and the superlattice are present, as has been shown by the fabrication of synthetic samples.

Today nanophase engineering expands in a rapidly growing number of structural and functional materials, both inorganic and organic, allowing to manipulate mechanical, catalytic, electric, magnetic, optical and electronic functions. The production of nanophase or cluster-assembled materials is usually based upon the creation of separated small clusters which then are fused into a bulk-like material or on their embedding into compact liquid or solid matrix materials. e.g. nanophase silicon, which differs from normal silicon in physical and electronic properties, could be applied to macroscopic semiconductor processes to create new devices. For instance, when ordinary glass is doped with quantized semiconductor "colloids," it becomes a high performance optical medium with potential applications in optical computing.

3. Classification of Nanomaterials

Nanomaterials have extremely small size which having at least one dimension 100 nm or less. Nanomaterials can be nanoscale in one dimension (eg. surface films), two dimensions (eg. strands or fibres), or three dimensions (eg. particles). They can exist in single, fused, aggregated or agglomerated forms with spherical, tubular, and irregular shapes. Common types of nanomaterials include nanotubes, dendrimers, quantum dots and fullerenes. Nanomaterials have applications in the field of nano technology, and displays different physical chemical characteristics from normal chemicals (i.e., silver nano, carbon nanotube, fullerene, photocatalyst, carbon nano, silica).

According to Siegel, Nanostructured materials are classified as Zero dimensional, one dimensional, two dimensional, three dimensional nanostructures.

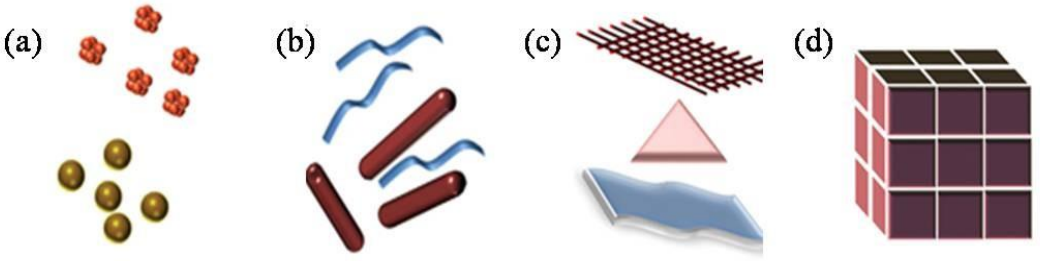


Fig. 3. Classification of Nanomaterials (a) 0D spheres and clusters, (b) 1D nanofibers, wires, and rods, (c) 2D films, plates, and networks, (d) 3D nanomaterials.

Nanomaterials are materials which are characterized by an ultra fine grain size (< 50 nm) or by a dimensionality limited to 50 nm. Nanomaterials can be created with various modulation dimensionalities as defined by Richard W. Siegel: zero (atomic clusters, filaments and cluster assemblies), one (multilayers), two (ultrafine-grained overlayers or buried layers), and three (nanophase materials consisting of equiaxed nanometer sized grains) as shown in the above figure 3.

4. Why are nanomaterials important?

These materials have created a high interest in recent years by virtue of their unusual mechanical, electrical, optical and magnetic properties. Some examples are given below:

(i) Nanophase ceramics are of particular interest because they are more ductile at elevated temperatures as compared to the coarse-grained ceramics.

(ii) Nanostructured semiconductors are known to show various non-linear optical properties. Semiconductor Q-particles also show quantum confinement effects which may lead to special properties, like the luminescence in silicon powders and silicon germanium quantum dots as infrared optoelectronic devices. Nanostructured semiconductors are used as window layers in solar cells.

(iii) Nanosized metallic powders have been used for the production of gas tight materials, dense parts and porous coatings. Cold welding properties combined with the ductility make them suitable for metal-metal bonding especially in the electronic industry.

(iv) Single nanosized magnetic particles are mono-domains and one expects that also in magnetic nanophase materials the grains correspond with domains, while boundaries on the contrary to disordered walls. Very small particles have special atomic structures with discrete electronic states, which give rise to special properties in addition to the super-paramagnetism behaviour. Magnetic nanocomposites have been used for mechanical force transfer (ferrofluids), for high density information storage and magnetic refrigeration.

(v) Nanostructured metal clusters and colloids of mono- or plurimetallic composition have a special impact in catalytic applications. They may serve as precursors for new type of heterogeneous catalysts (Cortex-catalysts) and have been shown to offer substantial advantages concerning activity, selectivity and lifetime in chemical transformations and electrocatalysis (fuel cells). Enantioselective catalysis was also achieved using chiral modifiers on the surface of nanoscale metal particles.

(vi) Nanostructured metal-oxide thin films are receiving a growing attention for the realization of gas sensors (NOx, CO, CO2, CH4 and aromatic hydrocarbons) with enhanced sensitivity and selectivity. Nanostructured metal-oxide (MnO2) finds application for rechargeable batteries for cars or consumer goods. Nanocrystalline silicon films for highly transparent contacts in thin film solar cell and nano-structured titanium oxide porous films for its high transmission and significant surface area enhancement leading to strong absorption in dye sensitized solar cells.

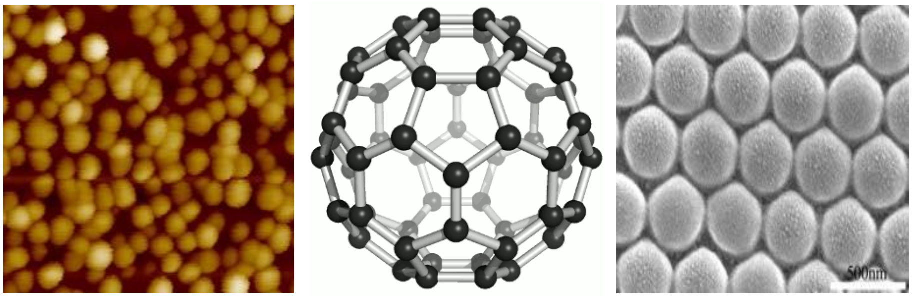
(vii) Polymer based composites with a high content of inorganic particles leading to a high dielectric constant are interesting materials for photonic band gap structure.

At the nanoscale, strange things happen to materials –their properties can change.

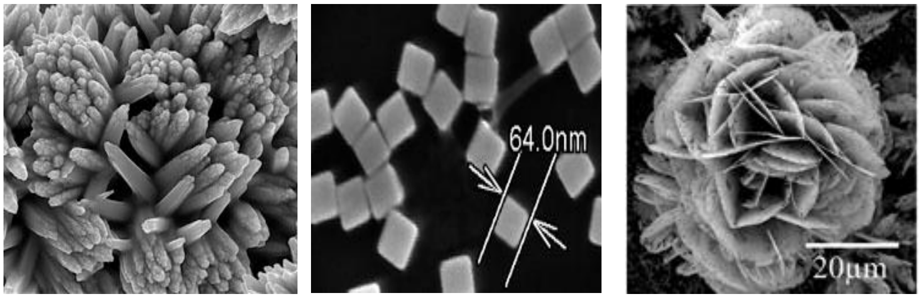
1. Reactivity - As particles get smaller they tend to react differently with their environment than larger particles.
2. Size - Smaller particles can have different optical properties: their colours change because different sizes of particle reflect and absorb light differently.
3. Magnetism - Smaller particles can have different magnetic properties than larger.

5. Examples of Nanomaterials

Nanomaterials (gold, carbon, metals, meta oxides and alloys) with variety of morphologies (shapes) are depicted in Fig. 4.



Au nanoparticle Buckminsterfullerene FePt nanosphere



Titanium nanoflower Silver nanocubes SnO2 nanoflower

Fig. 4. Nanomaterials with a variety of morphologies

6. Nanomaterial - synthesis and processing

Nanomaterials deal with very fine structures: a nanometer is a billionth of a meter. This indeed allows us to think in both the 'bottom up' or the 'top down' approaches (Fig. 5) to synthesize nanomaterials, i.e. either to assemble atoms together or to dis-assemble (break, or dissociate) bulk solids into finer pieces until they are constituted of only a few atoms. This domain is a pure example of interdisciplinary work encompassing physics, chemistry, and engineering upto medicine.

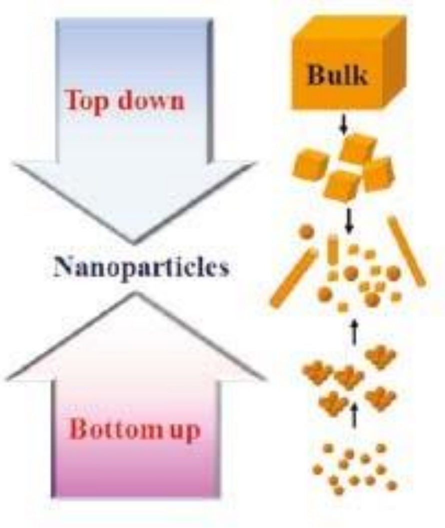


Fig. 5. Schematic illustration of the preparative methods of nanoparticles.

