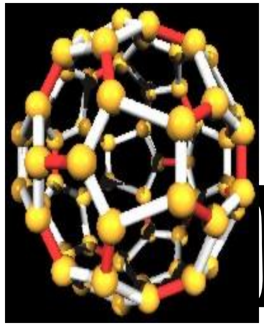


Nanomaterials

&

Its Applications

Dr. Sunita Goyal

- A nanometer is one billionth (10^{-9}) of a meter i.e.,

  1 meter is equal to 10^9 nanometers.

  (1 meter = 10^9 nanometers)

- Any material manipulated at the scale of nanometer is nanomaterial.

- In Nanotechnology, a nano particle is defined as a small object that behaves as a whole unit and has a size between 1 nm - 100 nm.

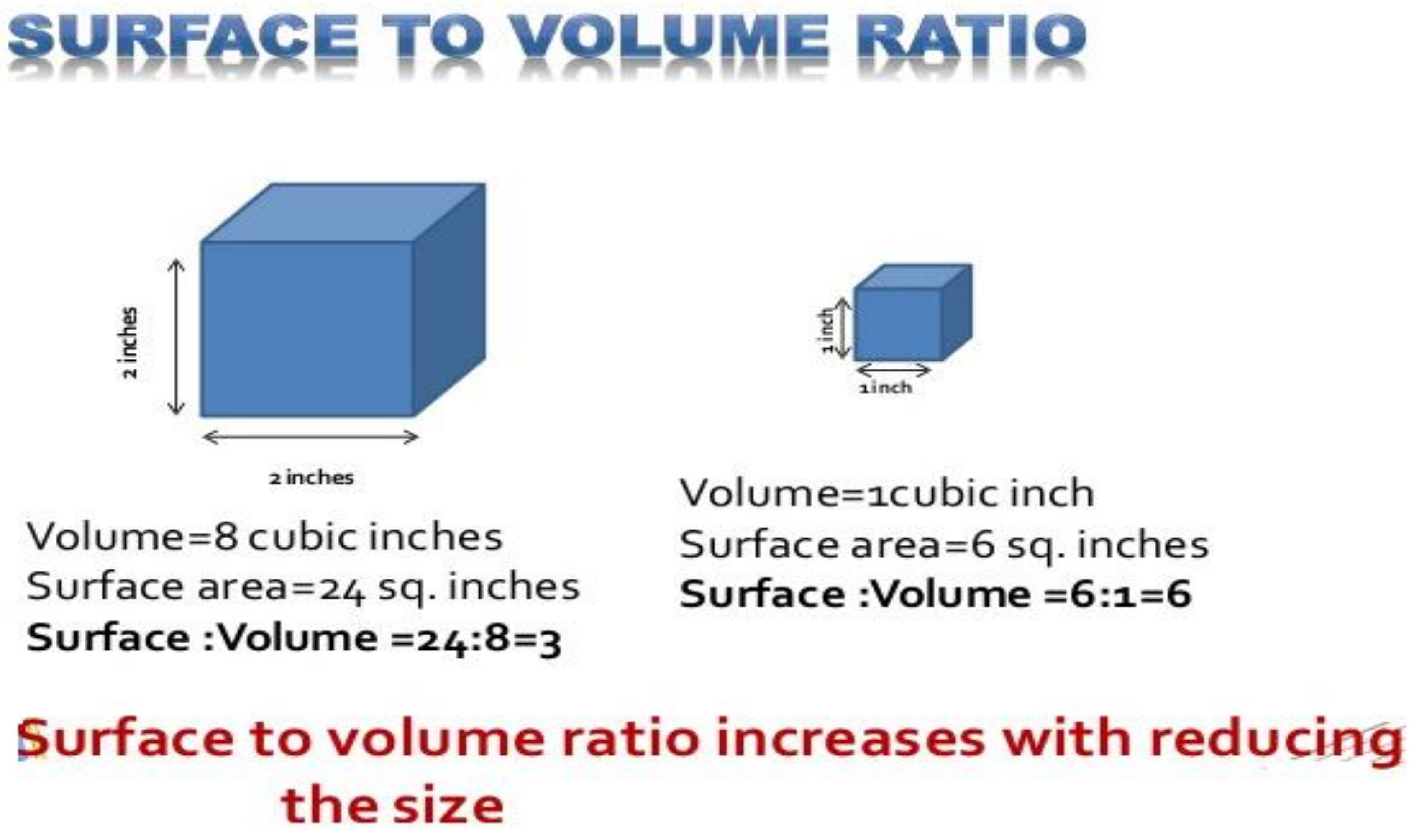
  They can be metals, ceramics, minerals, polymeric materials or composites, carbon allotropes etc.

Why the properties of nanomaterials differ significantly from bulk materials?

