Chemistry of nano-materials

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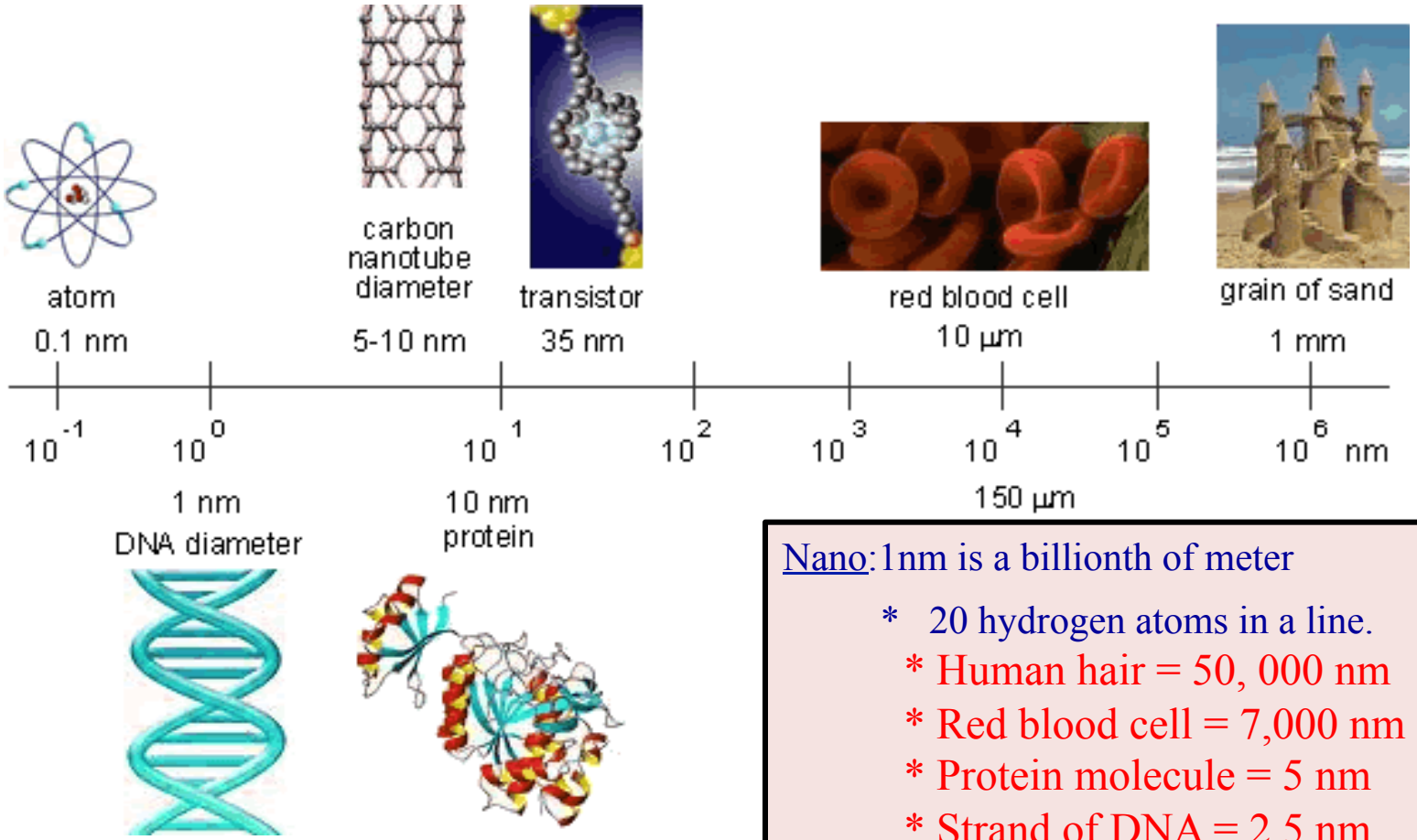
Chemistry of nanomaterials

MSRIT Syllabus (2019-20)

- Introduction to nanomaterials
- Synthesis methods :-
  - Solution combustion
  - Hydrothermal
- Characterization techniques
- Applications of nanomaterials in various fields.

What is nano ?

- A nanometer (nm) is one thousand millionth of a meter. People are interested in the nano scale because at this scale, the **Physical** and **Chemical** properties of nanomaterials differ significantly from those at a larger scale.