Lecture-2

NANOSTRUCTURES

1. **Zero-Dimensional Nanomaterials**
2. **One-Dimensional Nanomaterials**
3. **Two-Dimensional Nanomaterials**
4. **Three-Dimensional Nanomaterials**

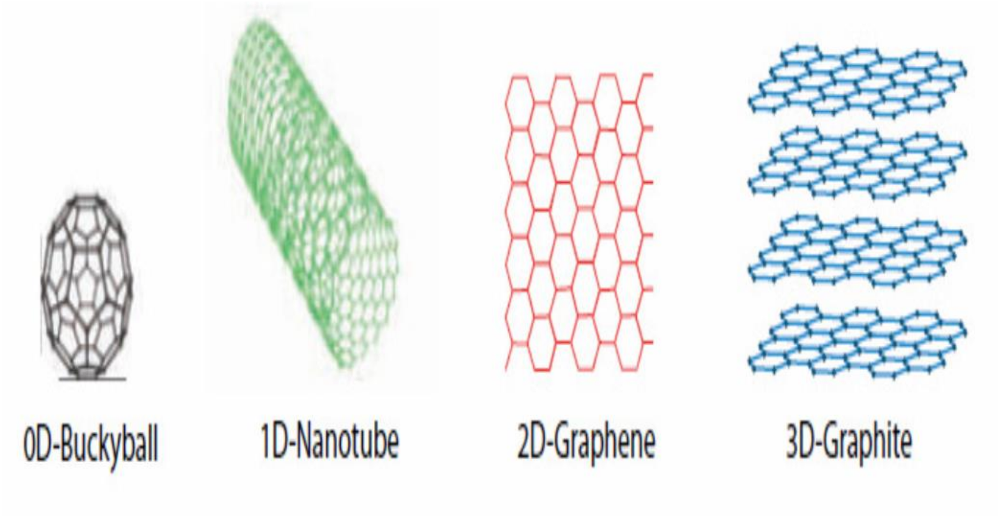


Fig. 6. Carbon nanostructures

1. Zero-Dimensional Nanomaterials

These materials have diameters <100 nm, and are denoted by nanoparticles, nanoclusters, or nanocrystals. The term nanoparticle is generally used to encompass all 0 D nanosized building blocks (regardless of size and morphology), or those that are amorphous and possess a relatively irregular shape.

For the fabrication of nanoparticles, a small size is not the only requirement. For any practical application, the processing conditions need to be controlled in such a way that resulting nanoparticles have the following characteristics:

- identical size of all particles (also called monosized or with uniform size distribution)
- identical shape or morphology,
- identical chemical composition and crystal structure (iv) individually dispersed or monodispersed, i.e. no agglomeration. If agglomeration does occur, nanoparticles should be readily redispersible

Materials wherein all the dimensions are measured within the nanoscale

- The most common representation of zero dimensional nanomaterilas are nano dots

2. One-Dimensional Nanostructures

Nanotube, Nanofiber, Nanowire, and Nanorod

The common thread among all of these structures is that their diameters must be within the 1–100 nm range; typically, their lengths are within the micron (or larger) regime.

One dimension is outside the nanoscale and other two dimensions
are in the nanoscale. This leads to needle like-shaped nanomaterials

- 1-D materials include nanotubes, nanorods and nanowires.
- 1-D nanomaterials can be a morphous or crystalline
- Single crystalline or poly crystalline
- Chemically pure or impure
- Metallic, ceramic or polymeric.

3. Two-Dimensional Nano Structured Materials

One dimension lies in the nanometer range and other two dimensions are not confined to the nanoscale

- 2D nanomaterials exhibit plate like shapes
- Two dimensional nanomaterials include nanofilms, nanolayers and nanocoating

4. Three-Dimensional materials

Three dimensional materials are not confined in the nanoscale in any dimension. These materials are thus characterized by having three arbitrarily dimensions above 100nm

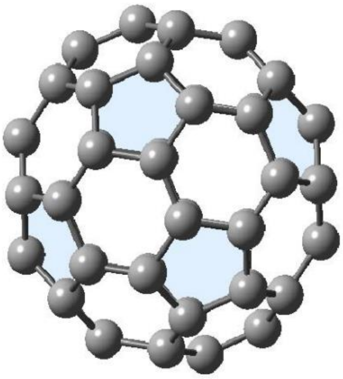
- Materials possess a nanocrystalline structure or involve the presence of features at the nanoscale
- Example: nanoballs (dendritic structures), nanocoils, nanocones, nanopillers and nanoflowers

➢ The first Nanostructures

In 1985, Harold W. Kroto, Robert F. Curl Jr. and Richard E. Smalley discovered the first important nanostructure the C-60 fullerene consisting of 60

Carbon atoms. They shared the 1996 Nobel Prize in Chemistry for this discovery

The C-60 particle was named ‘fullerene’ or ‘Buckyball’ after the name of R. Buckminister Fuller who invented geodesic domes. The structure of C-60 resembles the structure of these domes.



The C-60 Nano particle is about 0.7 nm wide and contains 12 pentagonal and 20 hexagonal faces arranged like in a soccer ball. The C-60 crystal lattice is fcc type in which the C-60 molecules are rotating rapidly at their locations.

- The melting point of C-60 crystal is 1180 deg C and it’s band gap is 1.7 eV. Average C-60–C-60 distance is 1.002 nm.

Fullerenes

- In 1990, Kratschmer and Huffman (University of Arizona) reported for the first time that C60 and other fullerenes (Cnc) can be produced in an electric arc apparatus

A special case of nanocrystal that is comprised of a semiconductor is known as a quantum dot.

Quantum dots

Typically, the dimensions of these nanostructures lie in the range 1–30 nm, based on its composition Quantum dots currently find applications as sensors, lasers, and LEDs. In fact, new high-density disks (e.g., HD-DVD and Blu-ray high-definition DVD formats) may only be read via blue lasers, which are fabricated from quantum dots. Long-term applications for these structures will likely include optical computing and high-efficiency solar cells.

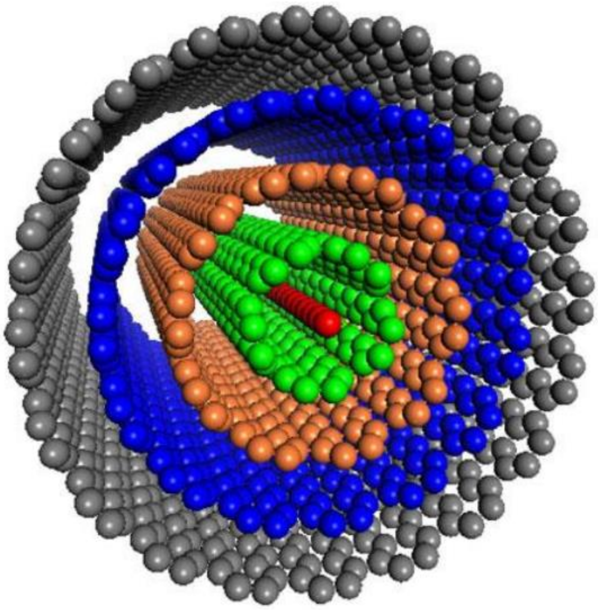
Another nanostructure -the CNT

The most widely studied 1D nanomaterial is the carbon nanotube (CNT). These structures were first discovered by Iijima in 1991, and consist of a graphitic sheet(s) rolled into a tubular array.

Based on the layers of graphene sheets that comprise the CNT, the structures are designated as single-walled, double-walled, or multiwalled nanotubes (SWNTs, DWNTs, or MWNTs respectively)

- In 1991, Sumio Iijima discovered the multiwall carbon nanotubes (MWCNTs) on the anode of a carbon discharge apparatus. The diameter of these nanotubes ranged between 4-30 nm and their lengths measured up to 1 mm.
- In 1993, Iijima et. al. reported the discovery of single walled carbon nanotubes (SWCNTs) with diameter as small as 1.37 nm.

The diameters of CNTs range from 1 nm (SWNTs) to >30 nm (MWNTs), with aspect ratios (length:width) ranging from 100 to greater than 1×10^6 .



- **Nanorods**

A nanorod is typically a crystalline 1D nanostructure, with an overall length comparable to its width (i.e., both dimensions are <100 nm). As their name implies, another feature of nanorods is their rigid sidewall structures. The term “nanocrystal” is probably more appropriate for these structures (or, more explicitly: “rod-like nanocrystals”).

- **Nanofibers**

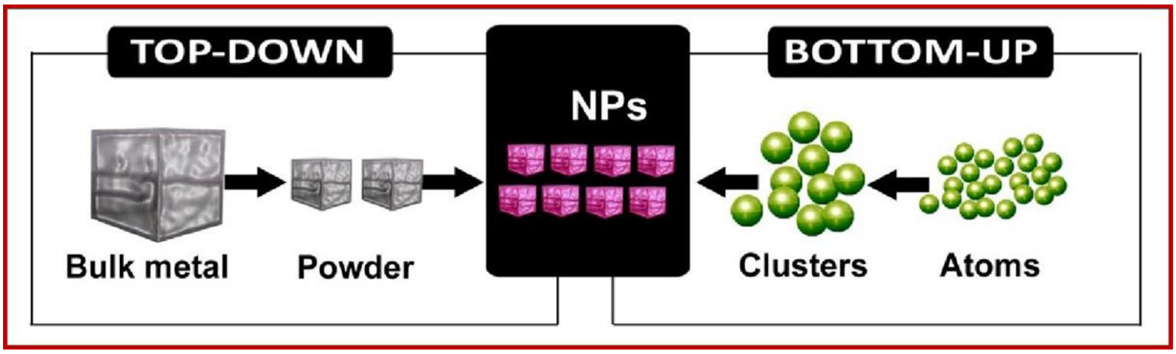
The term nanofiber should be reserved for 1D nanostructures that are amorphous (and usually nonconductive) such as polymers and other nongraphitized carbonaceous structures

LECTURE 3

Synthesis of Nanomaterials

Scientists are conducting research to develop novel materials with better properties, more functionality and lower cost than the existing one. Several physical, chemical methods have been developed to enhance the performance of nanomaterials displaying improved properties with the aim to have a better control over the particle size, distribution methods to Synthesis of Nanomaterials. In general, top-down and bottom-up are the two main approaches for nanomaterials synthesis.