Two principal factors are:

- The nanoparticles have very large surface to volume ratio than bulk materials.
- The quantum effects begin to dominate the behavior of matter at nano scale, affecting the optical, electrical, mechanical and magnetic properties of materials.

- The nanoparticles have very large surface to volume ratio than bulk materials.



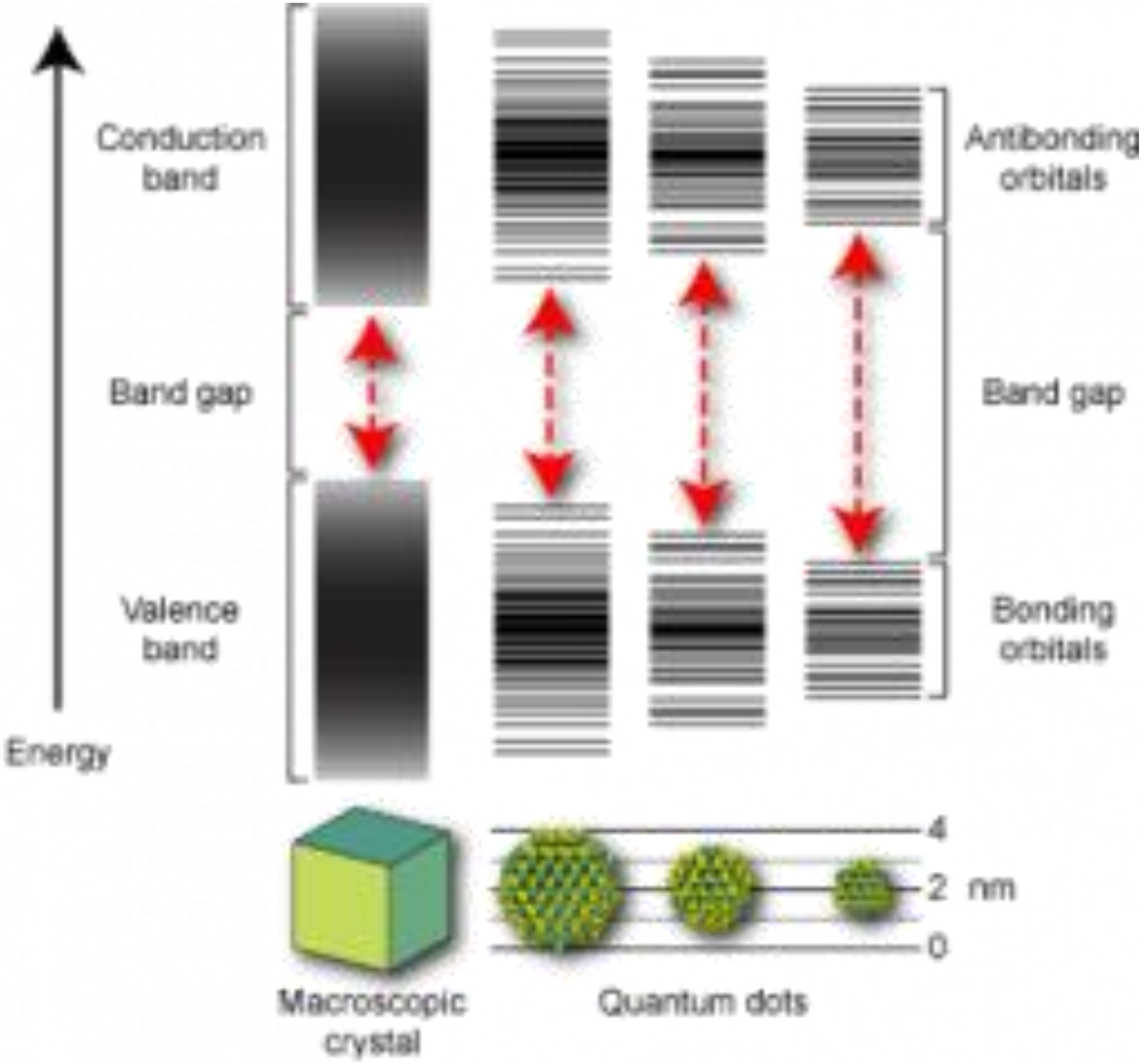


Figure 3: Quantum size effect in nanomaterials

Some surprising changes that may occur in nanomaterials are:

- Opaque substances can become transparent e.g., copper
- Inert material becomes catalyst e.g., platinum
- Stable material can turn combustible e.g., aluminum
- Solid turns to liquid at room temperature e.g., gold
- Insulators become conductors and conductors become insulators. e.g., CNT