Nano: 1nm is a billionth of meter

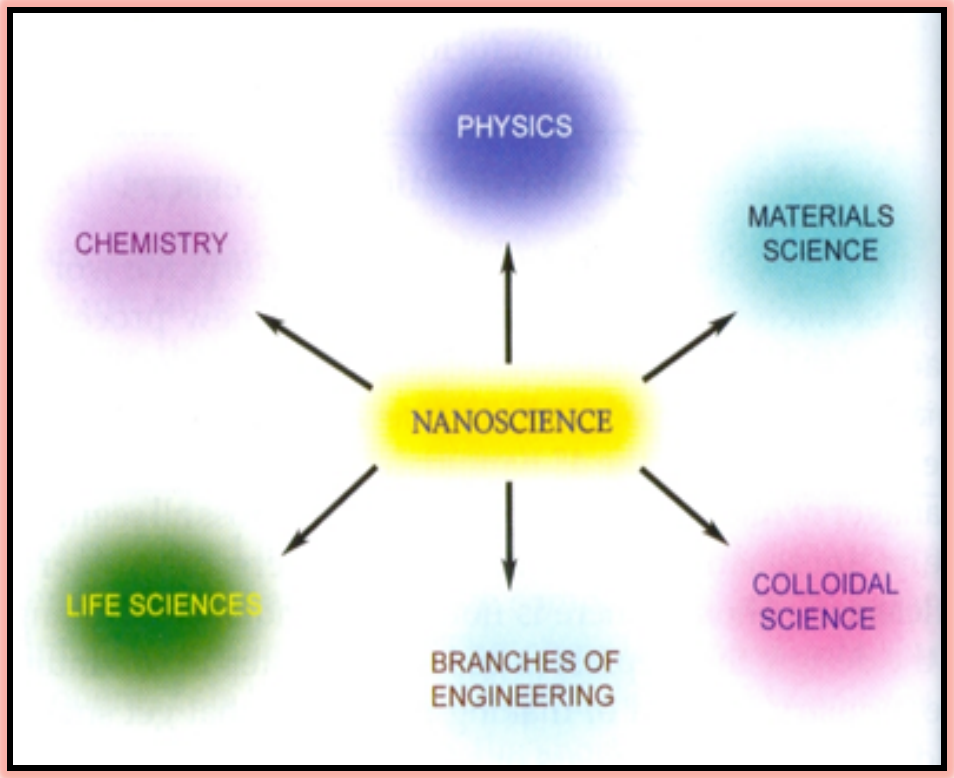
* 20 hydrogen atoms in a line.
* Human hair = 50, 000 nm
* Red blood cell = 7,000 nm
* Protein molecule = 5 nm
* Strand of DNA = 2.5 nm

Nanoscience & Nanotechnology

Nanomaterials: are defined as a set of substances where at least one dimension is less than approximately 100 nanometers.

Nanoscience: The study of phenomena and materials at the atomic, molecular and macromolecular scales, where properties differ significantly from those at the larger scale.

Nanotechnology: Design, characterization, production and application of structures, devices and systems by controlling **morphology** at the nano-scale.



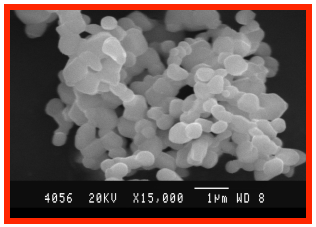
- **Nanotechnology** is already making **today's** products:
  - Lighter
  - Stronger
  - Faster
  - Smaller
  - More Durable

What is so unique about nanomaterials ?

- The properties like - Chemical - Physical - Mechanical – Optical properties are totally different from bulk
- So, nano-materials are exceptionally different from the bulk

Nano scale corresponds to a **size** > molecule but < bulk solid.

Therefore, a nanomaterial frequently exhibits physical and chemical **properties somewhere in between or completely different** and beyond to our imagination, sometimes.



atom **nanoparticle** **solid**

- **High surface/volume ratio leads to unique properties;**
- **The properties of nanoparticle lies in between that of a Single atom and that of bulk Solid.**

Why nano-materials are different from bulk materials?

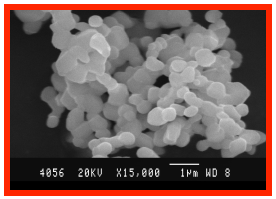
- *Quantum confinement* effects can begin to dominate the behavior at the nano-scale: affecting the optical, electrical and magnetic behavior of materials.

- As the size of the particle decreases, a **greater proportion of atoms** are found at the surface compared to those inside.

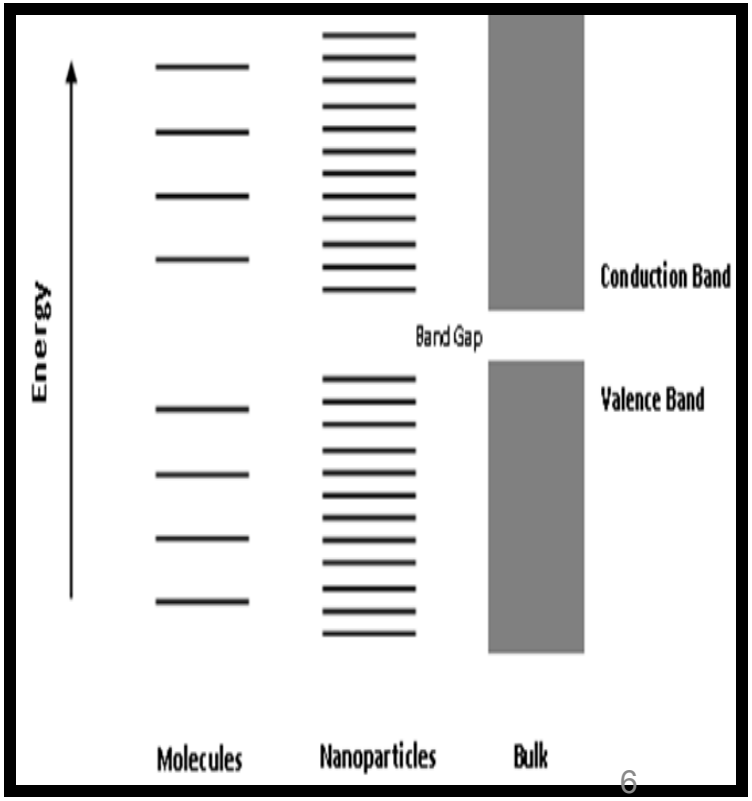
  For example, a particle of size

  - at 30 nm has 5 % of its surface,
  - at 10 nm 20 % of its atoms, and
  - at 3 nm 50 % of its atoms.

