

# INTRODUCTION TO NANOSCIENCE

## Nanomaterials

The concept of nanotechnology was first given by renowned physicist Richard Feynman in 1959 and earned Nobel Prize. The term was also popularized by the invention of scanning tunneling microscope and fullerene. Nanotechnology involves designing and producing objects at nanoscale size (~1 to 100 nm). One nanometer is one billionth ( $10^{-9}$ ) of a metre. Nanomaterials are one of the main products of nanotechnology as nanoparticles, nanotubes, nanorods, etc. It is also explained as nanoparticles have a high surface to volume ratio. Nanoparticles can display properties significantly different from the bulk material because at this level quantum effects may be significant. Simply we can say the mechanical, electrical, optical, electronic, catalytic, magnetic, etc. properties of solids are significantly altered with great reduction in particle size. For example:

- ✓ Silver foil does not react with dilute HCl but silver nanoparticles rapidly react with dilute HCl.
- ✓ Gold and silver both are chemically inert but their nanoparticles show catalytic property.
- ✓ Gold nanoparticles are deep red but its bulk material (gold pieces) is gold coloured.

## Classifications of Nanomaterials

The classification of nanomaterials is based on the number of dimensions as shown in Fig. 1. According to Siegel, nanostructured materials are classified as: zero dimensional (0D), one-dimensional (1D), two-dimensional (2D) and three dimensional (3D) nanomaterials.

- (i) Zero-dimensional nanomaterials: Here, all dimensions (x, y, z) are at nanoscale, i.e., no dimensions are greater than 100 nm. It includes nanospheres and nanoclusters.
- (ii) One-dimensional nanomaterials: Here, two dimensions (x, y) are at nanoscale and the other is outside the nanoscale. This leads to needle shaped nanomaterials. It includes nano fibres, nanotubes, nanorods, and nanowires.
- (iii) Two-dimensional nanomaterials: Here, one dimension (x) is at nanoscale and the other two are outside the nanoscale. The 2D nanomaterials exhibit platelike shapes. It includes nanofilms, nanolayers and nano coatings with nanometre thickness.
- (iv) Three-dimensional nanomaterials: These are the nanomaterials that are not confined to the nanoscale in any dimension. These materials have three arbitrary dimensions above 100 nm. The bulk (3D) nanomaterials are composed of a multiple arrangement of nano size crystals in different orientations. It includes dispersions of nanoparticles, bundles of nanowires and nanotubes as well as multi-nanolayers (polycrystals) in which the 0D, 1D and 2D structural elements are in close contact with each other and form interfaces

## Unique Characteristics of Nanoparticles

- ✓ Large surface to volume ratio.
- ✓ High percentage of atoms/molecules on the surface.
- ✓ Surface forces are very important, while bulk forces are not as important.
- ✓ 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.

## Timeline and milestone

- ✓ 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.



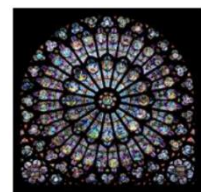
The Lycurgus Cup at the British Museum, lit from the outside (*left*) and from the inside (*right*)

- ✓ 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.



A Damascus saber

## Examples of Discoveries and Developments Enabling Nanotechnology in the Modern Era

- ✓ 1857: Michael Faraday discovered colloidal “ruby” gold, demonstrating that nanostructured gold under certain lighting conditions produces different-colored solutions.



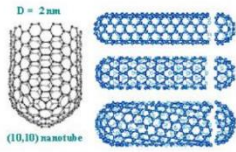
"Ruby" gold colloid (*Gold Bulletin* 2007 40,4, p. 267)

- ✓ 1936: Erwin Müller, working at Siemens Research Laboratory, invented the field emission microscope, allowing near-atomic-resolution images of materials.
- ✓ 1950: Victor La Mer and Robert Dinegar developed the theory and a process for growing monodisperse colloidal materials. Controlled ability to fabricate colloids enables many industrial uses such as specialized papers, paints, and thin films, even dialysis treatments.
- ✓ 1951: Erwin Müller developed the field ion microscope, a means to image the arrangement of atoms at the surface of a sharp metal tip; he first imaged tungsten atoms.
- ✓ 1956: Arthur von Hippel at MIT introduced many concepts of—and coined the term—“molecular engineering” as applied to dielectrics, ferroelectrics, and piezoelectrics.

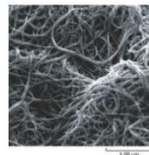
- ✓ 1958: Jack Kilby of Texas Instruments originated the concept of, designed, and built the first integrated circuit, for which he received the Nobel Prize in 2000.
- ✓ 1959: Richard Feynman of the California Institute of Technology gave what is considered to be the first lecture on technology and engineering at the atomic scale, "There's Plenty of Room at the Bottom" at an American Physical Society meeting at Caltech.
- ✓ 1974: Tokyo Science University Professor Norio Taniguchi coined the term nanotechnology to describe precision machining of materials to within atomic-scale dimensional tolerances.
- ✓ 1981: Gerd Binnig and Heinrich Rohrer at IBM's Zurich lab invented the scanning tunneling microscope, allowing scientists to "see" (create direct spatial images of) individual atoms for the first time. Binnig and Rohrer won the Nobel Prize for this discovery in 1986.

(Scanning Tunneling Microscopy, is an imaging technique used to obtain ultra- high resolution images at the atomic scale, without using light or electron beams).

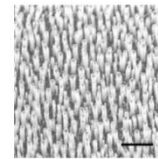
- ✓ 1981: Russia's Alexei Ekimov discovered nanocrystalline, semiconducting quantum dots in a glass matrix and conducted pioneering studies of their electronic and optical properties.
- ✓ 1985: Rice University researchers Harold Kroto, Sean O'Brien, Robert Curl, and Richard Smalley discovered the Buckminsterfullerene (C60), more commonly known as the buckyball, which is a molecule resembling a soccer ball in shape and composed entirely of carbon, as are graphite and diamond. The team was awarded the 1996 Nobel Prize in Chemistry for their roles in this discovery and that of the fullerene class of molecules more generally. (Artist's rendering at right.)
- ✓ 1985: Bell Labs's Louis Brus discovered colloidal semiconductor nanocrystals (quantum dots), for which he shared the 2008 Kavli Prize in Nanotechnology.
- ✓ 1986: Gerd Binnig, Calvin Quate, and Christoph Gerber invented the atomic force microscope, which has the capability to view, measure, and manipulate materials down to fractions of a nanometer in size, including measurement of various forces intrinsic to nanomaterials.
- ✓ 1990s: Early nanotechnology companies began to operate, e.g., Nanophase Technologies in 1989, Helix Energy Solutions Group in 1990, Zyvex in 1997, Nano-Tex in 1998...
- ✓ 1991: Sumio Iijima is credited with discovering the carbon nanotube (CNT), although there were early observations of tubular carbon structures by others as well. Iijima shared the Kavli Prize in Nanoscience in 2008 for this advance and other advances in the field. CNTs, like buckyballs, are entirely composed of carbon, but in a tubular shape. They exhibit extraordinary properties in terms of strength, electrical and thermal conductivity, among others.



Carbon nanotubes (courtesy, National Science Foundation). The properties of CNTs are being explored for applications in electronics, photonics, multifunctional fabrics, biology (e.g., as a scaffold to grow bone cells), and communications. See a 2009 [Discovery Magazine](#) article for other examples

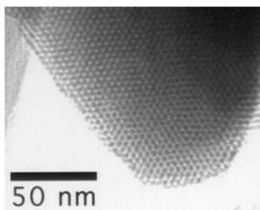


SEM micrograph of purified nanotube "paper" in which the nanotubes are the fibers (scale bar, 0.001 mm) (courtesy, NASA).

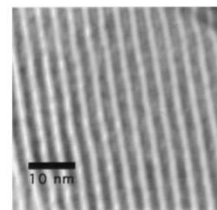


An array of aligned carbon nanotubes, which can act like a radio antenna for detecting light at visible wave-lengths (scale bar 0.001 mm) (courtesy, K. Kempa, Boston College).

- ✓ 1992: C.T. Kresge and colleagues at Mobil Oil discovered the nanostructured catalytic materials MCM-41 and MCM48, now used heavily in refining crude oil as well as for drug delivery, water treatment, and other varied applications.



MCM-41 is a "mesoporous molecular sieve" silica nanomaterial with a hexagonal or "honeycomb" arrangement of its straight cylindrical pores, as shown in this TEM image (courtesy of Thomas Pauly, Michigan State University).



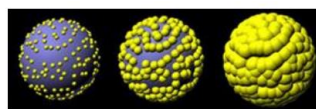
This TEM image of MCM-41 looks at the straight cylindrical pores as they lie perpendicular to the viewing axis (courtesy of Thomas Pauly, Michigan State University).

- ✓ 1993: Mounji Bawendi of MIT invented a method for controlled synthesis of nanocrystals (quantum dots), paving the way for applications ranging from computing to biology to high-efficiency photovoltaics and lighting. Within the next several years, work by other researchers such as Louis Brus and Chris Murray also contributed methods for synthesizing quantum dots.
- ✓ 1998: The Interagency Working Group on Nanotechnology (IWGN) was formed under the National Science and Technology Council to investigate the state of the art in nanoscale science and technology and to forecast possible future developments. The IWGN's study and report, *Nanotechnology Research Directions: Vision for the Next Decade* (1999) defined the vision for and led directly to formation of the U.S. National Nanotechnology Initiative in 2000.
- ✓ 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, deeppenetrating therapeutic cosmetics, scratch-resistant glass coatings, faster-recharging batteries for cordless electric tools, and improved displays for televisions, cell phones, and digital cameras.