A. Top-down: size reduction from bulk materials.
B. Bottom-up: material synthesis from atomic level.



- Top down approach refers to slicing or successive cutting of a bulk material to get nano sized particle.
- Bottom up approach refers to the build-up of a material from the bottom: atom by atom, molecule by molecule
- Atom by atom deposition leads to formation of Self-assembly of atoms/molecules and clusters. These clusters come together to form self- assembled monolayers on the surface of substrate

A. Top-down routes

are included in the typical solid –state processing of the materials. This route is based with the bulk material and makes it smaller, thus breaking up larger particles by the use of physical processes like crushing, milling or grinding. Usually this route is not suitable for preparing uniformly shaped materials, and it is very difficult to realize very small particles even with high energy consumption. The biggest problem with top-down approach is the imperfection of the surface structure. Such imperfection would have a significant impact on physical properties and surface chemistry of nanostructures and nanomaterials. It is well known that the conventional top down technique can cause significant crystallographic damage to the processed patterns.

Top – Down used to produce

- ➢ optical (semiconductor industry)
- ➢ electron (master production, research)
- ➢ scanning probe (mainly research)

- **In Top-down techniques, the starting material is solid state**

Physical processing methods:

- Mechanical methods :
  - cutting , etching, grinding
  - ball milling
- Lithographic techniques:
  - Photo Lithography
  - Electron Beam Lithography

ADVANTAGES

- Large scale production: deposition over a large substrate is possible
- Chemical purification is not required

DISADVANTAGES

Yields:

- broad size distribution (10-1000 nm)
- varied particle shapes or geometry
- Control over deposition parameters is difficult to achieve
- Impurities: stresses, defects and imperfections get introduced
- Expensive technique

B. Bottom –up approach

refers to the build-up of a material from the bottom: atom-by-atom, molecule-by-molecule or cluster-by-cluster. This route is more often used for preparing most of the nano-scale materials with the ability to generate a uniform size, shape and distribution. It effectively covers chemical synthesis and precisely controlled the reaction to inhibit further particle growth. Although the bottom-up approach is nothing new, it plays an important role in the fabrication and processing of nanostructures and nanomaterials.

Bottom – Up used to produced supramolecular level

- **All the Bottom-up techniques, the starting material is either gaseous state or liquid state of matter**

- Physical and chemical processing methods: Physical techniques

  Physical Vapor Deposition (PVD): involves condensation of vapor phase species

  - Evaporation (Thermal , e-beam)
  - Sputtering
  - Plasma Arcing,
  - Laser ablation,

Chemical techniques

CVD: Deposition of vapor phase of reaction species

PECVD(RF-PECVD,MPECVD)
Self-assembled Monolayer :
Electrolytic deposition, Sol-gel method, Microemusion route, pyrolysis.

ADVANTAGES

- Ultra-fine nanoparticles, nanoshells, nanotubes can be prepared
- Deposition parameters can be controlled
- Narrow size distribution is possible (1-20 nm)
- Cheaper technique

DISADVANTAGES

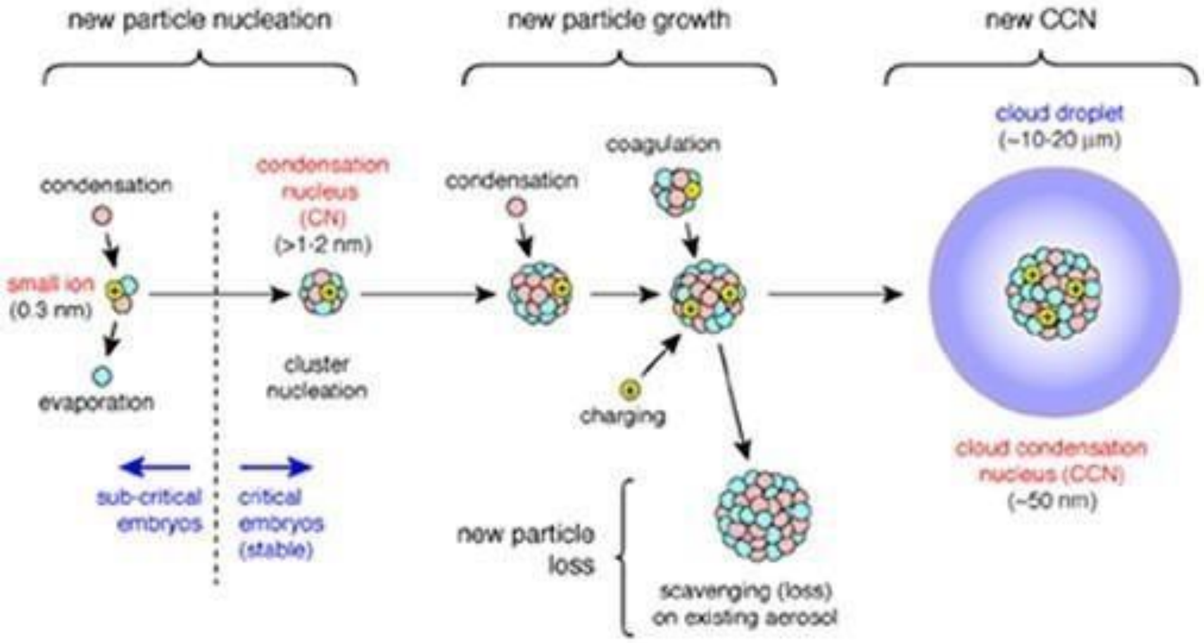
- Large scale production is difficult
- Chemical purification of nanoparticles is required

Growth Kinetics: Nucleation and Growth processes

Synthesis of nanoparticles is a combination of two stage process, nucleation and growth.

Most phase transformations begin with the formation of numerous small particles (clusters) of the new phase that increase in size until the transformation is complete.

Nucleation is the process whereby nuclei (seeds) act as templates for crystal growth.



Nucleation is the first step in the formation of either a new thermodynamic phase or a new structure via self-assembly or self-organisation.

There are two different categories of Nucleation:

- Heterogeneous nucleation –
- **Homogenous nucleation**

LECTURE FOUR

Unique Characteristics of Nanoparticles

- Large surface to volume ratio
  5. High percentage of atoms/molecules on the surface
  6. Surface forces are very important, while bulk forces are not as important.
  7. Metal nanoparticles have unique light scattering properties and exhibit plasmon resonance.
- Semiconductor nanoparticles may exhibit confined energy states in their electronic band structure (e.g., quantum dots)
- Can have unique chemical and physical properties
- Same size scale as many biological structures

Examples of Unusual Properties

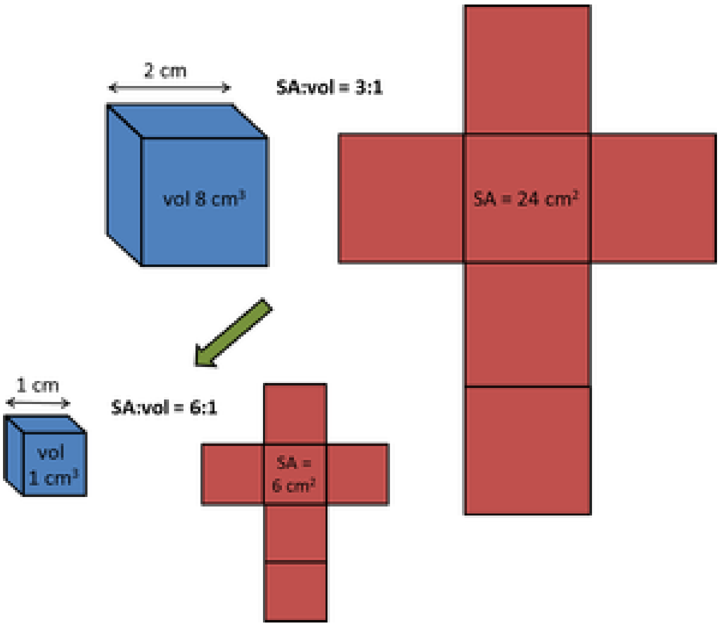
- Lowered phase transition temps
- Increased mechanical strength
- Different optical properties
- Altered electrical conductivity
- Magnetic properties
- Self-purification and self-perfection

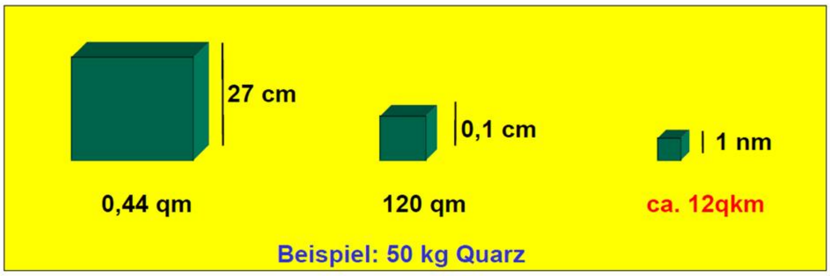
Physical Properties of Nanoparticles

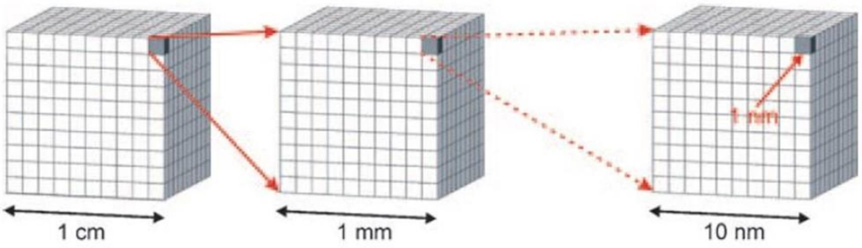
Physical properties of nanoparticles are dependent on:

– Size
– Shape (spheres, rods, platelets, etc.)
– Composition
– Crystal Structure (FCC, BCC, etc.)
– Surface ligands or capping agents
– The medium in which they are dispersed

Surface-to-Volume ratio increases with decreasing size:







- Consider a Cube with length of each side = 1m Since it has six faces, its surface area = 6 sq.m. Its volume = 1 cubic meter

Surface Area to Volume Ratio = 6/1 = 6

If we cut the cube into 8 (=23) pieces that are of 0.5m per side , then the surface area of each piece = (1/2)x(1/2) x6 = 1.5 sq.m. But there are 8 pieces, total surface area = 1.5x8 = 12 sq.m.