- Thus nanoparticles have a much greater surface area per unit mass compared the larger particles. As growth and chemical reactions occur at surface this means The materials with large **surface area** make the materials more *chemically reactive.*



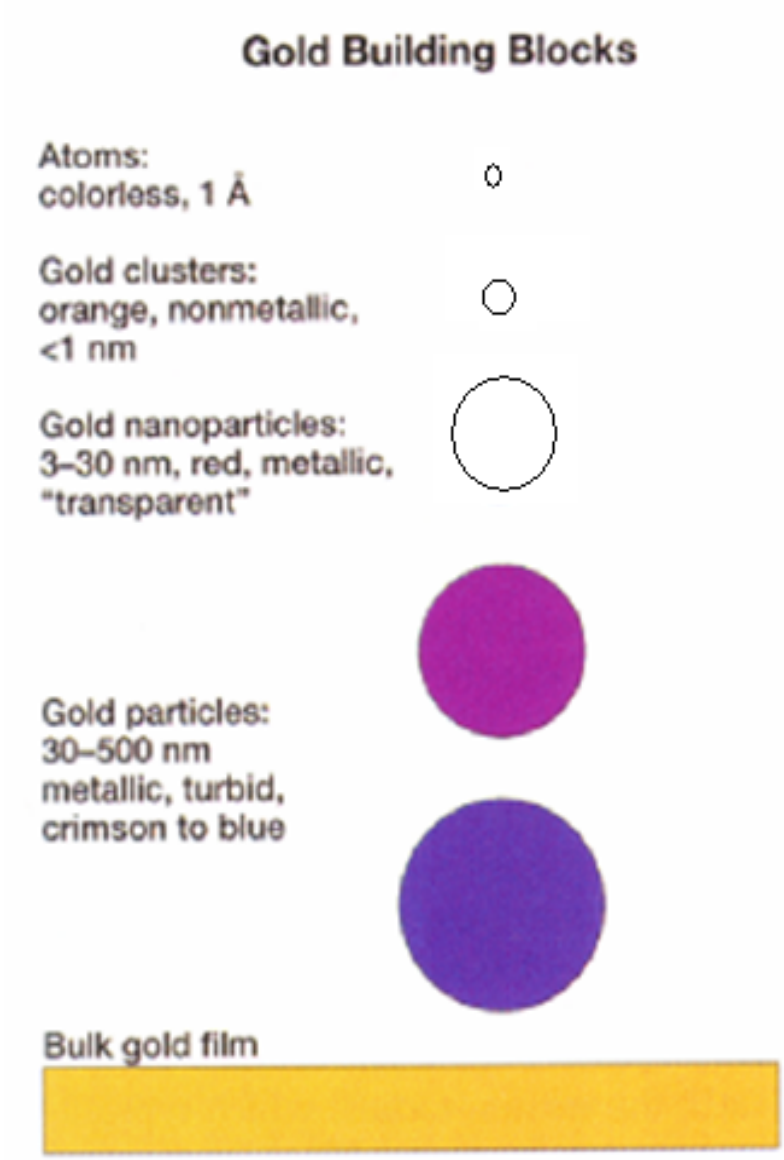
Nanoparticle **Bulk**



Size dependent properties of nanomaterials

Properties vary with size are :-

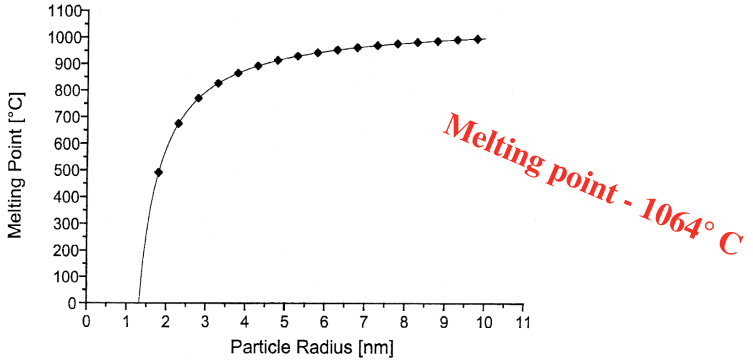
- Surface area
- Electrical property
- Optical property
- Catalytic property
- Magnetic property
- Etc.,



Gold Exhibit different color due to different mode of interaction of light

Properties:

- ✓ Bulk gold melts at **1064 °C,** but particles in the 5 nm size range melts at about **830 °C**.
- ✓ Electronic band of a crystal is gradually quantised as the size is reduced, resulting in an **increase in the band-gap** energy.
- ✓ Cobalt normally has a **hexagonal** lattice arrangement, but this is transformed to **FCC** for cobalt particles smaller than 20 nm.



The melting point decreases dramatically as the particle size gets below 5 nm

Synthesis of nanomaterials

Synthesis of nanomaterials

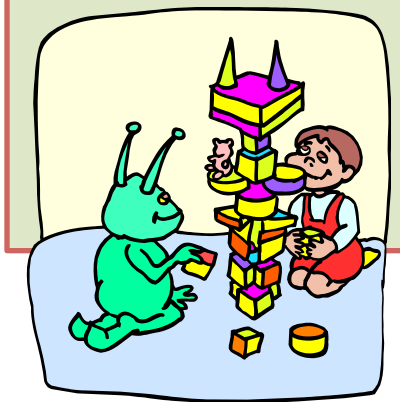
Several synthetic routes are practiced, that either break larger particles to nanosize or employ nucleation and growth.

Chemist route (Building-up process)

- ✓ Hydrothermal
- ✓ Sol-gel method
- ✓ Co-precipitation
- ✓ ** **Combustion synthesis**

Physisist route (Breaking-down process)

Ball Milling
Inert gas condensation
Ion beam technique
Laser ablation
Lithography
Mechanical attrition
Plasma pyrolysis
Sputtering
Hot thermolysis



Bottom ⇨ Up: Building what you want by assembling it from small prefabricated units such as atoms and molecules

- **Top ⇨ Down:** Start with the big chunk and cut away material to make the what you want.