- ✓ 2000: President Clinton launched the National Nanotechnology Initiative (NNI) to coordinate Federal R&D efforts and promote U.S. competitiveness in nanotechnology. Congress funded the NNI for the first time in FY2001. The NSET Subcommittee of the NSTC was designated as the interagency group responsible for coordinating the NNI.
- ✓ 2003: Congress enacted the 21st Century Nanotechnology Research and Development Act (P.L. 108-153). The act provided a statutory foundation for the NNI, established programs, assigned agency responsibilities, authorized funding levels, and promoted research to address key issues.
- ✓ 2003: Naomi Halas, Jennifer West, Rebekah Drezek, and Renata Pasqualin at Rice University developed gold nanoshells, which when “tuned” in size to absorb near-infrared light, serve as a platform for the integrated discovery, diagnosis, and treatment of breast cancer without invasive biopsies, surgery, or systemically destructive radiation or chemotherapy.
- 2004: The European Commission adopted the Communication “Towards a European Strategy for Nanotechnology,” COM(2004) 338, which proposed institutionalizing European nanoscience and nanotechnology R&D efforts within an integrated and responsible strategy, and which spurred European action plans and ongoing funding for nanotechnology R&D.

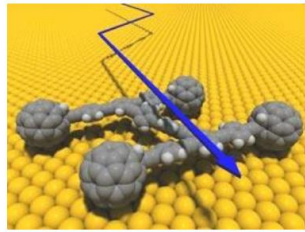


Computer simulation of growth of gold nanoshell with silica core and over-layer of gold (courtesy N. Halas, [Genome News Network](#), 2003)

- ✓ 2004: Britain’s Royal Society and the Royal Academy of Engineering published *Nanoscience and Nanotechnologies: Opportunities and Uncertainties* advocating the

need to address potential health, environmental, social, ethical, and regulatory issues associated with nanotechnology.

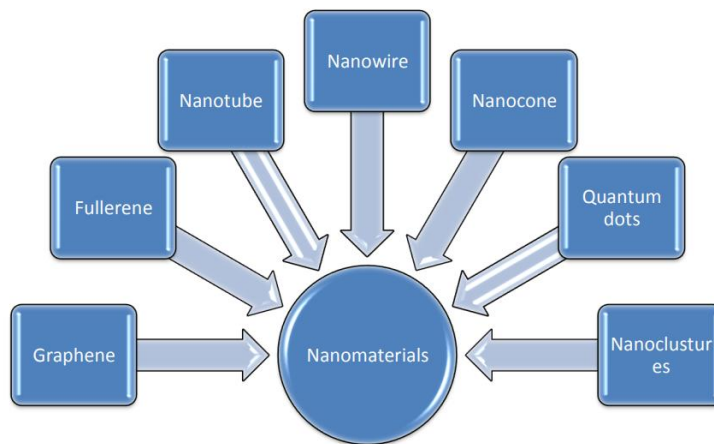
- ✓ 2004: SUNY Albany launched the first college-level education program in nanotechnology in the United States, the College of Nanoscale Science and Engineering.
- ✓ 2005: Erik Winfree and Paul Rothemund from the California Institute of Technology developed theories for DNA-based computation and “algorithmic 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.



Nanocar with turning buckyball wheels (credit: [RSC, 29 March 2006](#)).

- ✓ 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.
- ✓ 2008: The first official NNI Strategy for Nanotechnology-Related Environmental, Health, and Safety (EHS) Research was published, based on a two-year process of NNI-sponsored investigations and public dialogs. This strategy document was updated in 2011, following a series of workshops and public review.
- ✓ 2009–2010: Nadrian Seeman and colleagues at New York University created several DNA-like robotic nanoscale assembly devices.
- ✓ 2012: The NNI launched two more Nanotechnology Signature Initiatives (NSIs)-- Nanosensors and the Nanotechnology Knowledge Infrastructure (NKI)--bringing the total to five NSIs.
- ✓ 2013: -The NNI starts the next round of Strategic Planning, starting with the Stakeholder Workshop. -Stanford researchers develop the first carbon nanotube computer

## OVERVIEW OF DIFFERENT NANOMATERIALS AVAILABLE



For the better understanding, nanomaterials are again organized into four types as follows. Some types of nanomaterials are shown in Fig. 2.

- (i) Carbon based materials
- (ii) Metal based materials
- (iii) Dendrimers
- (iv) Composites

- (i) **Carbon based materials:** These are composed of carbon, taking the form of hollow spheres, ellipsoids or tubes. The spherical and ellipsoidal forms are referred as fullerenes, while cylindrical forms are called nanotubes.
- (ii) **Metal based materials:** These include quantum dots, nanogold, nanosilver and metal oxides like TiO<sub>2</sub>. A quantum dot is a closely packed semiconductor crystal comprised of hundreds or thousands of atoms, whose size is on the order of a few nanometers to a few hundred nanometers.
- (iii) **Dendrimers:** Dendrimers are repetitively branched molecules. The name comes from the Greek word 'dendron' (tree). These nanomaterials are nanosized polymers built from branched units. The surface of a dendrimer has numerous chain ends, which can perform specific chemical functions. Dendrimers are used in molecular recognition, nanosensing, light harvesting, and opto-electrochemical devices. They may be useful for drug delivery.
- (iv) **Composites:** Composites are combination of nanoparticles with other nanoparticles or with larger, bulk-type materials. Nanoparticles like nanosized clays are added to products (auto parts, packaging materials, etc.) to enhance mechanical, thermal, and flame-retardant properties.

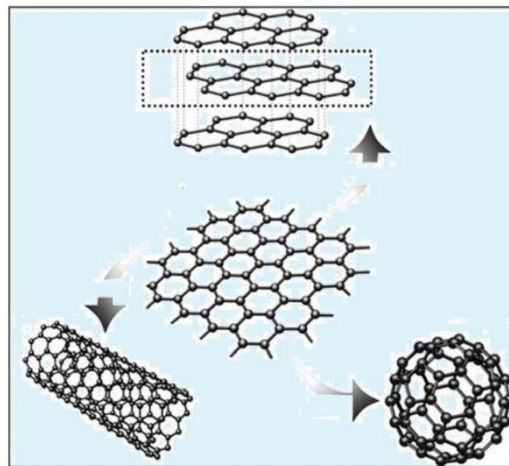




**Fig. 2** Some types of nanomaterials

## GRAPHENE

Graphene was first isolated by A.K. Geim and K.S. Novoselov at the University of Manchester in 2004. They got Nobel Prize in 2010 for their pioneering work. Graphene is a crystalline allotrope of carbon with two-dimensional, atomic scale, hexagonal pattern. Here each carbon atom forms four bonds, three  $s$  bonds ( $sp^2$  hybridized) with its three neighbours and one  $p$  bond oriented out of plane. It is the basic structural element of other allotropes like graphite, fullerene, nanotubes, nanocones, etc. hence called mother of all carbon nanomaterials (Fig. 3).



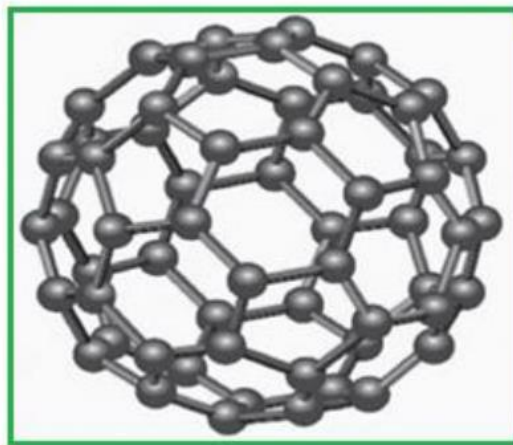
**Fig. 3** Graphene and other carbon nanomaterials

## Properties:

- It is nearly transparent.
- It is 200 times stronger than steel by weight due to its tightly packed carbon atoms.
- It conducts heat and electricity with great efficiency due to presence of  $p$  electrons.
- Nowadays, it is commonly used in semiconductors, batteries, electronics, composite industries, and many more.

## FULLERENE

The first fullerene was discovered by Harold Kroto, Richard Smalley and Robert Curl in 1985 by using a laser to vaporise graphite rods in an atmosphere of helium gas. The fullerenes (allotropes of carbon) are graphene sheets rolled into tubes or spheres. It is a cage like molecule composed of 60 carbon atoms ( $C_{60}$ ) joined together by single and double bonds to form a hollow sphere with 20 hexagonal and 12 pentagonal faces (a design that resembles a football). It was named as buckminsterfullerene or buckyball after the name of American architect Buckminster Fuller, the inventor of the geodesic dome. The structure of fullerene ( $C_{60}$ ) is shown in Fig. 4.



**Fig. 4** Fullerene ( $C_{60}$ )

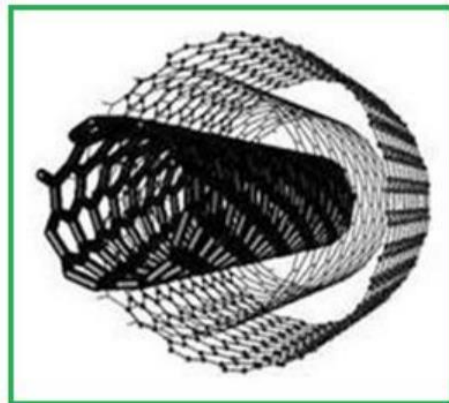
### Applications

The recent research has suggested that fullerene has many uses, including medical applications, superconductors, fiber-optics, etc. Some of the important applications are listed as follows:

- Fullerenes ( $C_{60}$ ) and their derivatives have potential antiviral activity, and may be used for the treatment of HIV-infection.
- They have potential medicinal applications as they can bind specific antibiotics and target certain types of cancer cells such as melanoma.
- They are used as biological antioxidants.
- They are also used as potential photosensitizers in photodynamic therapy and catalysts for hydrogenation.
- Fullerenes incorporated with sulphides of tungsten and molybdenum exhibit excellent solid-lubricant properties.