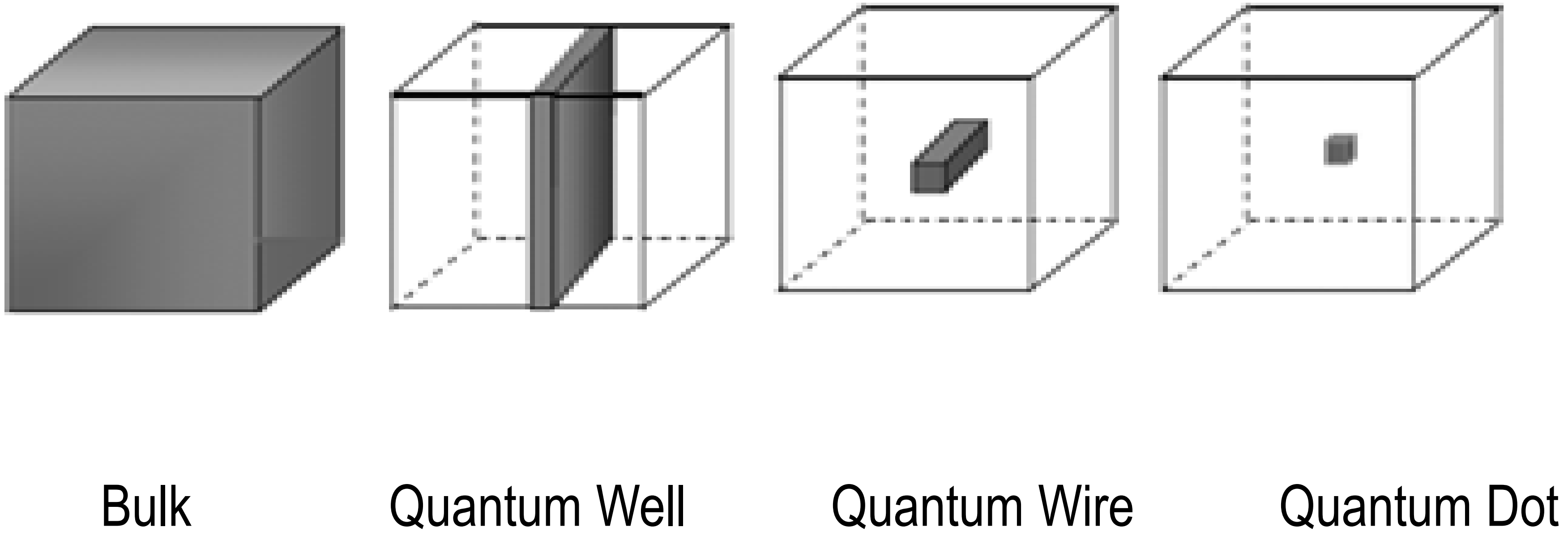
Progressive generation of rectangular Nanostructures:

- **Quantum Well**: If one dimension of the material is reduced to nano range while the other two dimensions remain large.

- **Quantum Wire:** If the two dimensions of the material are reduced to nano range while third remains large.

- **Quantum Dot**: If all the three dimensions are reduced to nano range.

Progressive generation of rectangular Nanostructures:



Properties of Nanomaterials:

- Only by varying the particle size of material, properties like melting point, solubility, colour and transparency change.

- With different surface properties of the nanoparticles, the properties like conductivity, catalytic behavior and optical properties change.

- With decrease in size and surface area, the no. of reactive sites increase which enhance their catalytic activity.