Low temperature *Solution combustion*

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Low temperature *Solution combustion* is best method for synthesis of metal oxides

Why metal oxides ???

- **Most abundant in nature**
- **Highly stable and high physical constants**
- **More than 10^6 oxides are known**
- **Wide range of *technological* applications**

Oxide materials & their Technological Applications

• Superconductors	Magnetic Sensing, MRI's
• Magnetic Materials	Data Storage, Power Conversion
• Semiconductors	Computers, Electronics
• Dielectric Materials	Non-volatile Computer Memory, Cellular Phones, Radar and Telecommunications
• Piezoelectric Materials	Actuators, Microphones
• Luminescent Materials	Flat Panel Displays
• 2nd Harmonic Generation	Lasers
• Phosphors	Imaging Devices used in Science & Medicine
• Thermoelectric Materials	Remote Energy Conversion
• **Catalysts** **	**Chemical Production, Power plants**
• Alloys	Automobiles, Bicycles, Spacecrafts
• Ionic Conductors	Fuel Cells, Batteries, Gas Sensors

Applications of Nano-crystalline Oxide Materials

Oxides	Property	Applications
Al_2O_3, CeO_2,	Hardness	Abrasive
TiO_2, CeO_2, Fe_2O_3, M/ Al_2O_3, M/CeO_2, Pt/TiO_2	Catalysts , photocatalyst	Air and water pollution control
TiO_2, ZnO other oxides	UV-vis sunlight absorbing	Photocatalyst, Sun screen and paint, sensors, switching property
$BaTiO_3$, ZnO, Al_2O_3, PZT	Dielectric	Sensors, MEMS
γ - Fe_2O_3, $BaFe_{12}O_{19}$, MFe_2O_4	Magnetic	Cancer detection and remediation, Sensors and memory devices
TiO_2, Fe_2O_3, Cr_2O_3, MAl_2O_4, M/Al_2O_3, M/ZrO_2, RE/$ZrSiO_4$ (RE= Rare earth ion, M = transition metal ions)	Colours	Ceramic pigments
Eu^{3+}/Y_2O_3(Red), Eu^{2+}, Tb/Ba- Hexaaluminate	Luminescence	Phosphors CFL, Colour TV picture tube
Al_2O_3, ZrO_2, ZTA, Mullite, Cordierite, Tialite	Refractory	Toughened ceramics
MgO, CaO & ZnO	Adsorbent	Defluoridation & COD from paper mill effluents
YSZ(Y_2O_3-ZrO_2), Ni/YSZ La(Sr)MO_3, M=Mn, Cr	Electrolyte Anode Cathode/Interconnect	Solid Oxide Fuel Cell Materials

Solution combustion method (Patil's Method)

➢The solution combustion synthesis was first developed by Prof. K.C. Patil (I.I.Sc.), at I.I.Sc, Bangalore during 1986. It is a *wet chemical* method that, involves the exothermic reaction of metal nitrates and an organic fuel.

➢Solution combustion process is a self-propagating high temperature synthesis in which exothermic reaction takes place accompanied by the evolution of gases.

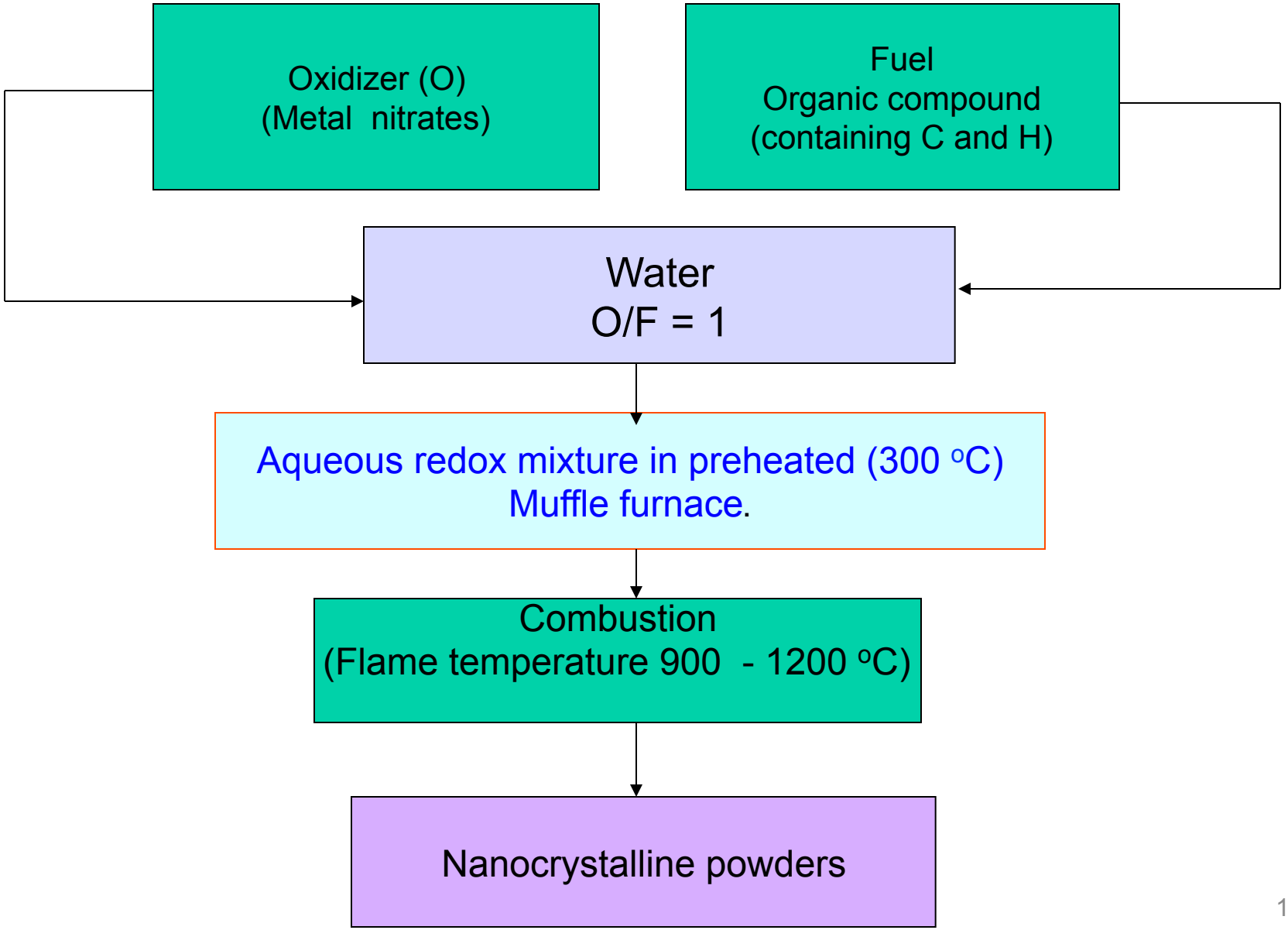
- Metal nitrates (aq) + Fuel (aq) ⟶ Combustion product (s) + Heat + Gases.