Surface Area to Volume Ratio = 12/1 = 12

If we further cut into 27 (=33) pieces, then the surface area of each piece = (1/3)x(1/3) x6 = (2/3) sq.m.

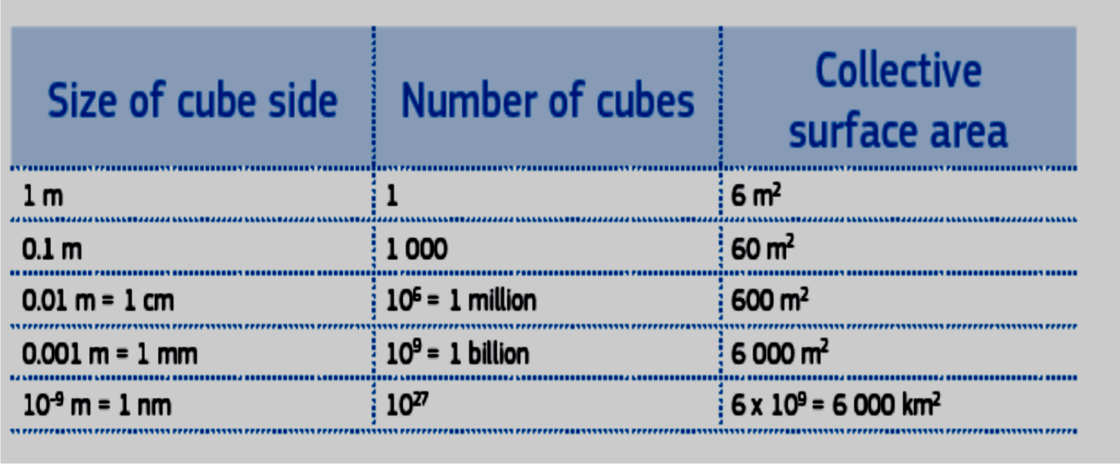
But there are 27 pieces, total surface area = (2/3)x27 = 18 sq.m.

Surface Area to Volume Ratio = 18/1 = 18

- A block made from 64 sugar cubes is 4 cm on a side and has a surface area of 6 x 16 cm^2 or 96 cm^2 and a volume of 64 cm^3. This is a surface area to volume ratio of 1.5 cm^2/cm^3. If you compute the surface of all 64 individual cubes, you would have 64 x 6cm^2 or 384 cm^2 or 4 times more surface area with the same total volume.

The consequence is that the surface-to-volume ratio of the material — compared to that of the parent bulk material — is increased.

How would the total surface area increase if a cube of 1 m3 were progressively cut into smaller and smaller cubes, until it is composed of 1 nm3 cubes? Table (2) summarizes the results.



Size of cube side	Number of cubes	Collective surface area
1 m	1	6 m^2
0.1 m	1 000	60 m^2
0.01 m = 1 cm	10^6 = 1 million	600 m^2
0.001 m = 1 mm	10^9 = 1 billion	6 000 m^2
10^{-9} m = 1 nm	10^{27}	6 x 10^9 = 6 000 km^2

Lecture 5

Characterization Methods

This lecture summarizes some of the methods used for imaging and characterization of nanomaterials, meaning materials with at least one dimension at the nanoscale level (1–100 nm). These include nanostructured surfaces, nanoparticles, nanoporous materials, etc. The aim of this lecture is to answer the question: How are nanomaterials imaged and characterized?

There are many methods available to image nanostructured materials (e.g. a nanostructured surface) and to characterize their physical and chemical properties. Here, only a short review and description of these methods is provided.

In general, two fundamental types of characterization methods exist: imaging by microscopy and analysis by spectroscopy. The methods employed have been developed specifically to meet the characterization needs of nanomaterials.

Microscopy

An optical microscope uses visible light (i.e. electromagnetic radiation) and a system of lenses to magnify images of small samples. For this reason, it is also called a light microscope. Optical microscopes are the oldest and simplest of the microscopes. The resolution limit of an optical microscope is governed by the wavelength of visible light (As a general rule of thumb, the resolution is about half the wavelength used in the measurement). Visible light is the part of the electromagnetic spectrum with wavelengths between 400 and 700 nm and the resolving power of an optical microscope is around 0.2 μm or 200 nm: thus, for two objects to be distinguishable, they need to be separated by at least 200 nm. Single objects smaller than this limit are not distinguishable: they are seen as fuzzy objects‘. This is known as the _diffraction limit‘ of visible light.

In order to overcome the limitations set by the diffraction limit of visible light, other microscopes have been designed which use other beams: rather than light, they use **electron beams** to illuminate the sample. **Electron microscopes** have much greater resolving power than light microscopes that use electromagnetic radiation and can obtain much higher magnifications of up to two million times, while the best light microscopes are limited to magnifications of 2000 times. Both electron and light microscopes have resolution limitations, imposed by the wavelength of the radiation used. The greater resolution and magnification of the electron microscope is because the wavelength of an electron (its de Broglie wavelength) is much smaller than that of a photon of visible light.

There are various types of electron microscopes, such as the **scanning electron microscope** (SEM) and or the **transmission electron microscope** (TEM). Conceptually, these microscopes are similar to an optical microscope in the sense that they use radiation to visualise a sample: photons in the case of an optical microscope, and electrons (i.e. particles) in the case of electron microscopes.

In 1981, a totally new concept of imaging was introduced by Binning and his co-workers from IBM. They used a small metal tip placed at a minute distance from a conducting surface: when the two are placed very close together, but not actually touching, a bias between the two can allow electrons to tunnel through the vacuum between them. This creates a tunnelling current, which can be measured and which is a function of the electron density on the surface. Electron density is the probability of finding an electron in a particular place: there is high electron density around the atoms and bonds in molecules.

This type of microscope is called the **Scanning Tunnelling Microscope** (STM). Variations in current as the probe passes over the surface are translated into an image. The STM can create detailed 3D images of a sample with atomic resolution. This means that the resolution is actually so high that it is possible to see and distinguish the individual atoms (0.2 nm = $2 * 10^{-10}$ m) on the surface. The invention of the STM earned Binning and his co-worker Heinrich Rohrer (at IBM Zürich) the **Nobel Prize in Physics in 1986**.

1. Scanning tunnelling microscope (STM)

The STM is a fundamental tool in nanoscience and nanotechnologies. It is used in both industrial and fundamental research to obtain atomic-scale images of metal and semiconducting surfaces (**Figure 29**). It provides a three-dimensional profile of the surface roughness, allowing the observation of surface defects and the determination of the size and conformation of molecules and aggregates.

Another astonishing property of the STM is that it can be used to manipulate (move!) individual atoms, trigger chemical reactions, as well as performing electronic spectroscopy.

➢ Operational principle of the STM

STM is a **Scanning Probe Microscopy** (SPM) technique. SPM provides images of surfaces by scanning the surface line by line with a probe. Scanning works very similarly to the way the blind read Braille, line by line, by moving a finger over buds on the paper. In an STM, the probe is a very thin needle called the ‗tip‘ that is so small that its point is just a few atoms across. The tip is made of a conducting material (e.g. metal, typically tungsten). The precise movement of the tip is controlled by a piezomotor.

The tip of an STM is about 3 mm ($3 * 10^{-3}$ m) long and should be located very close to the surface to be scanned. In practice, the distance between the end of the tip and the surface must be less than 0.1 nm (10^{-10} m), without the tip actually hitting the surface. To visualize how small and precise this actually is, it corresponds to placing the 300 m tall Eiffel Tower ($3 * 10^{2}$ m) top down with a distance of 0.01 mm ($1 * 10^{-5}$ m) over a neighbourhood and scanning across it without actually touching it (**Figure 30**). One of the fundamental elements of the STM is the tip of the probe that scans the surface, which must be sharpened to a very fine tip (**Figure 31**). The fabrication of sharper probes allows for better resolution of surface features. Ultimately, a probe tip sharpened to one atom would provide the best resolution.