## NANOTUBES

The carbon nanotubes (elongated form of fullerenes) were identified in 1991 by Iijima Sumio of Japan. A carbon nanotube is a tube-shaped material, made up of carbon, having a diameter ranging from  $< 1$  nm to 50 nm. Simply we can say, carbon nanotubes (CNTs) are cylinders of one or more layers of graphene (lattice). Carbon nanotubes show a unique combination of stiffness, strength, and tenacity compared to other fibre materials. Thermal and electrical conductivity are also very high as comparable to other conductive materials. Carbon nanotubes may be categorized as follows: Single-wall nanotubes (SWNT): These may be zigzag, armchair and chiral depending on the manner in which the graphene sheets are rolled. Multi-wall nanotubes (MWNT): It consists of several single-walled nanotubes with different diameters. A multi-wall nanotube is shown in Fig.5



**Fig. 5:** Multi-walled nanotube

### Applications

Carbon nanotube technology can be used for a wide range of new and existing applications, which are as follows:

- Nanotubes can potentially replace indium tin oxide in solar cells to generate photocurrent.
- SWNTs are used in transistors and solar panels.
- MWNTs are used in lithium ion batteries to enhance cycle life.
- Parallel CNTs have been used to create loudspeakers.
- CNTs can serve as a multifunctional coating material.
- CNTs can be used to produce nanowires.

- CNTs are also used for applications in energy storage, automotive parts, boat hulls, water filters, thin-film electronics coatings, ultra-capacitors, biosensors for harmful gases, extra strong fibers, etc.

## **NANOWIRES**

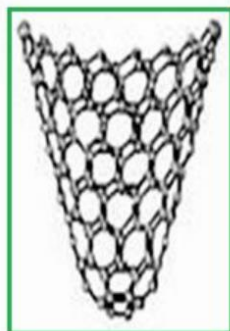
These are defined as the structures which have the diameters of the order of a nanometre and an unconstrained length. i.e., nanowires are much longer than their diameters. These are also called quantum wires because at this scale they have different quantum mechanical effects. There are different types of nanowires. For example: carbon nanowires, molecular nanowires, metallic nanowires, etc.

## **Applications**

- They are useful in digital computing.
- These are used for the preparation of active electronic components like p-n junction, logic gates, etc.
- They have potential applications in high-density data storage.
- Silver chloride nanowires are used as photocatalysts to decompose organic molecules in polluted water.

## **NANOCONES**

Carbon nanocones (Fig. 6) are conical structures made from carbon and have at least one-dimension of the order one micrometre or smaller. These are obtained from the wrapped graphene sheets. These are different from nanowires as nanocones have height and base diameter of the same order of magnitude. From electron microscopy, it is clear that the opening angle (apex) of the cones is not arbitrary, but has preferred values of approximately 20°, 40°, and 60°



**Fig. 6:** Carbon nanocone

## Applications

- They have interesting applications in nanolithography.
- These are used in chemical sensors, biosensors, spectroscopy, etc.
- They are used as electrode material in lithium ion batteries.

## QUANTUM DOTS

Quantum dots (QDs) were first discovered by A. Ekimov in glass matrix and by L. Brus in colloidal solutions (Fig. 7). These are the semiconductor nanoparticles between 10 and 100 atoms in diameter. The properties of QDs can vary depending on its shape and size. These are not all uniform. In spite of having a variety of applications, QDs are a source of toxic compounds containing in their core. The QDs toxicity may be due to the leaching of toxic heavy metals from the colloid form. The toxicity may also be originated from intrinsic properties of the size and surface chemistry of quantum dots. Such materials might have potential risks to human health but still the use of these materials is growing quickly.

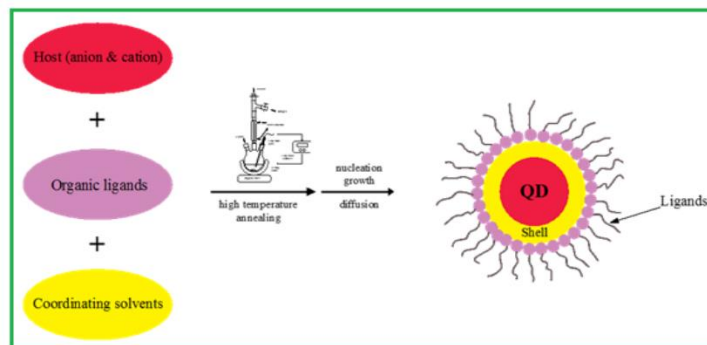
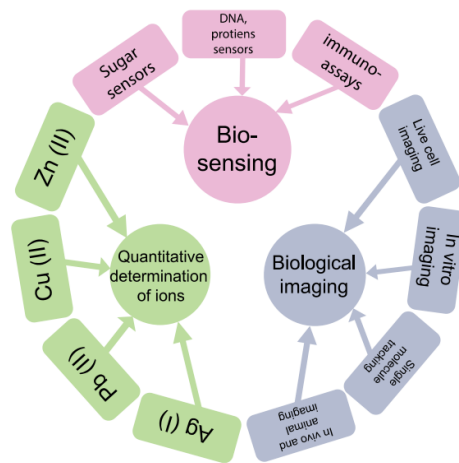


Fig. 7: Synthesis of Quantum dots (QDs)

## Applications (Fig. 8)

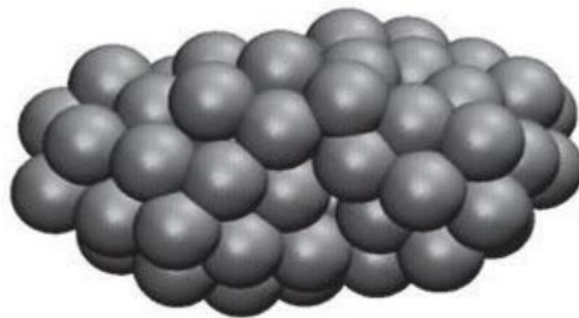
- These are used in transistors, solar cells, diode lasers, LEDs, etc.
- These may increase the efficiency of silicon photovoltaic cells.
- These are also significant for optical applications like amplifiers, biological sensors, etc.
- These are used as photocatalysts.
- They have potential applications in spectroscopy and fluorescent biomedical imaging.



**Fig. 8:** Schematic representation of QDs' applications.

## NANOCLUSTURE

It is the grouping of a number of nanoparticles (Fig. 9) in a narrow size distribution having at least one-dimension between 1 and 10 nm. Simply, they are fine aggregates of atoms or molecules. Nanoclusters contain a couple of hundred atoms but the larger aggregates may have more than 1000 atoms (called nanoparticles). The number of atoms in the clusters of critical size with higher stability is called magic number. The nanoclusters are bridge between bulk materials and atomic or molecular structures.



**Fig. 9:** Nanocluster

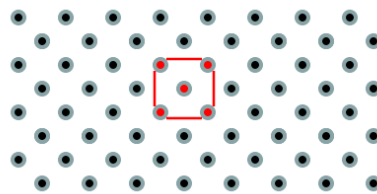
### Applications

- A bulk material has constant physical properties but at the nanoscale, it has many properties.
- It is used in biotechnology and pharmacology.
- It has potential applications in microelectronics, telecommunications, sensors, transducers, electroluminescent displays, catalysis, etc.

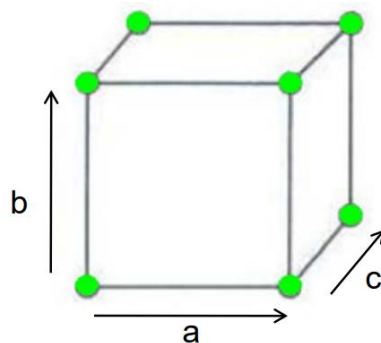
# INTRODUCTION TO SOLID STATE PHYSICS

## Crystal structure

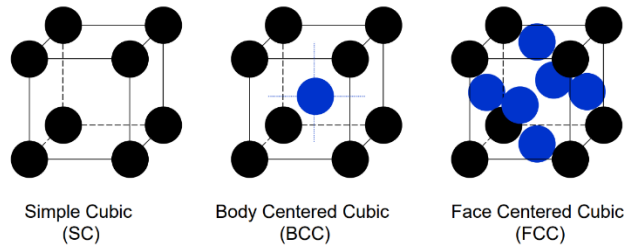
- Most solids are crystalline with their atoms arranged in a regular manner.
- This arrangement of atoms impacts the functionality of the material.
- Some solids have this order presented over a long range as in a crystal.
- Amorphous materials such as glass and wax lack long range order, but they can have a limited short range order, defined as the local environment that each atom experiences.
- The spatial arrangement of atoms in a crystal lattice is described by its unit cell.
- The unit cell is the smallest possible volume that displays the full symmetry of the crystal.
- Many materials have a “preferred” unit cell.



- In 3 dimensions, unit cells are defined by 3 lattice constants and 3 angles.
- This leads to 14 Bravais lattices, each having characteristic restrictions on the lattice constants, angles, and centering of atoms in the unit cell



For cubic unit cells, there are three centering types:



- Most metals in the solid form close packed lattices
- Ag, Al, Cu, Co, Pb, Pt, Rh are Face Centered Cubic (FCC)
- Mg, Nd, Os, Re, Ru, Y, Zn are Hexagonal Close Packed (HCP)
- Cr, Li, Sr can form Body Centered Cubic (BCC) as well as (FCC) and (HCP) depending upon formation energy
- How does crystal structure impact nanoparticles?
- Nanoparticles have a “structural magic number”, that is, the optimum number of atoms that leads to a stable configuration while maintaining a specific structure.
- Structural magic number = minimum volume and maximum density configuration
- If the crystal structure is known, then the number of atoms per particle can be calculated.