✓ Metal nitrates are oxidizers

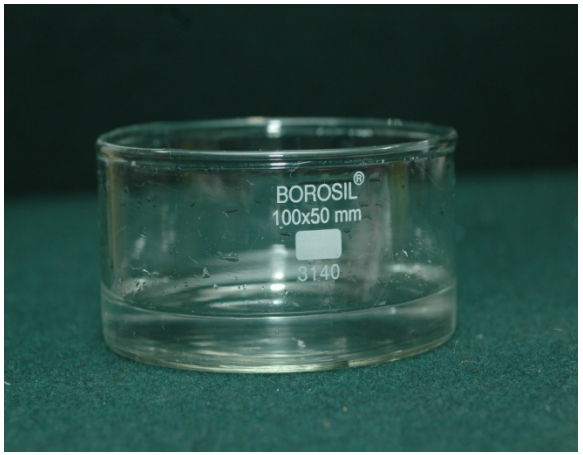
✓ Organic compounds are fuels

(Ex: urea, glycine, hydrazine, carbohydrazide)

The flow chart for synthesis of nano materials by solution combustion

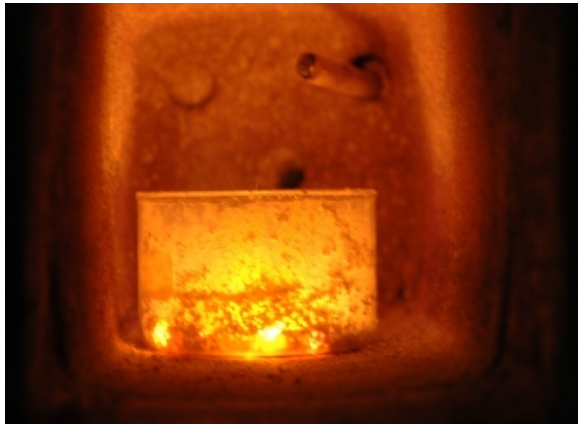


Combustion synthesis: Typical stages:



Metal nitrate and fuel in distilled water

Redox mixture boils at 300 °C



The incandescent combustion of redox mixture

High surface area combustion product

General procedure of combustion synthesis:

- In combustion synthesis process the stoichiometric amounts of metal nitrates (Oxidizers) and Carbonaceous fuels (Urea (U), glycine, carbohydrazide(CH), oxalyldihydrazide(ODH), tetrafarmaltrisazine(TFTA) hexamethylenetetramine(HMT) and other derivatives of hydrazine) are mixed in a minimum quantity of distilled water. The resulting solution is transferred into a cylindrical petri dish and heated over a hot plate to boil off the excess water. The petri dish containing wet powder is introduced into a muffle furnace maintained at $300^0 \pm 10^0$C. Initially, the wet powder undergoes thermal dehydration followed by decomposition of metal nitrates and fuel and then ruptures into flame after about 3 – 5 min. and yield voluminous, weakly agglomerated, nano powder.

Synthesis of ZnO nanoparticles by solution combustion method :

- Zinc nitrate (5.0g) and sugar (1.2 g) are dissolved in a minimum quantity of distilled water taken in a cylindrical petri dish and stirred well using magnetic stirrer for ½ hr. The resulting solution is heated over a hot plate to boil off the excess water. The petri dish containing wet powder is introduced into a muffle furnace maintained at 300 $\pm$ 10^0C. The redox mixture boils, froths, dehydrates forming a honey like gel and burns with an incandescent flame. The whole process is completed in less than 5 minutes. The procedure of combustion was voluminous, foamy, fluffy and porous. Weigh the product and find out the % of yield of the product. The theoretical reaction may be written as -

  $\mathbf{Zn(NO_3)_2\ (aq) + C_{12}H_{22}O_{11}\ (aq) \rightarrow ZnO\ (s) + N_2\ (g) + 11H_2O\ (g) + 12CO_2\ (g)}$