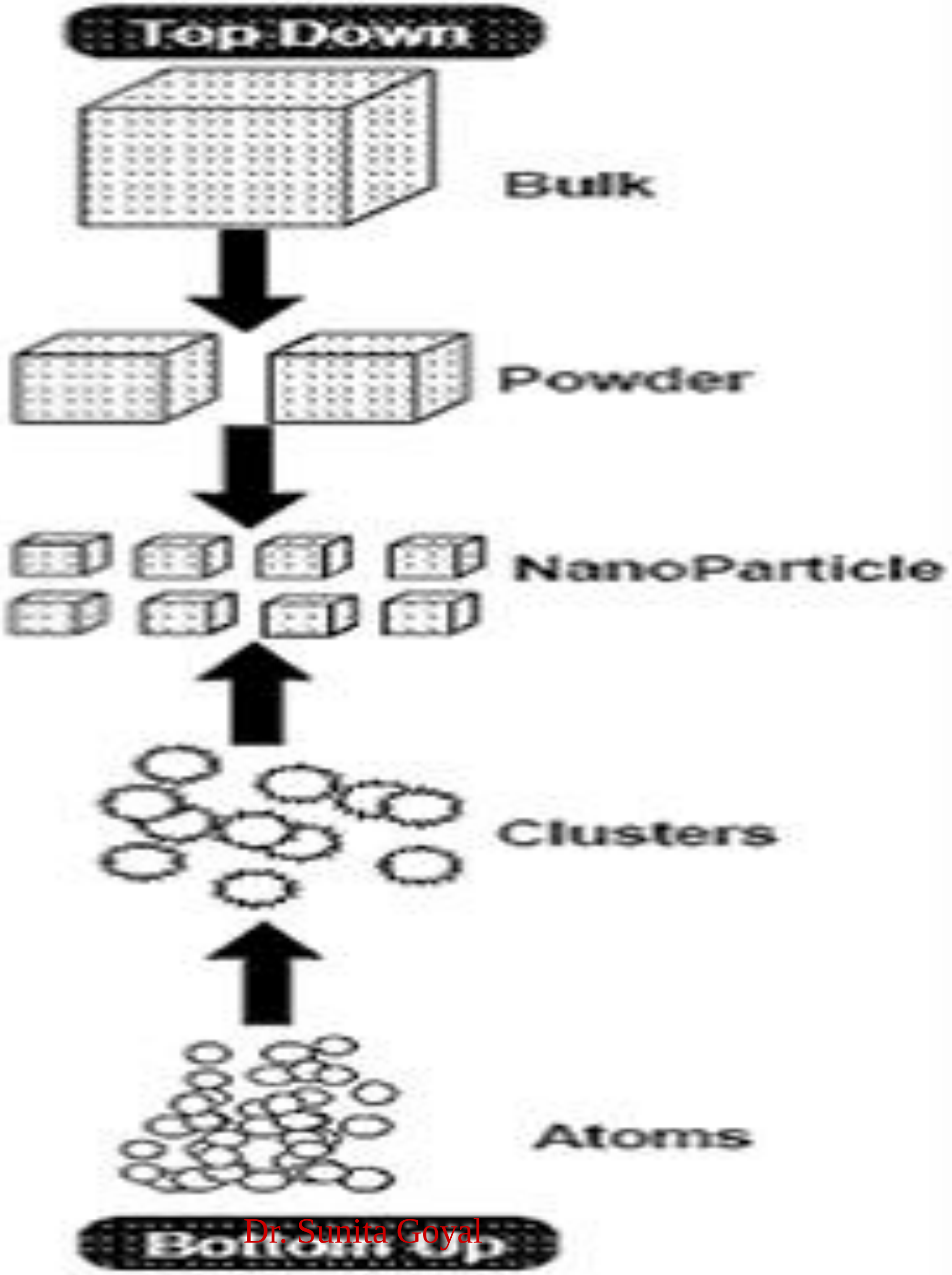
- A semiconductor, which shows conductivity at normal particle size level, becomes insulator due to increase in energy band gap by reducing the particle size.

- Due to the change in energy level separation, the colour of the material changes, as the colour of a material depends on the wavelength of light (photons) absorbed by it. For e.g., gold is golden in colour but it turns into pink or blue with decrease in size in nanorange.

Methods of Preparation of Nanomaterials:

- **Top-Down** Approach: In this approach we begin with a pattern generated on a large scale then reduced to nanoscale . It involves the production of very small structures from larger piece of material.

- **Bottom-Up Approach** : In this approach we begin with very small units . Single atoms and molecules are assembled into larger nanostructures.