### Close-Packed Magic Number Clusters

Full-shell "magic number" clusters	1	2	3	4	5
Number of shells	1	2	3	4	5
Number of atoms in cluster	13	55	147	309	561
Percentage of surface atoms	92	76	63	52	45

- Magic Number = Cluster has a complete, regular outer geometry
- Formed by successively packing layers around a single metal atom.
- Number of atoms ( $y$ ) in shell ( $n$ ):  $y = 10n^2 + 2$  ( $n = 1, 2, 3, \dots$ )
- Maximum number of nearest neighbors (metal-metal hcp packing)
- Decreasing percentage of surface atoms as cluster grows
- For  $n$  layers, the number of atoms  $N$  in an approximately spherical FCC nanoparticle is given by the following formula:

$$N = \frac{1}{3}[10n^3 - 15n^2 + 11n - 3]$$

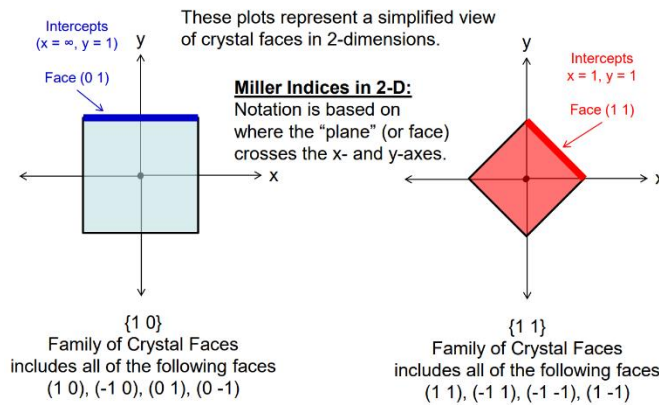
- The number of atoms on the surface  $N_{\text{surf}}$



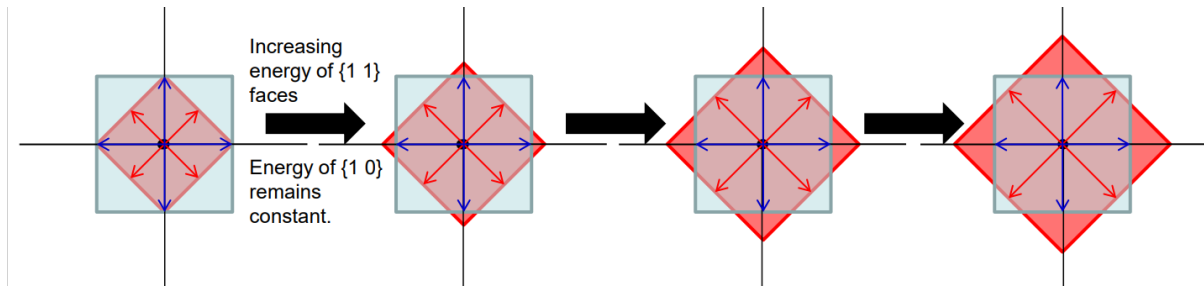
$$N_{\text{surf}} = 10n^2 - 20n + 12$$

## Wulff Crystal Shapes

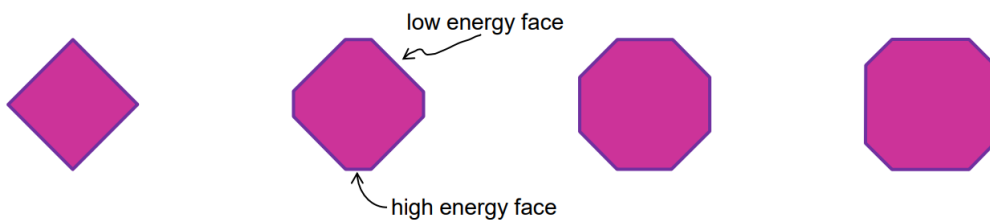
- Used to determine the shape of a crystal when formed under thermodynamic equilibrium conditions.
- Surfaces = areas of high energy
- Different facets have different surface energies.
- Objective is to minimize the total surface energy of the crystal.



Wulff Plots: Length of arrow is proportional to surface energy of that face. Longer arrows denote higher energy surfaces



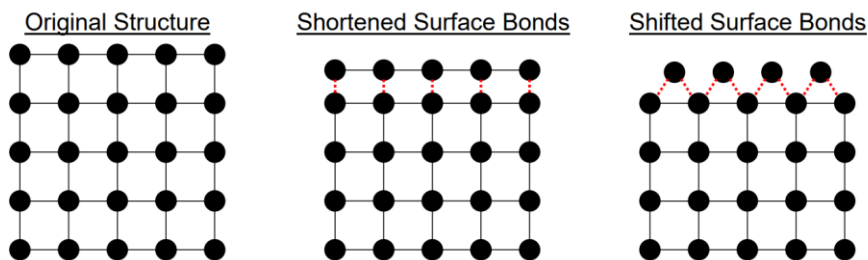
Crystal Shapes: Draw outline of inner-most facets to determine shape of the crystal. The result is that high energy faces expose less surface area to the external environment.



- Often, nanoparticles (nanocrystals) do not form welldefined crystal facets.
- The Wulff crystal shapes are idealized cases where the crystal surface energies determine the shape (thermodynamic control).
- Kinetic factors often play a major role in crystal growth. This explains why different processing conditions can lead to different morphologies for the same material.
- Roughening Temperature: Above this temperature, surface atoms on a growing crystal have increased mobility (liquid-like surface) and well-defined facets do not form.
- At elevated temps, all faces tend to have similar energy (e.g., on macroscale consider the C-Z process for Si)

## Altered Lattice Constants

- Compare lattice structure of nano and bulk materials
- Shortening of bonds near the surface
- Surface reconstruction



## Introduction to magnetism

- Magnetic nanoparticles are nanomaterials consists of magnetic elements, such as Fe, Ni, Co, Cr, Mn and their chemical compounds
- Magnetic nanoparticles can be selective attached to a functional molecule and allow transportation to a targeted location under an external magnetic field from an electromagnetic or permanent magnet.
- In order to prevent aggregation and minimize the interaction of the particles with the system environment, surface coating may be required.
- Coated magnetic nanoparticles have been widely used in several medical applications such as cell isolation, immunoassay, diagnostic testing and drug delivery.
- The properties of magnetic nanoparticles depend on the synthesis method and chemical structure.

- In most cases, the magnetic nanoparticles range from 1 to 100 nm in size and can display superparamagnetism.
- Superparamagnetism is caused by thermal effects that the thermal fluctuations are strong enough to spontaneously demagnetize a previously saturated assembly. In this state an external magnetic field is able to magnetize the nanoparticles with much larger magnetic susceptibility. When the field is removed, magnetic nanoparticles exhibit no magnetization. This property can be useful for controlled therapy and targeted drug delivery.
- Some magnetic material heat up when they are placed in a magnetic field and cool down when they are removed from a magnetic field, which is defined as the magnetocaloric effect (MCE). In magnetic nanoparticles this property increases because of their particle size dependent superparamagnetic features and the large surface area, which can provide better heat exchange with the surrounding environment.

## **Applications of magnetic nanoparticles**

### **(1) Magnetic separation**

In a biomedical study isolation and separation of specific molecules including DNAs, proteins and cells. In the process the biological molecules are labelled by magnetic nanoparticles colloids and then subjected to separation by an external magnetic field, which may be applied for cell isolation, protein purification, RNA/DNA extraction and immunoprecipitation.

### **(2) Diagnostics**

MRI (Magnetic Resonance Imaging) is widely used as diagnostic tools to present a high spatial resolution and great anatomical detail to visualize the structure and function of tissues. Several kinds of magnetic nanoparticles have been developed to improve contrast agents in MRI imaging with significant benefits of improved sensitivity, good biocompatibility and ready detection at moderate concentration.

### **(3) Sensors**

Many types of magnetic nanoparticles-based biosensors have been used to recognize specific molecular targets. Due to different composition size and magnetic properties magnetic nanoparticles can be used in a variety of instruments for biosensing.

### **(4) Drug delivery**

Magnetic nanoparticles have been developed and applied in localized drug delivery to tumors. The magnetic nanoparticles first act as a carrier of the drug, which are attached to its outer surface or dissolve in the coating. Once the drug coated particles have been introduced into blood stream of the patient, a magnetic field gradient is created by strong permanent magnet to retain the particles at the targeted region. Magnetic nanoparticle coated with a drug could

be injected intravenously, transported and retained at targeted sites, which make them highly promising system for drug delivery.

#### **(5) Therapy**

Magnetic nanoparticles have currently been explored as a technique for targeted therapeutic heating of tumors which is called hyperthermia. Various types of super paramagnetic nanoparticles with different coatings and targeting agents are used for specific tumor sites.

### **Introduction to super conductivity**

- ✓ The nanoscale superconductors are as 'nanosuperconductors' and are classified as a **superconducting material developed at the scale of a nanometer.**
- ✓ Superconductivity occurs when a quantum condensate of paired electrons (Cooper pairs) is formed.
- ✓ Superconductivity is a fantastic property. At some temperature, electrons flow without resistance, forever. Below the superconducting transition temperature, electrons anti-correlate strongly their motions in pairs. As a result, scattering cannot change their center of mass motion. At present the temperature of superconductors is about half way to absolute zero. This makes it difficult to use on a large scale. A long-term goal of research in superconductivity is to raise the superconducting temperature to room temperature. This would have enormous practical consequences, for energy efficiency and storage.
- ✓ Recent researches reveal that, as the electrons are confined in a small volume, the interaction changes. Some of the effect of confinement might help, such that having more electrons at the same energy, or the increase of the electron-phonon coupling, while others hurt such as the net decrease of the number of electrons.

### **Applications of Nanosuperconductors**

- ✓ Nanosuperconductors first found many uses within electrical components, and their discovery helped to develop innovations in currently-existing semiconductors.
- ✓ They also enabled the conversion of non-superconducting materials into superconducting units. While nanosuperconductors are generally utilized in metrology or high-frequency applications such as amplifiers, magnetometers, and imaging, they have a broad range of uses across many industries.
- ✓ Nanosuperconductors are primarily utilized in the field of medicine and biophysics in the form of improved imaging techniques (e.g., magnetic resonance imaging, nuclear magnetic resonance). The developments in these techniques using

nanosuperconductors could lead to more accurate diagnoses of physiological abnormalities or improved disease monitoring.