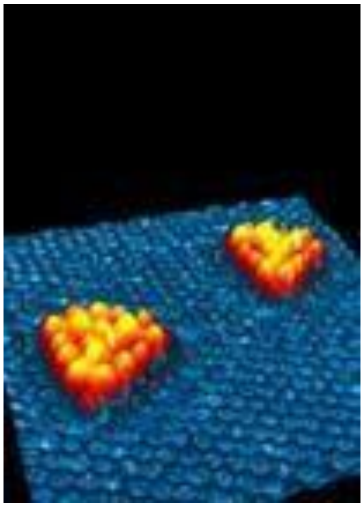


Figure 29: Nanocatalyst used for cleaning sulphur from crude oil: this STM image shows two molybdenum-disulfide nanoclusters consisting each of 15 Mo atoms and 42 S atoms.

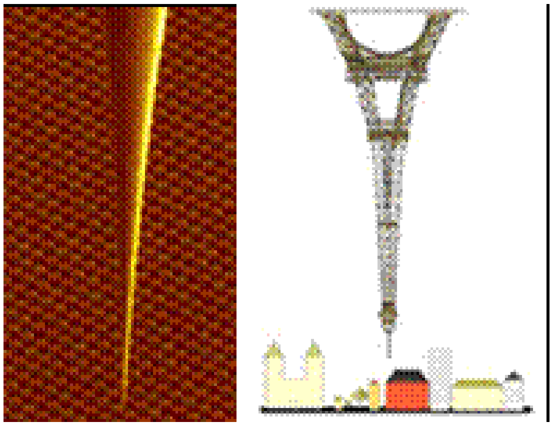


Figure 30: Left: 3 mm tip positioned 0.1 nm above the surface; right: macroscopic analogy: a 300 m high Eiffel Tower located 0.01 mm above the city

Figure 31: SEM image of a tungsten tip for STM imaging

When a conducting tip is brought very near to a metallic or semiconducting surface, at a distance of about 0.1 nm, it can induce the formation of a tunnel current between the tip and the surface: a bias between the two atoms (tip and surface) can allow electrons to tunnel through the vacuum between them and induce the formation of a current. Variations in current as the probe passes over the surface are translated into an image (**Figure 32**).

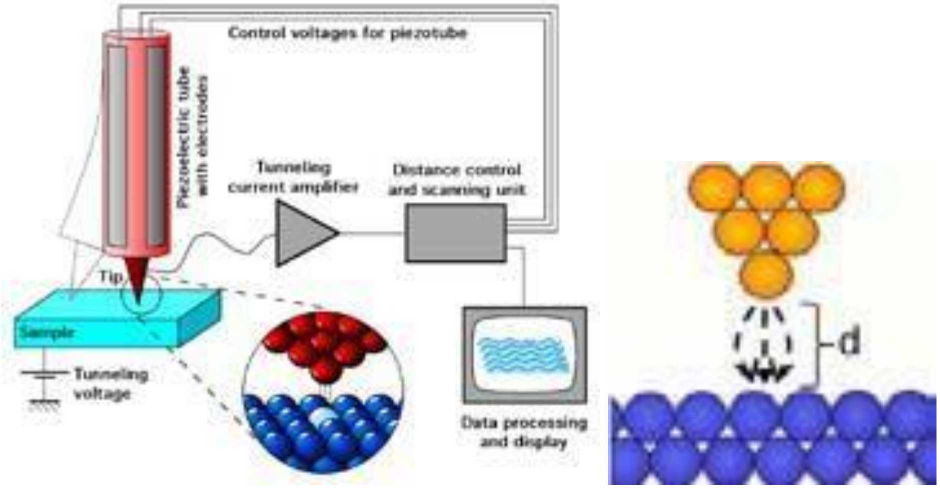


Figure 32: Schematic representation of STM scanning over a surface: (left) overview of an STM; (right) close-up of the tunnelling effect between the tip of the probe and the surface atoms. The intensity of the tunnel current depends on the distance d.

As the conducting tip of an STM scans over a conducting or semiconducting surface, a _tunnel current‘ is formed, which arises from electrons jumping from the surface to the tip of the STM probe. The probability of this happening depends largely on the distance **d** between the surface and tip, thus the size of the current depends on this distance. Small changes in the distance between the probe tip and the substrate surface translate into large changes in tunnel current: atomic scale resolution by STM is possible in the x, y and z directions due to this phenomenon.

➢ How are images created?

One way of using the STM to image the surface of the substrate is to keep the tunnel current constant, typically nanoamps (nA) (10^{-9} A) by applying a constant tunnel current, the tip of the probe is kept at a specific distance above the surface. When the tip scans a surface, it will rise when it scans over an atom and drop when scanning between two atoms in the surface, as shown in **Figure 33**, where the STM tip moves from left to right.

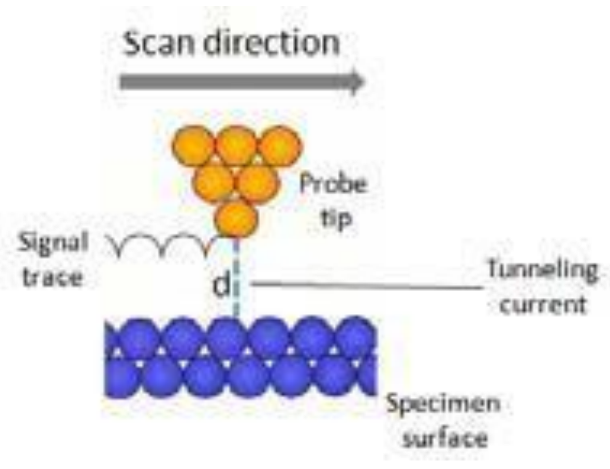


Figure 33: Schematic representation of the signal trace as a tip of an STM probe scans a surface

The movement of the tip can be transformed into a **coloured height map** of the surface. This map corresponds to an atlasmap, where each colour indicates a specific height, as in **Figure 34**.

Using the STM, surfaces can be scanned by moving the tip in steps of 0.1 nm (10-10 m), thus providing a very accurate representation of the surface. For the technique to work, it is necessary that, as the tip scans the surface, a tunnel flow is induced. **Thus, the surface must be conductive to some extent** (the substrate must be a conductor or semiconductor).

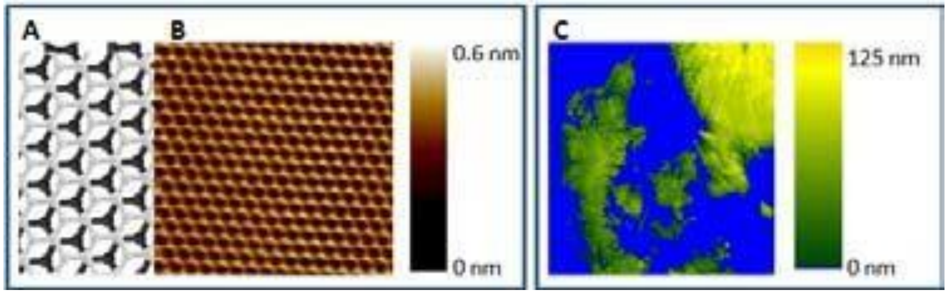


Figure 34: (A) model of two layers of graphite; (B) STM image of a graphite sheet (height scale on the right, note how the image fits the model); (C) relief map of Denmark (height scale on the right)

If it is necessary to scan a surface which in itself is **not electrically conductive**, it can be coated with a very thin layer of a conductive material such as gold. This does, however, imply that the STM is less suitable for some studies (e.g. to study biological molecules such as DNA (which is not conductive)). For these types of samples, other SPM techniques are more suitable, such as the **Atomic Force Microscope** (AFM). An AFM does not measure the tunnel current, but the forces between the tip and the surface and, therefore, does not require the surface to be conductive. The AFM was developed in 1985, also by Binning and co-workers at IBM Zürich. It was developed specifically to image materials that are insulating.

2. Atomic force microscope

The **Atomic Force Microscope** (AFM) was developed specifically to overcome the intrinsic limitations of the STM, which is not suitable for imaging surfaces coated with biological entities such as DNA or proteins. The AFM operates in air and not under a vacuum. Some versions of the instrument also allow operation in liquid, which is very advantageous when imaging biological samples that often need buffers to remain biologically active.

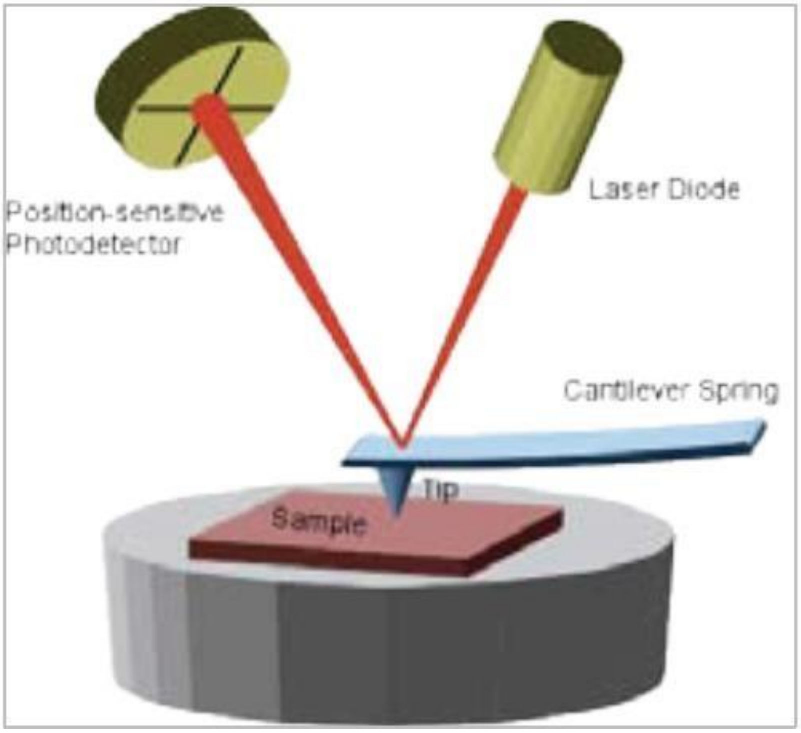


Figure 35: Operation principle of an AFM source

The AFM measures the **interaction force** (attractive or repulsive) between the probe and the surface. The solid probe is located at the end of a very flexible cantilever; an optical system detects the deflection of a laser beam that bounces off the reflective back of the cantilever, thus reporting cantilever fluctuations, which are proportional to the applied force. The probe is continuously moved along the surface and the cantilever deflection is constantly monitored. A feedback loop continuously changes the height of the probe on the surface in order to keep the applied force constant. The vertical movement of the probe is recorded to create a **topographic map** of the surface under study.