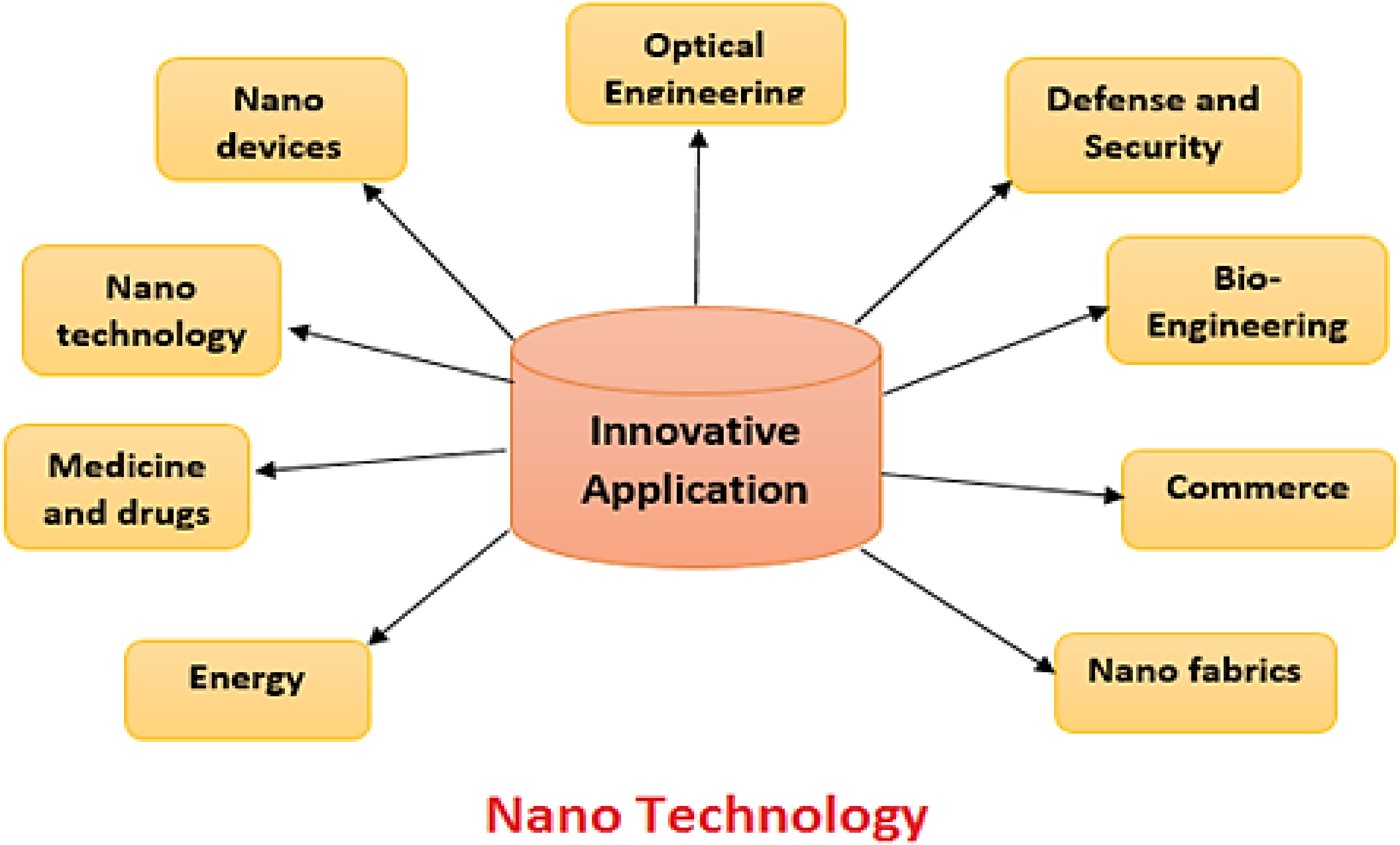

Top Down
Bulk
Powder
NanoParticle
Clusters
Atoms
Bottom Up

Example of Nanomaterials:

- **Carbon Nanotubes (CNT):** Sheets of graphenes are rolled up to make a tube of 0.4 nm in diameter.

- **Fullerenes:** These belong to a class of cage-like carbon compounds, composed of fused, pentagonal and hexagonal sp^2 hybridized carbon rings.

General applications of Nanomaterials:



General applications of Nanomaterials:

- **Nanosized TiO_2 and ZnO are used in sunscreens as they absorb UV rays.**
- **Silicate nano layer and nanotubes can be used as reinforced fillers to increases the mechanical properties of composites and impart new properties.**
- **Nano coatings improve properties like wear resistance, scratch resistance and hydrophobic properties of the materials.**