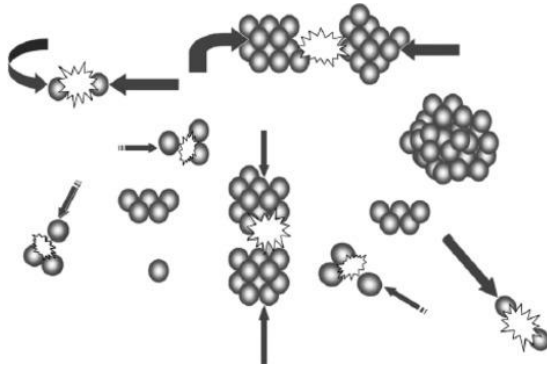
- ✓ For example, nanosuperconductors are already being used to magnetically tag antibodies in humans, which enables better diagnostics and therefore, more effective treatment. They are also currently being utilized in the development and research of gradiometers. By improving the abilities of the gradiometers, nanosuperconductors could help physicians and parents measure and assess fetal heart signals more accurately in real time.
- ✓ Prior research has often suggested that superconductivity is a necessary consideration when looking into improving and developing enhanced power solutions.
- ✓ Therefore, nanosuperconductors have unsurprisingly been found useful in the development of power transmissions, strong magnets, and small and compact motors.
- ✓ Present studies on nanosuperconductors are mostly aimed at expanding the applicability of the material. In particular, researchers are committed to developing new uses for the nanosuperconductors through the use of nano-cells; ranging from singular cellular materials to complex arrays of nanostructures.
- ✓ For example, currently being tested is the applicability of high-temperature nanosuperconductors in ceramic. Current findings promote the viability of nanosuperconductors against varying temperatures, which implies that the material can operate appropriately regardless of increasing temperatures. This also suggests that nanosuperconductors could be implemented in other high-temperature applications.
- ✓ In another study, it was found that the flux line pinning in superconductors - used to improve the transport properties of superconductors - could be better facilitated using nanoparticles. The experimental result suggested that critical current density becomes higher by a factor of 3 and the  $J_c$ - $B$  behavior significantly improves when nanosuperconducting units are utilized. This finding supports other studies by displaying the wide use of nanosuperconductors in various areas.

## **Novel physical chemistry related to nano particles**

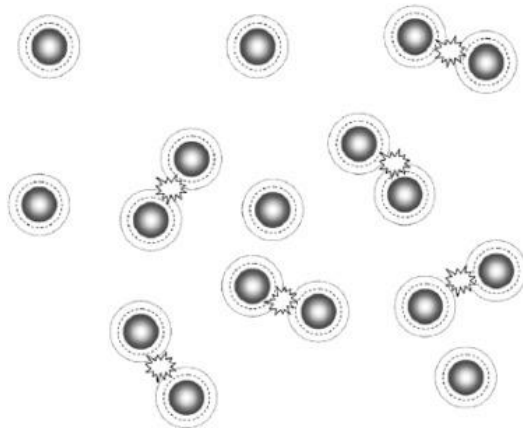
### **Colloidal nanoparticles**

- ✓ Typical colloidal nanoparticle sols are aqueous or alcoholic solutions/suspensions of oxide nanoparticles with sizes of a few nanometers to tens of nanometers.
- ✓ Colloidal nanoparticles in aqueous solution have recently gained much attention for their potential applications.
- ✓ Particle agglomeration may either be required to occur in a controllable manner or needed to be avoided, depending on particular applications.
- ✓ In order to understand particle agglomeration, it is important to understand the surface forces at the interface of the particle and aqueous portion of the colloid.

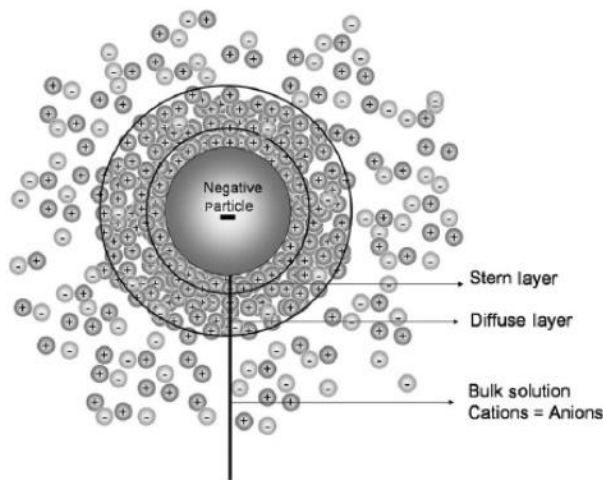
- ✓ Particles with zero charge are induced aggregation; large particles can be obtained by combining them, and they settle by gravitational force. Fig. represents nanoparticles with zero charge in liquid phase, in which it is easy for them to collide and form larger clusters.



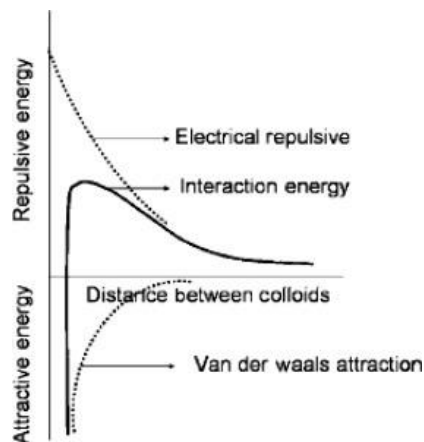
- ✓ If particles are carrying like electrical charges, a force of mutual electrostatic repulsion between adjacent particles is produced (Yu et al., 2008). This process is shown in Fig.



- ✓ Encapsulation of the particles by silica in a 7.4 pH buffer is a way to produce stable and homogenous nanoparticles. These particles do not aggregate due to the lower isoelectric point of the silica, rendering the overall particle charge negative. Particles possessing high charges can induce double layers in aqueous environments and are discrete, disperse, and in suspension (Yu et al., 2008). The double layers of colloidal and electrostatic principle are presented in Fig.



- ✓ In contrast with the repulsive energy, there is van der Waals attraction. The combination of an attractive force and a repulsive force induces net interaction energy as shown in Fig. (Yu et al., 2008).



## Nanoparticles in colloids and human diseases

- ✓ Several neurodegenerative diseases are linked to colloidal deposits in the brain containing nanoparticles. These are activated within the brain by colloidal or particulate material of exogenous origin. While the sites of damage and types of aggregate involved can vary widely, the sequence of events triggered by their chronic presence with the brain is more or less common.
- ✓ These diseases commonly have genetic origins that involve accumulation of complex carbohydrates and lipids, such as galactosidoses and sphingolipidoses. These insoluble deposits are intolerable to the brain and its vital functions.

- ✓ The growing exposure of the population to nanoparticles from a variety of sources thus is a cause for concern. The major route of contact with such materials is not by way of inhalation of ambient air and fumes, but increasingly by the use of nanoparticles in consumer products, food additives and medical drugs. The final effects of these exposures are unknown.

The ability of colloids and nanoparticles to initiate inflammatory events within the brain may be based on factors like:

- The particulate deposits are chemically inert but if they are of the critical size, they can lead to the initiation of immune responses from glial cells or the defence cells of the brain.
- These colloidal nanoparticles have a large surface area and thus can serve as an attractant of metal ions. When these include transition metals capable of expressing more than one valence state under physiological conditions (for example Fe, Cu, Mn), this forms an effective platform for Fenton-like cycling activity. This can lead to production of reactive oxygen species and cause oxidative damage to the brain.

## Nano clusters

- ✓ **Nanoclusters** are atomically precise, crystalline materials most often existing on the 0-2 nanometer scale. They are fine aggregates of atoms or molecules. They bound by forces which may be metallic, covalent, ionic or hydrogen bonds or vander waals forces. Different types of clusters can be distinguished by the nature of forces between the atoms.
- ✓ The **key difference between nanoparticles and nanoclusters** is that nanoparticles are particles having dimensions between 1 to 100 nm, whereas nanoclusters are collections of nanoparticles.
- ✓ Nanoclusters behave like molecules and do not show plasmonic behaviour. They are the link between atoms and nanoparticles. Therefore, a synonym for nanoclusters is **molecular nanoparticles**. All the nanoclusters are not stable components. This stability depends on the number of atoms in the nanocluster and valence electron count.
- ✓ Clusters are small aggregates of atoms and molecules. Small means really tiny pieces of matter—they are composed of a few to thousands of units and have a diameter of nanometers. Nanoclusters have at least one dimension between 1 and 10 nm and a narrow size distribution. Nanoclusters are composed of up to 100 atoms, but bigger ones containing 1000 or more are called nanoparticles.



- ✓ They are often considered kinetically stable intermediates that form during the synthesis of comparatively larger materials such as semiconductor and metallic nanocrystals.
- ✓ The majority of research conducted to study nanoclusters has focused on characterizing their crystal structures and understanding their role in the nucleation and growth mechanisms of larger materials.
- ✓ These nanoclusters can be composed either of a single or of multiple elements, and exhibit interesting electronic, optical, and chemical properties compared to their larger counterparts.
- ✓ Materials can be categorized into three different regimes, namely bulk, nanoparticles and **nanoclusters**.
- ✓ Bulk metals are electrical conductors and good optical reflectors and metal nanoparticles display intense colors due to surface plasmon resonance.
- ✓ However, when the size of metal nanoclusters is further reduced to form a nanocluster, the band structure becomes discontinuous and breaks down into discrete energy levels, somewhat similar to the energy levels of molecules.
- ✓ This gives nanoclusters similar qualities as a singular molecule and does not exhibit plasmonic behavior; nanoclusters are known as the bridging link between atoms and nanoparticles.
- ✓ Nanoclusters may also be referred to as molecular nanoparticles.
- ✓ Nanoclusters have potential uses in chemical reactors, telecommunications, microelectronics, optical data storage, catalysts magnetic storage, spintronic devices, electroluminescent displays, sensors, biological markers, switches, transducers and many other fields. The fluorescence silver nanoclusters have been extensively used as biological markers for photodynamic therapy.
- ✓ **Magic numbers** : it is the number of atoms in the clusters of critical size with the higher stability.