The AFM probe tip is very sharp, with a radius of curvature in the range of tens of nanometres. If the surface under analysis is soft, the probe can penetrate it, with the risk of damaging it and degrading the spatial resolution of the resulting micrograph. To overcome this limitation, instruments working in dynamic modes have been developed. In these systems, the probe is not simply dragged on the surface but oscillated vertically with respect to the surface while it is scanned. These techniques (tapping mode and non-contact mode) significantly reduce the damage that can be caused by the probe and allow the imaging of soft, compressible samples, such as biomolecules and cells. On the other hand, the tip of an AFM can be used to **deliberately _scratch‘ and remove some molecules from a surface** or to write with an **_ink**‘. Both are _writing‘ methods in the sense that they allow the creation of nanostructures on a surface with any geometry. This technique is called Dip Pen Nanolithography (DPN).

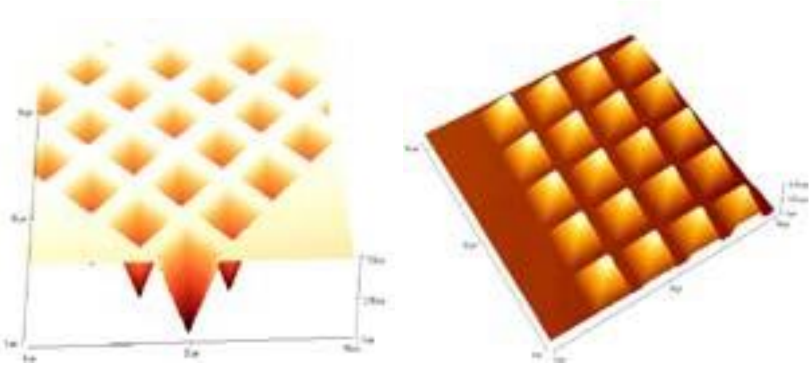


Figure 36: AFM image of an array of pyramidal wells (left) and pyramidal posts (right): the tips of the posts are about 100 nm wide

Spectroscopy methods

Spectroscopy is defined as the branch of science that is concerned with the investigation and measurement of spectra produced when matter interacts with or emits electromagnetic (EM) radiation. Depending on the wavelength of the electromagnetic used and the type of interaction with matter that occurs (absorption, scattering, etc.), different spectra are measured from which much information can be inferred.

Next, the spectroscopy methods that are most relevant in the characterization of nanomaterials (particles and surfaces) are briefly reviewed.

1. X-ray methods

X-ray methods involve exciting a sample either with X-rays (creating more X-rays)or with electrons (creating X-rays). X-rays can be also generated by bombarding a sample with alpha particles. The energy of emitted X-rays is equal to the difference between the binding energies of the electrons involved in the transition. There are various methods that use X-rays: **X-ray fluorescence** (XRF), **X-ray diffraction** (XRD), etc. In the context of nanomaterials, the most important method is **small-angle X-ray scattering** (SAXS) analysis. Like XRD, this method is based on the principle of scattering of X-rays. Diffraction of X-rays is a result of scattering from atoms configured in regular arrays. In conventional XRD, only crystalline materials can be visualized, as it is necessary to have a periodicity in the structure in the long-range, which nanomaterials lack (owing to their size). XRD is used for bulk crystals. With SAXS, particle sizes of the order of 1–100 nm can be analyzed.

The method can be used to image powders in the dry state or suspended in a medium. The method can also be used to measure the nanoparticle size.

2. UV-visible plasmon absorption and emission

Metal nanoparticles, in particular gold and silver, are characterized by a plasmon resonance absorption that gives rise to intensely coloured solutions.

The absorption band is due to electrons confined at the particle surface that collectively oscillate at a specific frequency, commonly referred to as the surface plasmon resonance frequency. As examples, the plasmon band of a 20 nm silver (Ag) particle is centred at 395 nm, resulting in a yellow solution, while a 20 nm gold (Au) particle absorbs at 520 nm resulting in a red solution. The **plasmon absorption effect** occurs for particles up to approximately 50 nm in diameter and scales with particle volume. Absorption can in be in the visible and UV area of the spectrum. Particles can be visualised by absorbance in solution at nanomolar and picomolar concentrations.

➢ Plasmon resonance light scattering

In **larger metal nanoparticles** (> 30 nm) another effect, light scattering, is observed. When illuminated with white light, metal nanoparticles in the 50–120 nm diameter size range scatter light of a specific colour at the surface plasmon resonance frequency. This effect is called **plasmon resonance light scattering**. As in the case of plasmon absorbance, light scattering scales with particle volume, but the scattered light can be detected at much lower concentrations than absorbed light. For example, light scattered by a solution of 80 nm diameter gold particles is detectable down to 5 fM concentration (fM = 10-15 M). For this reason, metal nanoparticles are interesting materials for use in techniques that rely on labelling (such as microarray technology).

Surface-enhanced Raman scattering

Metal surfaces with nanometre scale roughness have the property of amplifying the Raman scattering signals of absorbed molecules. In simple terms, Raman scattering is the inelastic scattering of photons. Normally, when light is scattered from an atom or molecule, it has the same energy (frequency) and wavelength as the incident light (Rayleigh scattering). This is an elastic scattering. However, a small fraction of the scattered light (approximately 1 in 10 million photons) is scattered by excitation, with the scattered photons having energy (frequency) different to the frequency of the incident photons. Metal surfaces with nanoscale roughness increase the Raman scattering of molecules absorbed on them. This effect is due to chemical and electromagnetic factors, as well as increased surface area. The details of this effect will not be considered here: what is important is that the **surface-enhanced Raman scattering** (SERS) effect can induce a signal enhancement of up to 108 times. In one specific case, it has been possible to achieve a Raman enhancement effect of 1015 times! This means that the SERS effect makes it possible to push the detection limit of surface detection techniques. The SERS signal depends on the characteristics of the nano-substrate: the size, shape, orientation, and composition of the surface nano-roughness. Advancements in SERS technology will allow detection at the attomole (10-18 mol) level, and single molecule detection

- **Dynamic Light Scattering (DLS)**

Dynamic light scattering is a well-established technique for measuring the size and size distribution, typically in the submicron range, of molecules and particles which are dispersed or dissolved in a liquid. The Brownian motion of these particles or molecules causes the intensity of the light they scatter to fluctuate rapidly. Analysis of these short-term intensity fluctuations yields the speed of the Brownian motion and hence the particle size, using the Stokes-Einstein relationship. DLS is a highly flexible sizing method which is rapid, accurate and repeatable. It requires only small volumes of sample for analysis, and is non-destructive. DLS is material-independent and therefore widely applicable.

Lecture-6

Applications

Over 600 nanotech enabled products are on the market today. Some examples are:

Nano-size particles of titanium dioxide and zinc oxide are less visible than the whitish particles of the older sunscreens. They block UV light more effectively without turning your skin white. Older sunscreen leaves a white sheen behind

- Self-cleaning glass uses UV light to energize nanoparticles to break down and loosen dirt on glass. Particles are also hydrophilic so water spreads across the glass evenly and helps wash the glass clean.
- Coating fabric with nanoparticles helps repel the water and other materials to make clothes stain resistant.
- Nanoparticles of silver in antimicrobial bandages block the microbe's cellular respiration, thus killing them.

Application of CNT

There are many potential applications of carbon nanotubes owing to its remarkable properties. They have potential to be used in electronics, textile industry as waterproof and tear proof fabric, sensor based on the property of thermal conductivity and many more. Carbon nanotubes in bike frames and tennis rackets make the products stronger and lighter.

Nanoparticle Applications: ZnO

Zinc Oxide has opaque and antifungal properties. Used as UV blocking pigments in sunscreens, cosmetics, varnishes, and fabrics. Incorporated in foot powders and garden supplies as an antifungal. ZnO nanowires can improve the elastic toughness of bulk materials

Nanoparticle Applications: TiO2

Titanium Dioxide is used as an inorganic white pigment for paper, paints, plastics, and whitening agents. TiO2 nanoparticles are used as UV blocking pigments in sunscreens, cosmetics, varnishes, and fabrics. TiO2 has unique photocatalytic properties that make it suitable for a number of advanced applications: Self-cleaning glass and antifogging coatings, Photoelectrochemical cells (PECs) Detoxification of wastewater and Hydrolysis

Nanoparticle Applications: Fe

50-100nm Iron nanoparticles are used in magnetic recording devices for both digital and analogue data. Decreasing the diameter to 30-40nm increases the magnetic recording capacity by 5-10 times per unit**.** Low-energy, catalyst-free carbon nanotube synthesis at room temperature. Ultra-high sensitivity oxygen sensors. Carbon overcoat on rigid magnetic disks (tribology)

Nanoparticle Applications: Iron Oxide

Iron Oxide nanoparticles have unique magnetic and optical properties. Iron oxide nanoparticles can be translucent to visible light while being opaque to UV light.