- **Used in fuel cells to improve their efficiency by catalytic processes.**

- **For the preparation of light weight and high energy density batteries.**

- **Used for large amount of data storage.**

- **Provide efficient water purification techniques.**

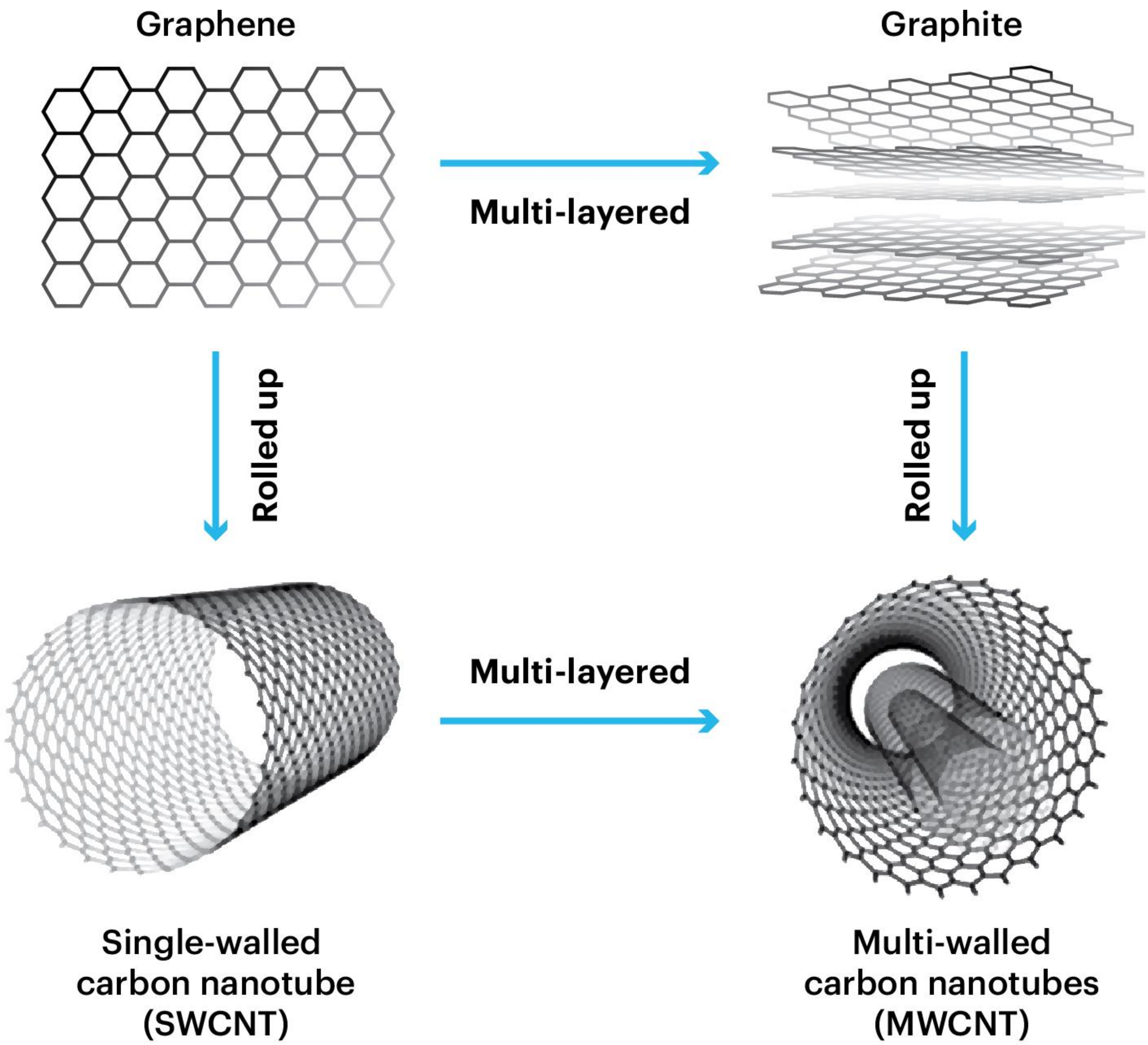
Carbon Nanotube

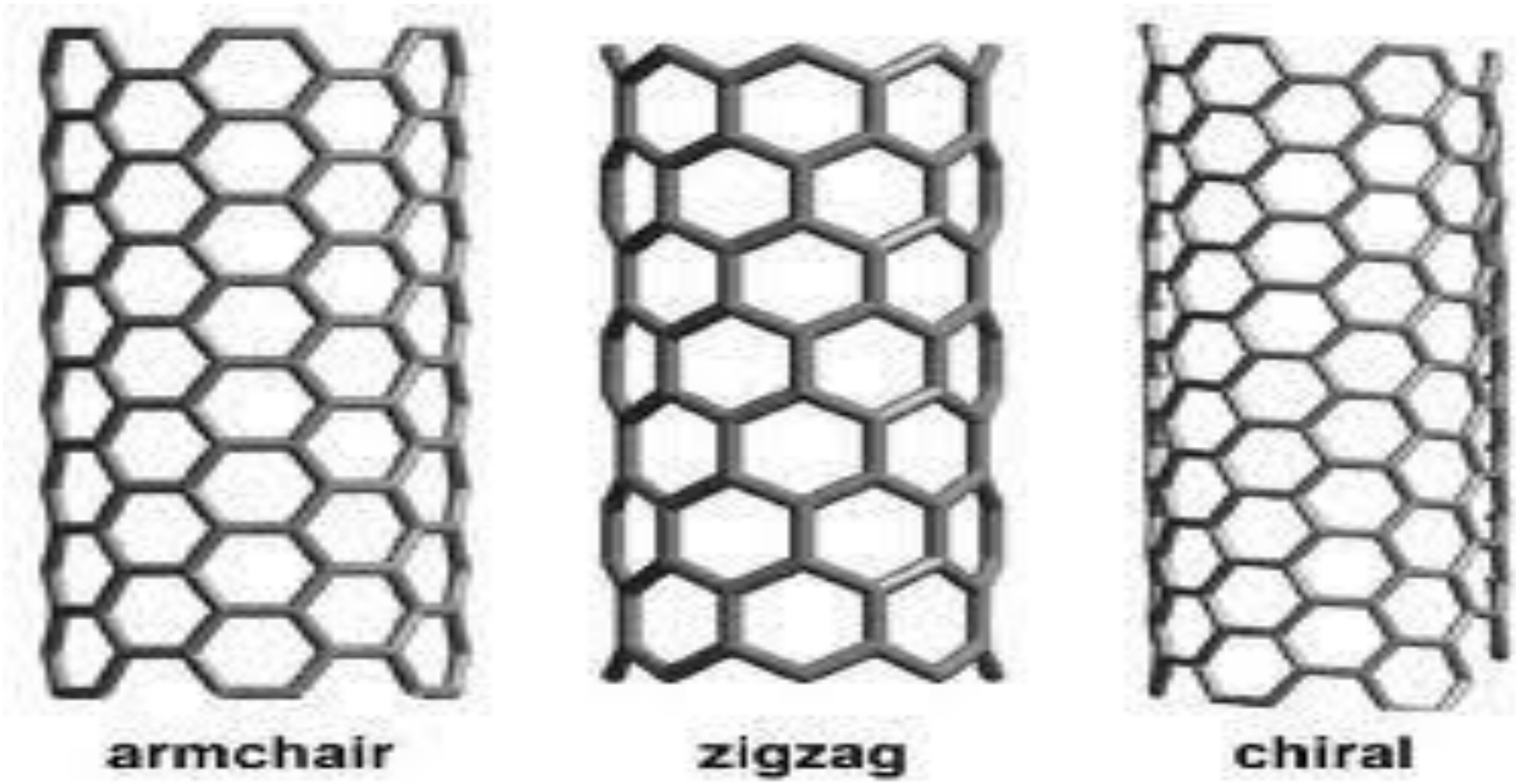
- **A carbon nanotube is an allotrope of carbon that resembles a tube of carbon atoms. Their appearance is like rolled tubes of graphite with diameter as small as 1nm and length few nm to microns.**
- **These cylindrical carbon molecules have unusual properties which are valuable for nanotechnology, electronics, optics and other fields of material science and technology.**
- **Buckytube is another name for carbon nanotubes.**
- **A carbon nanotube is a tube shaped material, made of carbon, having a diameter measuring on the nanometer scale.**
- **"Carbon nanotube" was discovered in 1991 by Japanese researcher Sumio Iijima.**