### **Metal nanoclusters**

- ✓ Metal nanoclusters (NCs) are composed of a small number of atoms, up to dozens. These nanoclusters can consist of a single element or multiple elements, usually smaller than 2 nm. Compared with their larger counterparts, this nanocluster exhibits attractive electronic, optical and chemical properties.
- ✓ These particles have quasi-continuous energy levels and display intense colors due to surface plasmon resonance. If their dimension is further reduced to the size approaching the Fermi wavelength of electrons, the band structure becomes discrete energy levels. The ultrasmall metal nanoparticles display molecule-like properties and no longer exhibit plasmonic behavior. Metal NCs, such as AuNCs, AgNCs, CuNCs, and PtNCs, exhibit a marked photoluminescence property due to quantum confinement. The most studied among these metal NCs are AuNCs, AgNCs, and CuNCs.

- ✓ Clusters containing the transition metal atoms have unique chemical electronic and magnetic properties.

## Sources of clusters

There are many kind of cluster sources. Two of them are

- (1) Gas aggregation source
- (2) Super sonic nozzle source.

### Gas aggregation source

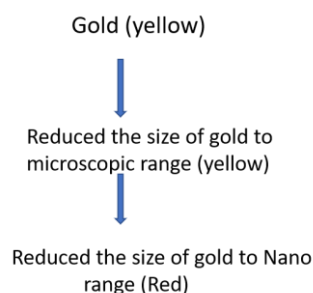
The vapours generated by any method are introduced into a cold inert gas at higher pressure. The gas phase is super saturated with the species and they aggregate. These source produce continuous beam of clusters of low to medium boiling metals.

### Super sonic nozzle source.

In this method metal is vapourised in an oven and the vapours are mixed with an inert carrier gas at a pressure of several atmospheres and a temperature of 75-1500k. the metal gas mixture is then allowed through a nozzle into a high vacuum, which creates a supersonic beam. Seeding produce large clusters while in the absence of a carrier gas smaller clusters are formed.

## Quantum effects (Quantum size effect/Quantum confinement)

- ✓ Restricted motion of randomly moving electrons in specific energy levels when the dimensions of a material approaches the de Broglie wave length of electron.
- ✓ The effect does not come into play by going from macro to micro dimension.
- ✓ It become dominant when the nano meter size range is reached.
- ✓ The properties of matter also changes while moving from macro to nano size.
- ✓ This effect was first observed by Norio Taniguchi (in 1974), in his experiment on gold
- ✓ Examples: quantum well, quantum wire, quantum dots.



### Quantum well (Nano sheets):

- ✓ It is 2 dimensional.
- ✓ Confinement acts only in one direction.
  
- ✓ A quantum well is a nanometer-thin layer which can confine (quasi-particles (typically electrons or holes) in the dimension perpendicular to the layer surface, whereas the movement in the other dimensions is not restricted.
  
- ✓ The confinement is a quantum effect. It has profound effects on the density of states for the confined particles. For a quantum well with a rectangular profile, the density of states is constant within certain energy intervals.
  
- ✓ A quantum well is often realized with a thin layer of a semiconductor medium, embedded between other semiconductor layers of wider band gap (examples: GaAs quantum well embedded in AlGaAs, or InGaAs in GaAs). The thickness of such a quantum well is typically  $\approx 5\text{--}20$  nm. Such thin layers can be fabricated with molecular beam epitaxy (MBE) or metal–organic chemical vapor deposition (MOCVD). Both electrons and holes can be confined in semiconductor quantum wells.
  
- ✓ If a quantum well is subject to strain, as can be caused by a slight lattice mismatch (e.g., for InGaAs quantum wells in GaAs), the electronic states are further modified, which can even be useful in laser diodes.
  
- ✓ Semiconductor quantum wells are often used in the active regions of laser diodes, where they are sandwiched between two wider layers with a higher band gap energy. These cladding layers function as a waveguide, while electrons and holes are efficiently captured by the quantum well (*separate confinement*), if the difference in bandgap energies is sufficiently large. Quantum wells are also used as absorbers in semiconductor saturable absorber mirrors (SESAMs), and in electroabsorption modulators.
  
- ✓ If a large amount of optical gain or absorption is required, multiple quantum wells (MQWs) can be used, with a spacing typically chosen large enough to avoid overlap of the corresponding wave functions.

### Quantum wire:

- ✓ One dimensional structure
- ✓ Confinement in two dimensions

- ✓ In one direction free flow of electrons
- ✓ Areas of application: electronics, micro electromechanical system

### Quantum dots:

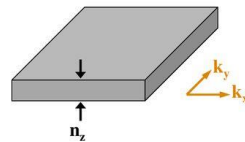
- ✓ Quantum dots are zero dimensional
- ✓ Confinement in 3 dimensions.
- ✓ Quantum dots are widely used for their unique optical properties, as they emit light of specific wavelengths if energy is applied to them. These wavelengths of light can be accurately tuned by changing various properties of the particle, including shape, material composition, and size.

### Quantum Confinement in Nanostructures

Confined in:

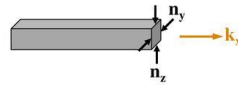
**1 Direction:** Quantum well (thin film)

Two-dimensional electrons



**2 Directions:** Quantum wire

One-dimensional electrons



**3 Directions:** Quantum dot

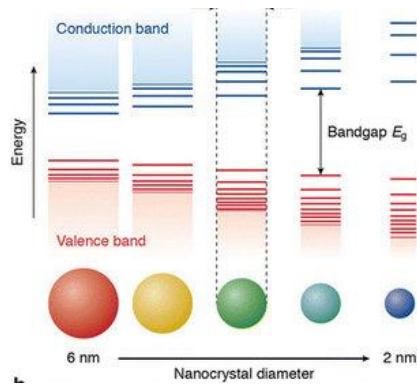
Zero-dimensional electrons



Each confinement direction converts a continuous  $k$  in a discrete quantum number  $n$ .

### Properties of Nanomaterials

- ✓ Properties of nanomaterials are different from their bulk counter part
- ✓ That is if the physical size of material is reduced its properties change
- ✓ This is because of
  1. Large fractions of surface atoms
  2. Large surface energy
  3. Surface volume ratio increases
  4. Quantum confinement (which leads to increase in band gap)
  5. Reduced imperfections.
- ✓ While moving from bulk to nanoscale the surface to volume ratio increases.
- ✓ The increase in surface is important in applications where surface to volume ratio play a critical role such as catalysis, semiconductors etc.
- ✓ The quantum confinement also lead to increase in band gap.



- ✓ In bulk material the valence band and conduction bands are continuous. When the size reduced to microscopic range number of atoms decreases. Therefore, the energy level of valence band and conduction band become moderately discontinuous and energy gap increases.
- ✓ If the material reaches the nano size the number of atoms again decreases and the energy level of valence band and conduction fully discontinuous and band gap again increases.
- ✓ That is discontinuity or band gap increases from bulk to nano and also within nano as the size decreases.

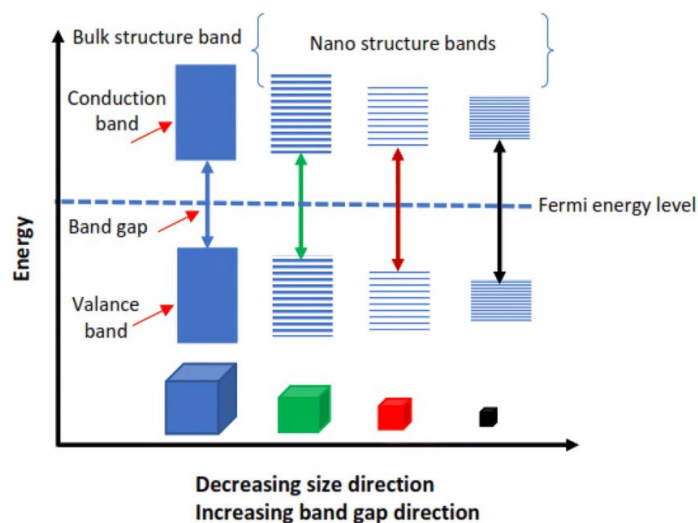
### Conductivity of nanoparticles

- ✓ The properties like conductivity or resistivity are come under category of electrical properties. These properties are observed to change at nanoscale level like optical properties.
- ✓ The examples of the change in electrical properties in nanomaterials are:  
Conductivity of a bulk or large material does not depend upon dimensions like diameter or area of cross section and twist in the conducting wire etc.
- ✓ However it is found that in case of carbon nanotubes conductivity changes with change in area of cross section.
- ✓ It is also observed that conductivity also changes when some shear force (in simple terms twist) is given to nanotube.
- ✓ Conductivity of a multiwalled carbon nanotube is different than that of single nanotube of same dimensions.
- ✓ The carbon nanotubes can act as conductor or semiconductor in behaviour but we all know that large carbon (graphite) is good conductor of electricity.
- ✓ In electrically conducting carbon nanotubes, only one electron wave mode is observed which transport the electrical current.
- ✓ There are three categories of materials based on their electrical properties: (a) conductors; (b) semiconductors; and (c) insulators. The energy separation between the valence band and the conduction band is called  $E_g$  (band gap).

- ✓ The ability to fill the conduction band with electrons and the energy of the band gap determine whether a material is a conductor, a semiconductor or an insulator.
- ✓ In conducting materials like metals, the valence band and the conducting band overlap, so the value of ( $E_g$ ) is small: thermal energy is enough to stimulate electrons to move to the conduction band.
- ✓ In semiconductors, the band gap is a few electron volts. If an applied voltage exceeds the band gap energy, electrons jump from the valence band to the conduction band, thereby forming electron hole pairs called excitons.
- ✓ Insulators have large band gaps that require an enormous amount of voltage to overcome the threshold. This is why these materials do not conduct electricity .