Applications include UV protective coatings, various electromagnetic uses, electro-optic uses, and data storage.

Nanoparticle Applications: Alumina

Alumina (Aluminum Oxide) is used in Chemical Mechanical Polishing (CMP) slurries, as well as ceramic filters. Nano-alumina is used in light bulb and fluorescent tube coatings because it emits light more uniformly and allows for better flow of fluorescent materials.

Nanoparticle Applications: Ag

Silver has excellent conductivity and has been used as an antimicrobial material for thousands of years. Silver’s anti-microbial potential increase with increased surface area. Applications include biocides, transparent conductive inks, and antimicrobial plastics, and bandages.

Applications

- Antibacterial effect of silver

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Nanoparticle Applications: Gold

Gold nanoparticles are relatively easy to produce compared to other types of nanoparticles due to its high chemical stability. Uses for gold nanoparticles are typically catalytic and include DNA detection and the oxidation of carbon monoxide. Gold has superior conductivity allowing gold nanoparticles to be used in various probes, sensors, and optical applications.

- Photo acoustic imaging
- Cancer therapy (safe, biocompatible target for photo thermal ablation)
- Explosion initiation (lower energy requirement and increase safety and portability – extension of use as a catalyst in combustion efficiency)
- Hydrogen storage and release at room temperature

General Application of Nanoparticales

- Catalysts
- Envirox™ cerium oxide
- Nanoremediation
- SAMMS technology to remove mercury

- Paper
- photographic paper
- Filters
- nanofibres
- Toothpaste
- to remineralise teeth
- Food
- packaging
- Paint
- improved adhesion and anti-fungal qualities/anti-graffiti
- Clothes
- non-staining and anti-radiation
- Batteries
- (Black & Decker) phosphate nanocrystal technology
- Cleaning products

Lecture 7

Application of Nano material for water / wastewater treatment

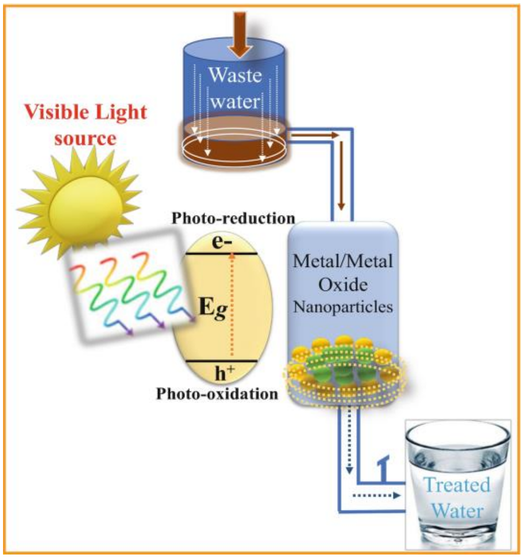
Nanotechnology for sustainable water supplies has been identified as a high priority theme because water purification techniques that contain Nano scale materials are already available and human development needs for clean water are vital, especially in arid and semiarid countries. It is better than other technique used in water treatment but today the knowledge about the environmental fate, transport and toxicity of nanomaterials is still in infancy

Applications of nanotechnology have been suggested for meeting the needs of poor people aimed at more effectively removing contaminants from water could potentially solve problems with conventional technologies.

Advantages of Nano Technology particles for water and wastewater purification

Wastewater is water that has been used and must be treated before it is released into another body of water. Wastewater comes from a variety of sources including water from baths, showers, sinks, dishwashers, washing machines, and toilets.

- Domestic wastewater” is wastewater that comes primarily from individuals and does not generally include industrial or agricultural wastewater.
- Wastewater has been a diversely contaminated by organic pollutants, bacteria and microorganisms, industrial effluent or any compound that deteriorated its initial quality.
- Treatment of wastewater must take into consideration all the aspects related to water contamination and has to ensure that the product water is free from any substance that might adversely affect the health of humans and the environment.

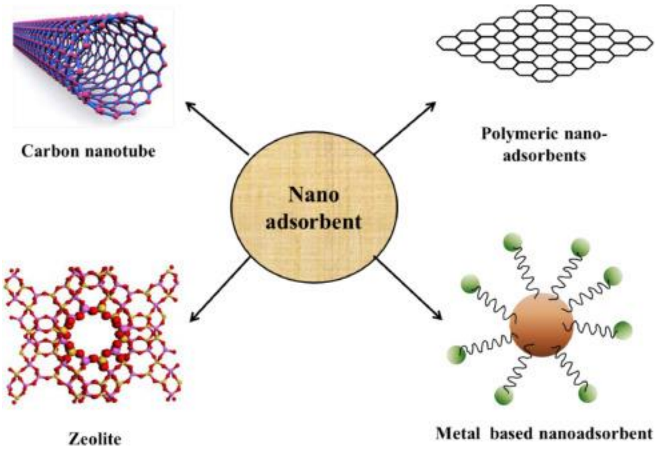


Scientists classified nano scale materials that are being evaluated as functional materials for water purification into four classes namely,

- dendrimers,
- metal-containing nanoparticles,
- zeolites and
- carbonaceous nanomaterials.

The application of nano technology in the cleaning up of contaminated water would summarized by (smith, 2006):

- Nano scale filtration technique
- The adsorption of pollutants on Nano particles
- The breakdown of contaminants by Nano particle catalysts.



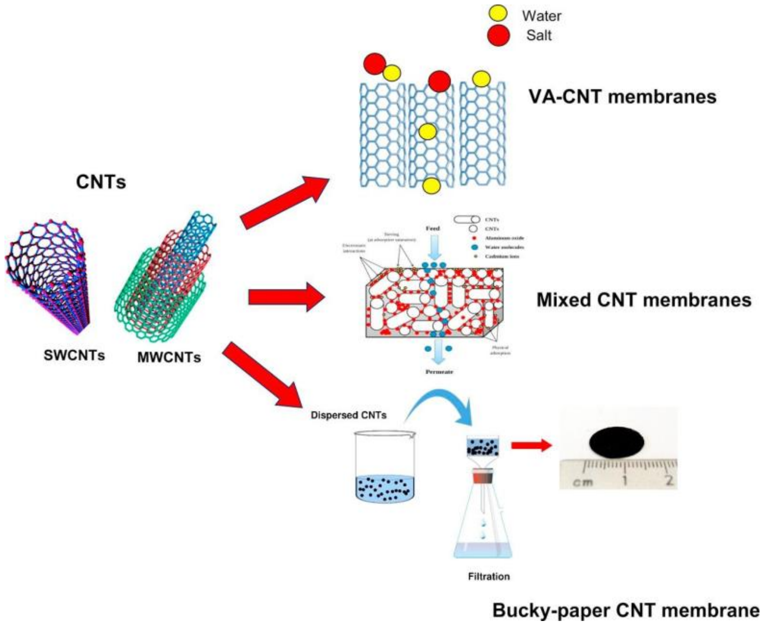
3.1. Adsorption

- Is one of the most well practiced techniques which commonly used to remove organic and inorganic contaminants in water and wastewater treatment.
- Nano adsorbents offer significant improvement with their extremely high specific surface area and associated sorption sites and tunable pore size (Xiaolei et al., 2013).
- Use of nano materials as adsorbent in treatment of wastewater is applicable in various forms like catalytic, absorptive, catalytic membrane, bioactive nanoparticles, and nano composite membrane etc.
- Types of nanoparticles have been investigated as adsorbents are
- metal-containing particles, metal oxides, carbon nanotubes and fullerenes, organic nanomaterials and zeolites.

3.1.1. Carbon Nano Tube (CNTs)

- CNTs are allotropes of carbon with a cylindrical nanostructure in which their adsorption capacity depends on both the surface functional groups and the nature of the sorbate.
- CNTs are the engineered materials exhibiting unique properties, such as electrical conductivity, optical activity, mechanical strength and surface morphologies. Their high porosity, light mass density, large specific area, hollow structure and strong interactions with pollutant molecules render them good adsorbents (Gadhave and Waghmare, 2014).
- Adsorption sites in CNT bundles are internal sites, interstitial channels, grooves and outside surface. Equilibrium is reached faster on external sites as compared to internal sites. The adsorption mechanism is mainly attributed to the chemical interactions between the surface functional groups of CNTs and the metal ions. Depending on the process of synthesis and purification, CNTs generally contain –OH, –C=O and –COOH groups (Gadhave and waghmare)

Generally, the sorption behaviours of CNTs mainly involve chemical interaction for polar compounds and physical interaction for non-polar compounds. Due to great capacity to adsorb carbon nanotubes are advantageous for water and wastewater treatment



3.1.2. Polymeric nano adsorbents

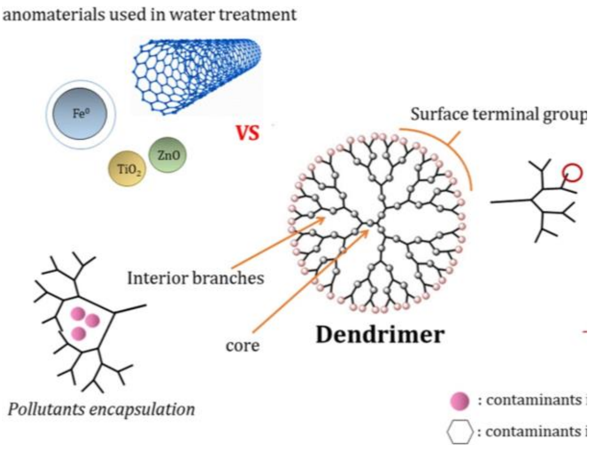
Are adsorbents such as dendrimers (repetitively branched molecules) are utilizable for removing organics and heavy metals.