Advantages of solution combustion synthesis

Among wet chemical routes, the low temperature ***solution combustion process*** is an attractive one and finds several advantages like-

1. The synthesis temperature (300°C) employed is lower than those currently used in conventional route.
2. Simple and energetically attractive process.
3. Ability to dope desired amounts of impurity ions with better homogeneity.
4. The powders are voluminous, foamy, sinteractive and in nanoscale having large surface area.
5. Short reaction time (few seconds to 5 minutes).
6. Chemical homogeneity

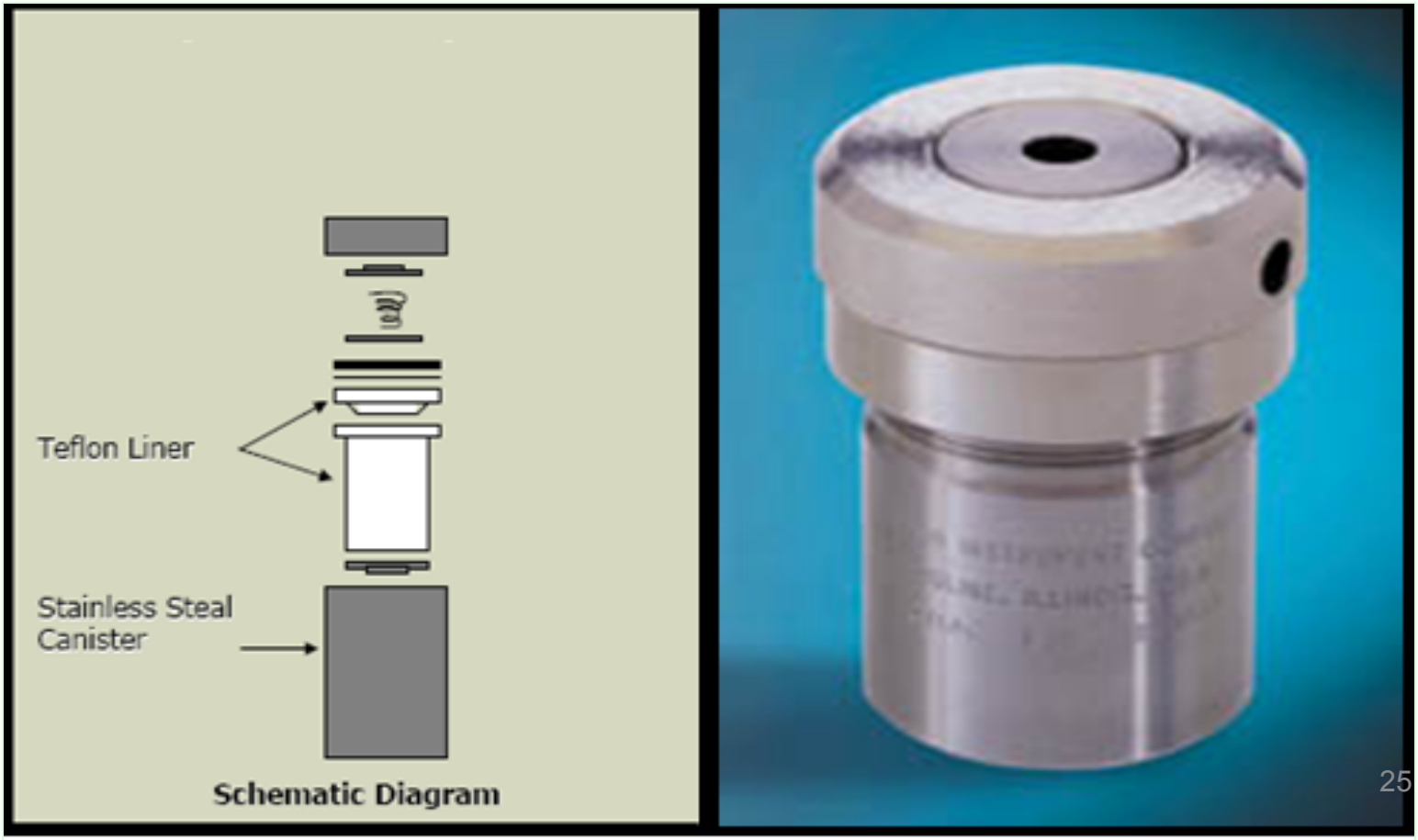
Hydrothermal Synthesis

Hydrothermal Synthesis

- Hydrothermal is a solution based method to prepare wide range of nanomaterials having diverse shapes and size. It is a method to produce different chemical compounds and materials using closed-system in aqueous solutions at temperatures above 100°C and pressures above 1 atm.

Hydrothermal Synthesis….

- In this method, reactants (Metal salts) are dissolved in water (hydrothermal) in a closed vessel called ***BOMB (autoclave)***.
- Bomb is heated above boiling point of water in hot air oven.



Synthesis of nano particles using hydrothermal method

- **Principle of hydrothermal method:** It is based on the principal of dissolution and recrystallizing substances from high temperature aqueous solutions at high vapour pressure. The crystal growth is performed in an apparatus consisting of a steel pressure vessel called autoclave, in which a nutrient (precursors) is supplied along with water. A gradient of temperature is maintained at the opposite ends of the growth chamber so that the hotter end dissolves the nutrient and the cooler end causes end causes seeds to take additional growth.