### Quantum confinement and its effect on material electrical properties:-

- ✓ Quantum confinement causes the energy of the band gap to increase as illustrated in Figure. Furthermore, at very small dimensions when the energy levels are quantified, the band overlap present in metals disappears and is actually transformed into a band gap. This explains why some metals become semiconductors as their size is decreased.



### Catalytic Activity of nano particles

- ✓ **Nanomaterial-based catalysts** are usually heterogeneous catalysts broken up into metal nanoparticles in order to enhance the catalytic process.
- ✓ **Due to** an increase in surface area with a decrease in particle size, nano material-based catalysts show increased catalytic activity.
- ✓ Nanoparticle catalysts can be easily separated and recycled.
- ✓ They are typically used under mild conditions to prevent decomposition of the nanoparticles.
- ✓ Example Pd, Pt metal nanoparticles used in hydrogenation reactions.
- ✓  $TiO_2$ , ZnO are used in photocatalysts.

- ✓ Gold in bulk form is unreactive, but gold nanoparticles are found to be a very good catalyst for various organic reactions.
- ✓ Main applications of nano catalysts in water purification, fuel cell, energy storage, biodiesel production, in medicine, in dye.
- ✓ Metallic nanoparticles can catalyze C-C coupling reactions such as the hydroformylation of olefins, the synthesis of vitamin E and Heck Coupling and Suzuki Coupling reactions.

### **Reasons for catalytic properties in nanomaterials**

- ✓ When materials are taken to the nanoscale, many of their properties change, such as electrical, optical, magnetic, etc.
- ✓ The emergence of the following three properties is one of these changes: very small size, very high surface-to-volume ratio, and increasing the number of atoms on the surface.
- ✓ These last three factors are the most important reasons for the emergence of catalytic properties in nanomaterials.
- ✓ Basically, when particles become very small (nanoscale), due to the very high curvature they find, they have many atoms on their surface, which are very weakly bonded to the lattice atoms of the lattice.
- ✓ Therefore, these particles have very high surface energy and are highly active, and it is said that surface atoms are in a state of physical instability and are chemically active, and are prone to perform many chemical reactions.
- ✓ It can be said that the main and determining reason for the emergence of catalytic properties in nanomaterials is their very high surface-to volume ratio.
- ✓ The higher this ratio, the higher the catalytic properties in nanomaterials due to the increase in surface energy.
- ✓ In principle, the reason for these changes is due to changes in the electronic structure of materials, which can be justified by quantum mechanics.
- ✓ When the particle size becomes too small, the density of the capacitance band states changes and a set of discrete levels is observed.
- ✓ Eventually, as the particles shrink, they become so large that the surface of the particles is spaced by an order of magnitude electron wavelength.
- ✓ In this situation, energy levels can be modeled by the quantum mechanical behavior of a particle in a box. This effect is called the quantum size effect.
- ✓ The emergence of new electron properties can be understood in terms of Heisenberg's uncertainty principle, which states that the more spatially an electron is trapped, the wider its range of motion.
- ✓ In semiconductors, the presence of oxyton has a large effect on the electronic properties.
- ✓ In a massive semiconductor with a photon whose energy is greater than the energy gap of matter, a pair of bound electron-hole pairs called oxytons can be produced.

- ✓ The photon removes the electron from the capacitance band and transfers it to the conduction band. As a result, a hole is created in the capacitance bar that is equivalent to one positive electron or charge. Due to the attraction between the positive hole and the negative electron, a pair of exaction bonds travels across the lattice, which greatly affects the electron and optical properties.
- ✓ If the radius of the nanoparticle is smaller than the electron-hole radius, the range of motion of the exciton is limited. As a result, oxytone uptake is observed and a shift towards lower wavelengths (blue shift, hypochromic effect) is observed.
- ✓ Since the electronic structure of nanoparticles depends on the particle size, their ability to react with other samples also depends on their size. These changes and their effect are very noticeable.
- ✓ For example, one of the metals that behaves very differently in mass and nanoscale is gold. Gold has a very low catalytic properties in the solid state and is one of the most inactive metals, but when taken to the nanoscale it exhibits very high catalytic activity and, interestingly, is one of the most common intermediate metals used in the synthesis of nanocatalysts. In the synthesis of catalysts used for the oxidation reaction of carbon monoxide and its conversion to carbon dioxide.

### **Factors affecting the catalytic properties of nanomaterial's**

Factors affecting the catalytic properties of nanomaterial's are:

1. The size of the nanoparticles.
2. The shape of the nanoparticles.
3. The distribution of the nanoparticles.
4. The preparation medium of the nanoparticles.
5. The reaction conditions.

#### **Nanoparticle size**

In most cases, the smaller the nanoparticle size, the greater the catalytic properties, but in some cases the catalytic properties do not increase with decreasing nanoparticle size. In the oxidation reaction of carbon monoxide using ruthenium nanoparticles in PVP substrate (PolyN-vinyl-2-pyrrolidone), it has been shown that when ruthenium nanoparticles are 6nm in size, their catalytic activity is eight times that of 2nm. It has also been proven that when gold nanoparticles with dimensions less than 5 nm are used, they show the highest activity and selectivity. Intermediate nanoparticles can have sizes in the range of less than 1 100 nm, but their greatest catalytic activity is observed when their size is around 1-10 nm.

#### **Nanoparticles distributed**

The spatial distribution of nanoparticles can also affect their catalytic properties. The higher the spatial distribution of the nanoparticles, the more catalytic properties increase as the number of surface atoms becomes available. In addition, it has been shown that the narrower the nanoparticle size distribution, the greater the catalyst activity.



## **The shape of nanoparticles**

Particles are said to have large curvatures when at the nanoscale, and their surface atoms are unstable. This effect is especially pronounced in non-spherical particles, particles that have many edge and corner locations, such as quadrilaterals, octagons, and cubes. In this case, as the surface-to-volume ratio increases significantly, the nanomaterial's show more catalytic properties; this has been confirmed in most research studies using the X-ray diffraction technique and the observed efficiencies. It is worth mentioning that in the synthesis of colloidal nanoparticles by Bradley method (the most common method of synthesis of colloidal nanoparticles) by controlling the concentration ratio of nanoparticles to stabilizers or using different reductant depending on the reaction, the desired shape can be synthesized.

## **Nanoparticle preparation bed**

Materials at the nanoscale have very high surface energy and tend to stick to each other. In most cases, nanoparticles are deposited on a substrate in different ways and then used in the reaction; The reason for this is that the substrate prevents the nanoparticles from accumulating and becoming so-called agglomerated, because when the nanoparticles accumulate, they become out of the nanoparticle state. The substrate traps nanoparticles on its surface through electrostatic and spatial interactions, reduces their surface energy, prevents their accumulation, and also stabilizes them. The effect that the substrate has on the catalytic properties of nanoparticles is different for different nanomaterial's and does not have a specific process and depending on the type of nanomaterial and the type of substrate used, the catalytic properties can be increased or decreased. It has been shown that when ligand is used as a substrate in the preparation of nanocatalysts, the catalytic property decreases in most cases and when it is used as a substrate, the catalytic property increases in most cases. Various substrates - including polymers, dendrites, metal oxides, carbon nanotubes, and some ligands - are used to make nanomaterials, but polymer substrates are more common than others. The formation of nanoparticles in polymer substrates has been shown to increase the control of nanoparticles and can determine the state of nanoparticles on the surface, and in most cases increases the catalytic properties of nanomaterials. Among polymeric substrates, PVP (PolyN-vinyl-2-pyrrolidone) is the most commonly used substrate and is an inexpensive, linear polymer on which nanoparticles are uniformly dispersed.

It was shown that the main reason for the catalytic properties of nanomaterials is their high surface-to-volume ratio. This change is due to a change in the electron properties and the fact that reducing the size of nanoparticles does not always increase their catalytic properties, and other factors, such as the shape and substrate used, are very effective. If these nano catalysts can be produced on an industrial scale, we can see a huge change in industries, especially the oil and petrochemical industries.

## Nanotechnology in Health care

**Nanobiotechnology** and **bionanotechnology** refer to the combination of ideas, techniques, and sciences of biology and nanotechnology.

Nanobiotechnology refers to the application of nanoscale objects for biotechnology while bionanotechnology refers to the use of biological components in nanotechnology.

Nanotechnology is already leading to dramatic improvements in health care. Scientists are using nanoparticles to **target tumors, in drug delivery systems, and to improve medical imaging**. Some nanoparticle-based treatments are multi-functional; they can both find tumors and carry drugs for treatment. Nanotechnology is also being used to cut the cost and increase the speed of **DNA sequencing** and **provide scaffolding for tissue regeneration** or **wound treatment**.

**Nanomedicine**, the application of nanotechnology in medicine, draws on the natural scale of biological phenomena to produce precise solutions for disease prevention, diagnosis, and treatment. Below are some examples of recent advances in this area:

1. **Cancer detection and treatment: Gold nanoparticles** as probes for the detection of targeted sequences of nucleic acids, and they are also being clinically investigated as potential treatments for cancer and other diseases. Gold 'nano shells' are useful to fight cancer because of their ability to absorb radiation at certain wavelength. Once the nano shells enter tumour cells and radiation treatment is applied, they absorb the energy and heat up enough to kill the cancer cells.
2. **Drug Delivery:** Nanotechnology researchers are working on a number of different therapeutics where a nanoparticle can encapsulate or otherwise help to **deliver medication directly to cancer cells** and minimize the risk of damage to healthy tissue. This has the potential to change the way doctors treat cancer and dramatically reduce the toxic effects of chemotherapy.
3. **Imaging and diagnostic tools:** Tools enabled by nanotechnology are paving the way for earlier diagnosis, more individualized treatment options, and better therapeutic success rates.
4. **Diagnosis and treatment:** Nanotechnology is being studied for both the diagnosis and treatment of **atherosclerosis, or the buildup of plaque in arteries**. In one technique, researchers created a nanoparticle that mimics the body's "good" cholesterol, known as HDL (high-density lipoprotein), which helps to shrink plaque.
5. **Genetics:** The design and engineering of advanced solid-state nanopore materials could allow for the development of novel **gene sequencing technologies** that enable single-molecule detection at low cost and high speed with minimal sample preparation and instrumentation.
6. **Regenerative medicine:** Research in the use of nanotechnology for regenerative medicine spans several application areas, including **bone and neural tissue engineering**. Novel materials can be engineered to mimic the

crystal mineral structure of human bone or used as a restorative resin for dental applications. Researchers are looking for ways to grow complex tissues with the goal of one-day **growing human organs for transplant**. Researchers are also studying ways to use **graphene nanoribbons** to help repair spinal cord injuries; preliminary research shows that neurons grow well on the conductive graphene surface.