Their interior shells can be hydrophobic for sorption of organic compounds while the exterior branches can be tailored (e.g., hydroxyl- or amine-terminated) for adsorption of heavy metals (Crooks et al., 2001).

Dendrimers are symmetrical and spherical macromolecules, which make them particularly attractive as functional materials for water purification (Ottaviani et al., 2000).

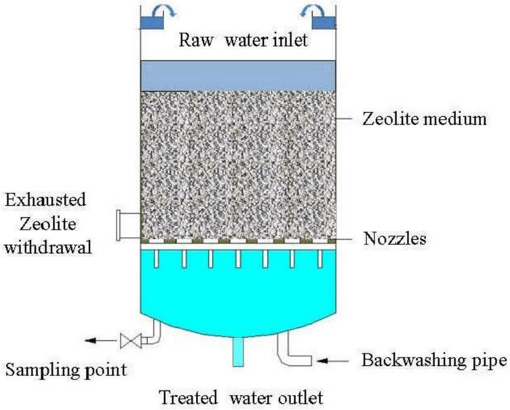
3.1.3. Metal and metal oxide nanoparticles

Nanoparticles can be synthesised from oxides of various metals such as iron, copper, titanium, manganese, magnesium, zinc, silica and aluminium. Metal elements have a distinct property to form oxides with a large variety of structural and electronic properties. In nanotechnology, the aim is to get nanostructures exhibiting distinct physical and chemical properties, different from bulk or single structured particles. This is because the band gap between the oxide particles decreases with decrease in average size of the particles, resulting in change in conductivity and chemical reactivity (Fernández-Garcia and José, 2007).



3.1.4. Zeolites

Zeolites are inorganic crystalline porous materials with a highly ordered structure which used in the removal of heavy metals such as chromium, copper, nickel, and zinc from waste waters (Theron J., et al., 2008). It can also use to separate harmful organics from water. A new class of nano porous polymeric materials that can be used to reduce the concentration of common organic contaminants in water to parts-per-trillion levels have been developed (M. C. Roco, et al. 999).



3.2 membrane and membrane process

A membrane is a thin layer of porous material that permits water molecules to pass through it. Membranes use either pressure-driven forces or electrical technologies (Sandeep K.et al., 2014). Membrane technology is well established in the water and wastewater area as a reliable and largely automated process. The performance of membrane system is largely defined by the membrane material (Sandeep K.et al., 2014).

3.2.1 .Nano Filtration Membrane

Membrane processes such as Nano filtration are emerging as key contributors to water purification. NF membranes are widely used in water treatment for drinking water or wastewater treatment. It is a low-pressure membrane process that separates materials in the 0.001-0.1 micrometer size (Bruggen & Vander casteele, 2003).

Nano filtration membranes are mostly applied for the reduction of hardness, color, odor, and heavy metal ions for removal of pesticides and other organic contaminants from surface and ground waters to help ensure the safety of public drinking water supplies (Karishma K., et al., 2015).

3.2.2. Nano fiber membranes

Nano fibers are produced by the process electro spinning which is an efficient and inexpensive way to make ultrafine fibers using various materials like polymers, ceramics, or some metals which form nano fiber mats with complex pore structure. Nano fiber membranes have a high flow rate and can remove pollutants, bacteria, viruses, and proteins from the liquid phase by means of electrostatic effects (Fur M. and Umwelt 2015).

Their potential area of application could therefore be the preliminary treatment of the water or wastewater prior to ultrafiltration or reverse osmosis w/c can result in an extension of the life of the reverse osmosis membranes. Another benefit of Nano fibers is their capacity to be tailored to specifics such as membrane thickness and an interconnected open pore structure.

3.3. Photo Catalysis

Photo catalytic oxidation is an advanced oxidation process for removal of trace contaminants and microbial pathogens. The major barrier for Photo catalysis wide application is the slow kinetics due to limited light flux (cloudiness of the water) (Fur M. and Umwelt., 2015).It is a useful pre-treatment for hazardous and non-biodegradable contaminants to enhance their biodegradability.

Photo catalysis has emerged as a green technology for the complete mineralization of hazardous organic chemicals to water, carbon dioxide and simple mineral acids (Tang, Z. and Ye J., 2004; Mohapatra D. P.et al., 2013) and occurs at room temperature.

When light radiation falls on the surface of metal, electrons absorb it and get excited. These electrons disperse on the surface of the photo catalyst and react with external substances, causing reductions and oxidations (Pankaj K.et al., 2012)

Lecture-8

Nanomaterials for photocatalytic water purification

Photocatalytic Nanoparticles

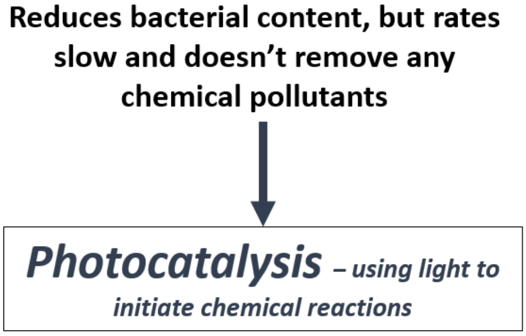
There is a clear necessity to develop a method of water purification for those living in areas most at risk of depending on poor quality water sources. This must be:

- Safe
- Cheap
- Simple
- Reliable
- Robust
- Point-of-source

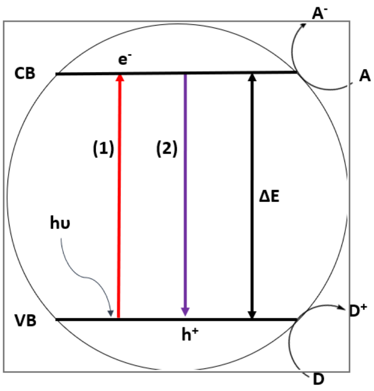
Some nanoparticles have photocatalytic properties that scientists can engineer to speed up reactions using a light source. Photocatalytic nanoparticles are organic, may have antimicrobial properties, and are considered cost-effective.

Solar Disinfection (SODIS)

The Sun’s natural disinfecting ability is utilised globally in areas where water resources are unsafe and resources are limited.



The Photocatalysis Process



Size of band gap important for the photon energy required to initiate the chemical processes involved.

For titania, **ΔE_{TiO2} = 3.2 eV ~ 390 nm**

↓

Problem of UV light being necessary to activate titania

(1) - Excitation of an electron from the VB to the CB
(2) - Charge recombination

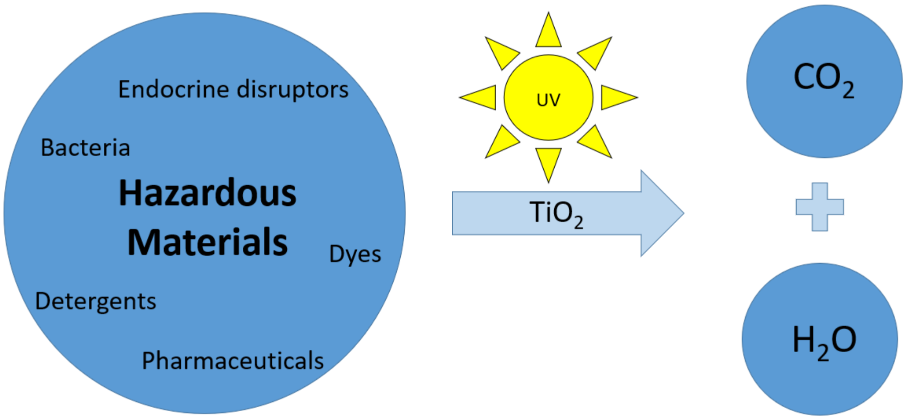
$$\mathbf{TiO_2 + h\upsilon \rightarrow TiO_2\,(e^- + h^+)}$$

$$e^- + M^{n+} \rightarrow M^{(n-1)+}$$
$$O_2 + e^- \rightarrow O_2^-$$
$$O_2 + 2e^- + 2H^+ \rightarrow H_2O_2$$
$$H_2O_2 + H^+ + e^- \rightarrow \cdot OH + H_2O$$

$$h^+ + H_2O \rightarrow \cdot OH + H^+$$
$$h^+ + OH^- \rightarrow \cdot OH$$
$$\cdot OH + R_{(ads)} \rightarrow \cdot R_{(ads)} + H_2O$$

Highly oxidising species – lead to advanced oxidation processes

Hazardous molecules → $CO_2 + H_2O$



Photocatalytic Nanoparticles

Advantage	Disadvantage
Low operational and installation cost	High energy lamps needed
Non-professional and unmanned operation is possible	Catalyst recovery from water
Can avoid use of dangerous chemicals	
Can work on small and large scale	