Types of Nanotubes:

(i) Single Walled Carbon Nanotube (SWNT) : The Single-walled Carbon nanotubes exist in a 1-d structure. Some examples of Single-walled CNT are armchair and zig-zag single-walled carbon nanotubes

(ii) Multi Walled Carbon Nanotube (MWNT): It is composed of several nested carbon nanotubes. In this MWNT multiple graphene layers fused into one another. This type of nanotubes has two diameters, one is known as outer diameter and another one is known as inner diameter. An example of Multi-walled Carbon nanotubes is chiral Multi-walled Carbon nanotubes.


Graphene
Graphite
Multi-layered
Rolled up
Rolled up
Multi-layered
Single-walled
carbon nanotube
(SWCNT)
Multi-walled
carbon nanotubes
(MWCNT)


armchair
zigzag
chiral

Properties of Carbon Nanotube

- Carbon nanotubes are ten times stronger than steel.
- The gravitational weight of the nanotube is very low.
- The density of the carbon nanotubes is one-fourth of that of steel.
- They exhibit extraordinary mechanical properties.
- Carbon nanotubes have a high thermal capacity. Therefore, it does not expand on heating like that of steel. Therefore carbon nanotubes uses in making bridges and aircrafts material.

Properties of Carbon Nanotube

- In carbon nanotubes, each carbon atom is surrounded by three other carbon atoms through covalent bonds.
- The crystalline structure of carbon nanotubes exists in the form of regular hexagons.
- Carbon nanotubes are elastic.
- Carbon nanotubes are good conductors of heat and electricity.
- Carbon nanotubes are chemically neutral. So, they are chemically stable. Therefore, carbon nanotubes resist corrosion.

Applications of Carbon Nanotubes

1. Cancer tumor destruction:

Nanotubes are used to destroy cancer tumors. They work with an antibody. The antibody along with nanotubes is attracted to the proteins by cancer cells in the body and nanotubes absorb the laser beam killing the bacteria of the tumor.

2. Windmill blades:

Nanotubes are also used in the windmill blades because of their low weight . It increases the efficiency of the windmill and helps to produce more electricity at a faster rate.

3. Filtration:

Carbon nanotubes can be used to separate particles of size greater than the diameter of carbon nanotubes during filtration through them. They can also be used to trap smaller sized ions from a solution.

4. Carbon nanotubes as Nano cylinders:

Gas like H_2, for energy (battery for vehicles) can be safely stored inside the carbon nanotubes and the problem of H_2 storage hazards can be solved.

5. Aircraft stress reduction:

Nanotubes are also used in space and aircraft to reduce the weight and stress of the various components working together.

6. They are also used in drug delivery systems.

7. Nanotubes have led to a new generation of electronic devices. Their use as ultra-sensitive electromechanical sensors.

Green Chemistry

- **Green chemistry is also known as sustainable chemistry.**
- **It is design, development, and implementation of chemical products and process to reduce or eliminate the use and generation of substances hazardous to human health and the environment.**

Example- Production of biodiesel.