7. **Vaccine development:** Nanomedicine researchers are looking at ways that nanotechnology can improve vaccines, including vaccine delivery without the use of needles. Researchers also are working to create a universal vaccine scaffold for the annual flu vaccine that would cover more strains and require fewer resources to develop each year.
8. **Smart pills:** The term 'smart pills' refers to nano-level electronic devices that are shaped and designed like pharmaceutical pills but perform more advanced functions such as sensing, imaging, and drug delivery. Nanotechnology has previously helped in developing various kinds of smart pills, such as the PillCam, a capsule with a miniature video camera, and dose-tracking pills.
9. **Nanobots:** Nanobots are micro-scale robots, which essentially serve as miniature surgeons. They can be inserted into the body to repair and replace intracellular structures. They can also replicate themselves to correct a deficiency in genetics or even eradicate diseases by replacing DNA molecules. This property is still under development.
10. **Nanofibres:** Nanofibers are being used in wound dressings and surgical textiles, as well as in implants, tissue engineering, and artificial organ components. Scientists are working on developing 'smart bandages', which when left on the site, will absorb itself into the tissue once the wound heals. Embedded nanofibres in these smart bandages can contain clotting agents, antibiotics, and even sensors to detect signs of infection.
11. **COVID-19:** For image-based and clinical diagnostic of [COVID-19](#), nanomaterials are emerging as promising substrates because of their unique optical, electronic, magnetic, and mechanical properties. Nanomaterials that have been proposed for viral detection include metal, silica, and polymeric nanoparticles, quantum dots, and carbon nanotubes.

#### **Concerns of using nanotechnology in healthcare:**

1. **Toxicity:** Scientists are primarily concerned about the toxicity, characterization, and exposure pathways associated with Nanomedicine that might pose a serious threat to human beings and the environment.
2. Lack of proper knowledge about the effect of nanoparticles on biochemical pathways and processes of the human body.
3. Expensive processes and treatments make them less desirable.

Nanotechnology helps to overcome the limitations of conventional dosage forms. This technology promises to be used in disease treatment as well as diagnostics with high efficacy. Therefore, nanomedicine has been gaining widespread popularity. However, nanoparticles and nanotechnology, in general, is a relatively novel concept, and very little experimental data is available about their harmful effects. This lack of information may lead

to impediments in the safety regulation of nanotherapeutics and present before us unique assessment challenges.

## **Nanotechnology and environment**

- ✓ **Environmental Nanotechnology is the application of nanotechnology techniques to reducing or preventing damage to our environment.**
- ✓ Nanotechnology has the potential to play a significant role in environmental protection and sustainability by enabling new and improved methods for monitoring, cleaning up, and mitigating environmental pollutants.
- ✓ It can also help to reduce resource consumption and energy use through the development of more efficient technologies.
- ✓ For example, nanoparticles can be used to clean up oil spills, remediate contaminated soil and groundwater, and capture and remove air pollutants.
- ✓ Nanotechnology can also be used to create more efficient and effective methods for solar energy capture and storage, as well as for producing biofuels from renewable resources.
- ✓ Additionally, nanotechnology-enabled products, such as stronger and lighter materials, can reduce energy consumption in transportation and manufacturing.
- ✓ However, it is important to consider the potential environmental and health impacts of nanotechnology, and to implement measures to minimize these risks. This includes ensuring that nanotechnology is developed and used in a responsible and sustainable manner, and that it is subject to proper regulation and oversight.
- ✓ Overall, nanotechnology has the potential to make a positive impact on the environment and sustainability, but it is essential to approach its development and application with caution and a commitment to responsible use.
- ✓ Note, however, that nanotechnology currently plays a rather subordinate role in environmental protection, whether it be in research or in practical applications. Environmental engineering companies themselves attach only limited importance to nanotechnology in their respective fields.

## **Potential environmental benefits**

- ✓ Rising prices for raw materials and energy, coupled with the increasing environmental awareness of consumers, are responsible for a flood of products on the market that promise certain advantages for environmental and climate protection. Nanomaterials exhibit special physical and chemical properties that make them interesting for novel, environmentally friendly products.
- ✓ Examples include the increased durability of materials against mechanical stress or weathering, helping to increase the useful life of a product; nanotechnology-based dirt- and water-resistant coatings to reduce cleaning efforts; novel insulation materials to improve the energy efficiency of buildings; adding nanoparticles to a material to reduce weight and save energy during transport.
- ✓ In the chemical industry sector, nanomaterials are applied based on their special catalytic properties in order to boost energy and resource efficiency, and

nanomaterials can replace environmentally problematic chemicals in certain fields of application.

- ✓ High hopes are being placed in nanotechnologically optimized products and processes for energy production and storage; these are currently in the development phase and are slated to contribute significantly to climate protection and solving our energy problems in the future.
- ✓ In most commercially available nano-consumer products, environmental protection is not the primary goal. Neither textiles with nanosilver to combat perspiration odor, nor especially stable golf clubs with carbon nanotubes, help protect the environment. Manufacturers often promise such advantages, typically without providing the relevant evidence. Examples include self-cleaning surface coatings or textiles with spot protection, which are advertised as reducing the cleaning effort and therefore saving energy, water and cleaning agents.
- ✓ Emphasis is often placed on the sustainable potential of where nanotechnology will take us. Nonetheless, this usually reflects unsubstantiated expectations. Determining the actual effects of a product on the environment – both positive and negative – requires examining the entire life cycle from production of the raw material to disposal at the end of the life cycle.
- ✓ As a rule, the descriptions of environmental benefits fail to consider the amount of resources and energy consumed in producing the products.

### **Specific examples of nanotechnology applications that benefit the environment**

- 1. *Nanotechnology could make battery recycling economically attractive***  
Many batteries still contain heavy metals such as mercury, lead, cadmium, and nickel, which can contaminate the environment and pose a potential threat to human health when batteries are improperly disposed of. Not only do the billions upon billions of batteries in landfills pose an environmental problem, they also are a complete waste of a potential and cheap raw material. Researchers have managed to recover pure zinc oxide nanoparticles from spent Zn-MnO<sub>2</sub> batteries alkaline batteries.
- 2. *Nanomaterials for radioactive waste clean-up in water.***  
Scientists are working on nanotechnology solution for radioactive waste cleanup, specifically the use of titanate nanofibers as absorbents for the removal of radioactive ions from water. Researchers have also reported that the unique structural properties of titanate nanotubes and nanofibers make them superior materials for removal of radioactive cesium and iodine ions in water.
- 3. *Nanotechnology-based solutions for oil spills.***

Conventional clean-up techniques are not adequate to solve the problem of massive oil spills. In recent years, nanotechnology has emerged as a potential source of novel solutions to many of the world's outstanding problems. Although the application of nanotechnology for oil spill cleanup is still in its nascent stage, it offers great promise for the future. In the last couple of years, there has been particularly growing interest worldwide in exploring ways of finding suitable solutions to clean up oil spills through use of nanomaterials.

#### **4. *Water applications***

The potential impact areas for nanotechnology in water applications are divided into three categories, treatment and remediation, sensing and detection, and pollution prevention and the improvement of desalination technologies is one key area thereof. Nanotechnology-based water purification devices have the potential to transform the field of desalination, for instance by using the *ion concentration polarization* phenomenon. Another, relatively new method of purifying brackish water is *capacitive deionization* (CDI) technology. The advantages of CDI are that it has no secondary pollution, is cost-effective and energy efficient. Nanotechnology researchers have developed a CDI application that uses graphene-like nanoflakes as electrodes for capacitive deionization. They found that the graphene electrodes resulted in a better CDI performance than the conventionally used activated carbon materials.

#### **5. *Carbon dioxide capture.***

Before CO<sub>2</sub> can be stored in *Carbon dioxide Capture and Storage* (CCS) schemes, it must be separated from the other waste gases resulting from combustion or industrial processes. Most current methods used for this type of filtration are expensive and require the use of chemicals. Nanotechnology techniques to fabricate nanoscale thin membranes could lead to new membrane technology that could change that.

#### **6. *Hydrogen production from sunlight – artificial photosynthesis***

Companies developing hydrogen-powered technologies like to wrap themselves in the green glow of environmentally friendly technology that will save the planet. While hydrogen fuel indeed is a clean energy carrier, the source of that hydrogen often is as dirty as it gets. The problem is that you can't dig a well to tap hydrogen, but hydrogen has to be produced, and that can be done using a variety of resources. The dirtiest method – at least until highly efficient carbon capture and sequestration technologies are developed – is the gasification of coal. The cleanest by far would be renewable energy electrolysis: using renewable energy technologies such as wind, solar, geo- and hydrothermal power to split water into hydrogen and oxygen. Artificial photosynthesis, using solar energy to split water generating hydrogen and oxygen, can offer a clean and portable source of energy supply as durable as the sunlight. It takes about 2.5 volts to break a single water molecule down into oxygen along with negatively charged electrons and

positively charged protons. It is the extraction and separation of these oppositely charged electrons and protons from water molecules that provides the electric power. Working on the nanoscale, researchers have shown that an inexpensive and environmentally benign inorganic light harvesting nanocrystal array can be combined with a low-cost electrocatalyst that contains abundant elements to fabricate an inexpensive and stable system for photoelectrochemical hydrogen production.