- **General Procedure:** In a typical hydrothermal synthesis, stoichiometric amount of precursors are added into ~ 20-25 ml of double distilled water. In few cases to maintain the basic pH alkali like NaOH or KOH are also added. Then the mixture is stirred well using magnetic stirrer to ensure complete homogenous mixing. Later, the solution is taken in an autoclave and sealed firmly and kept in a Hot air oven at a desired temperature (generally < 150 ^{O}C) and reaction is carried for desired time (Depending on material, time varies between 2 and 24 h). Then, after the reaction, the product is washed with water and ethanol to remove impurities and the products are dried at 110 ^{O}C for 2 h in a dust proof hot air oven to get nanocrystalline materials.

For example: Preparation of $BiFeO_4$ by hydrothermal method

- Equimolar mixtures of bismuth nitrate ($Bi(NO_3)_3.5H_2O$) and iron nitrate ($Fe(NO_3)_3.9H_2O$) are dissolved in distilled water. Add 8.0 M sodium hydroxide (NaOH) and stir for 30 min and poured into an autoclave. The hydrothermal treatment is conducted at 180^oC for 12 h. The produced powder is collected at the bottom of the autoclave after cooling to room temperature. The product is washed several times by repeated cycles of centrifugation in distilled water and ethanol. The obtained powder is heated at 80 ^oC for 1 hr.

Hydrothermal synthesis : Advantages :

1. High efficient and low-cost production of *advanced materials*
2. Crystalline, single and multi-component oxide materials
3. Environmentally safe and simple process, since water is used
4. It involves H_2O both as a catalyst and component of solid phases at elevated temperature (> 150 °C) and pressure (> a few atmosphere).

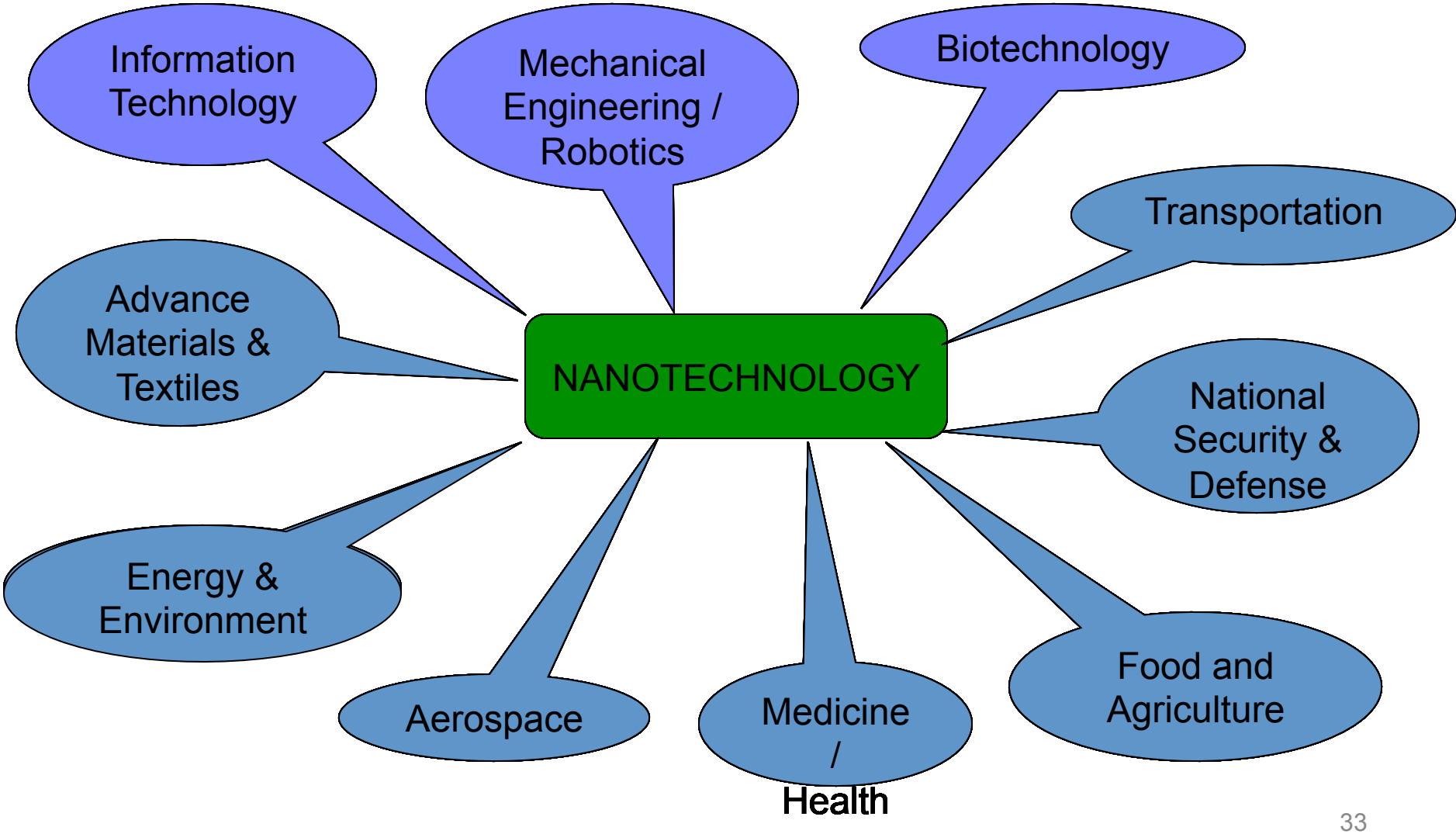
- **How do confirm, the prepared compound is *nano* in size ????**

Nano-size of the prepared compound is confirmed following characterization techniques

- Powder X-Ray diffraction – structure & Avg. crystallite size of materials
- SEM-Morphology(Shape) of the nanomaterials
- TEM-Morphology (shape) and particle size
- Etc.,

Applications of Nanomaterials

Nanotechnology – applicaions



Modern Nanotech - Sunblock

❖**Zinc oxide and titanium oxide are both employed as opaque sunblocks.**

❖**When particles are nanoscale, become invisible to the human eye, but still reflect UV light.**

❖**Modern sunblocks can provide a physical barrier without this classic appearance.**

- We use it in sunglasses – UV light damages our eyes!

- UV light can cause skin cancer, so we use it in sun lotion so it doesn't just sit on the skin it gets absorbed.

In Cosmetics

-Sunscreen

-nano Zinc Oxide

-Anti-Aging Creams

As Antibacterial agents

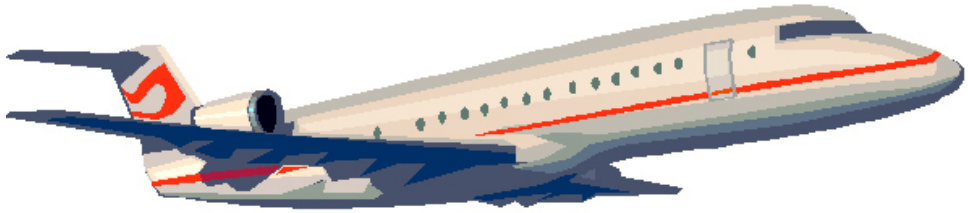
* Some fridges have the nanosized silver in the coating inside fridges.

- This will kill bacteria which can cause food poisoning

In transport

- More efficient catalytic converters
- Thermal barrier and wear resistant coatings

- Battery, fuel cell technology.
- Improved displays.



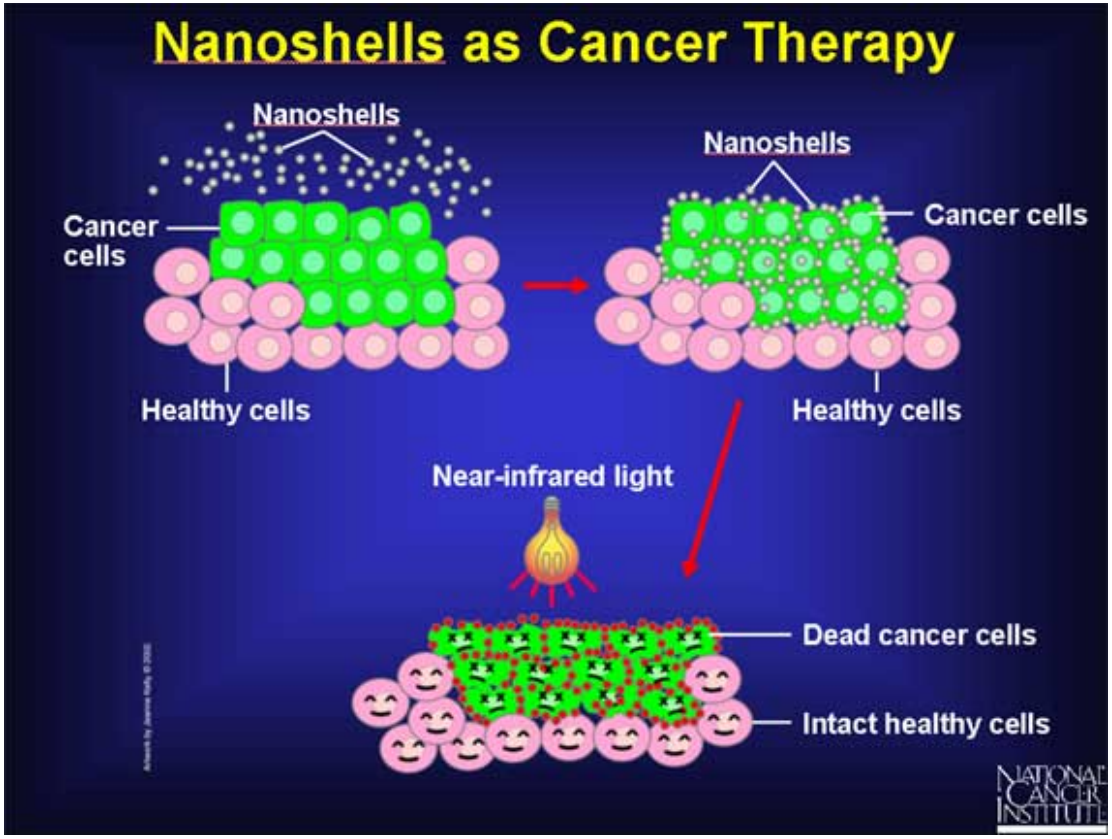
- High temperature sensors for ‘under the hood’; novel sensors for “all-electric” vehicles
- High strength, light weight composites for increasing fuel efficiency

Antifungal Properties

. Some

Nano shells as Cancer Therapy

Nano shells are injected into cancer area and they recognize cancer cells. Then by applying near-infrared light, the heat generated by the light-absorbing Nano shells has successfully killed tumor cells while leaving neighboring cells intact.



Other Applications of Nanotechnology: General Applications

Application	Examples
Medicine	Diagnostics, Drug delivery, Tissue engineering, Cryonics
Information and communication	Memory storage, Novel semiconductor devices, Novel optoelectronic devices, Displays, Quantum computers
Heavy Industry	Aerospace, Catalysis, Catalysis, Construction Vehicle manufacturers
Consumer goods	Foods, Household, Optics, Textiles, Cosmetics, Sports
Environment	Water treatment: The removal of colour, heavy metal, fluoride, etc

Thanks for your kind attention !