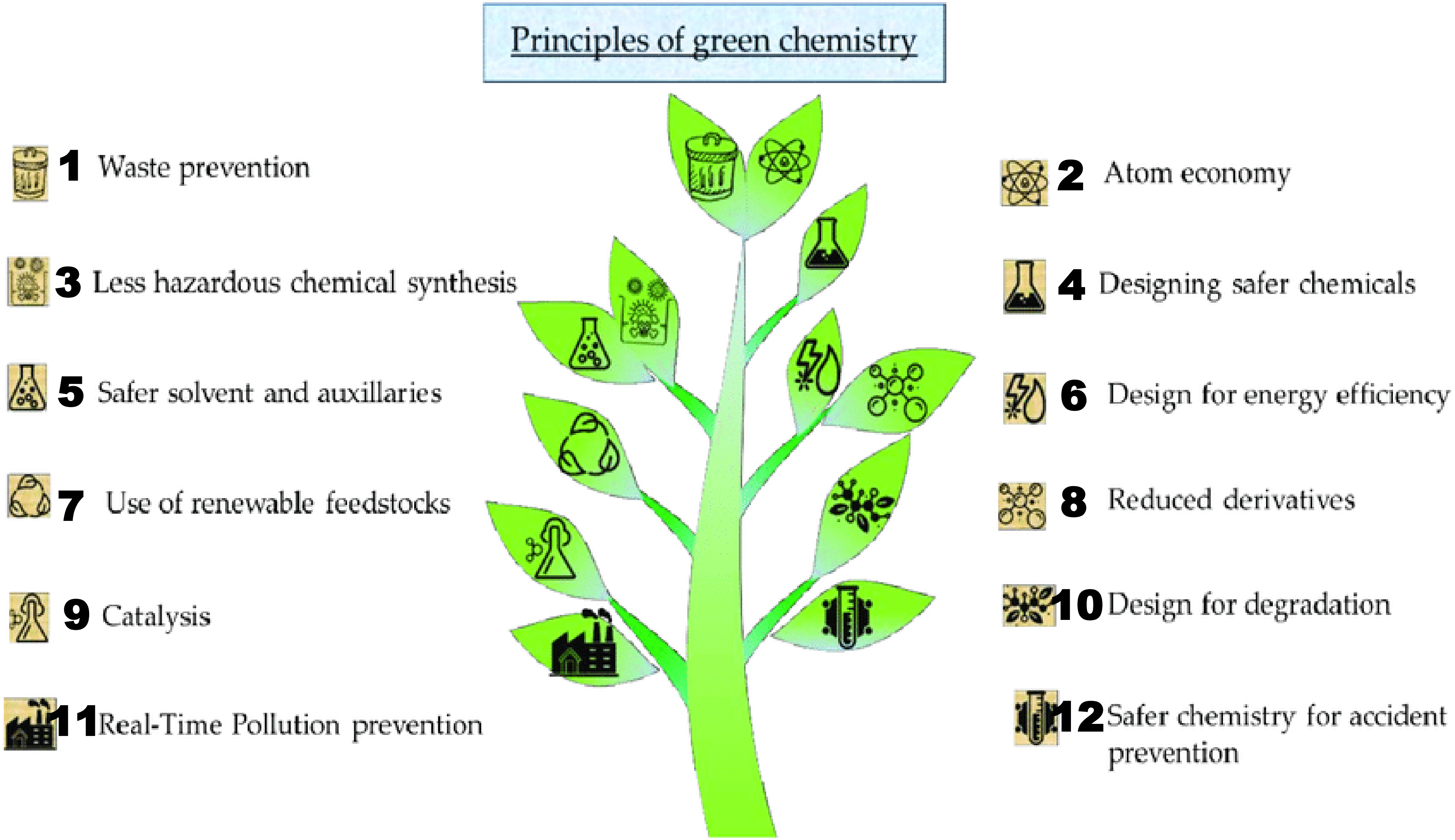
- **As fossil fuels are exhaustible and combustion of fuels causes air pollution therefore biodiesels are produced from plant oil / vegetable oil like soyabean , sunflower, palm oil .**

$$\textbf{Triglycerides + methanol} \xrightarrow{\textbf{Base}} \textbf{glycerol + ester}$$

$$
\begin{array}{lcccc}
CH_2OOCR_1 & & & R_1COOH_3 & CH_2OH \\
| & & & & | \\
CHOOCR_2 & + \; 3CH_3OH & \xrightarrow{KOH} & R_2COOH_3 \quad + & CHOH \\
| & & & & | \\
CH_2OOCR_3 & & & R_3COOH_3 & CH_2OH \\
\text{Triglyceride} & \text{Methanol} & & \text{Methyl Ester} & \text{Glycerol}
\end{array}
$$

12 Principles of Green Chemistry

12 Principles of Green Chemistry



12 Principles of Green Chemistry

1. **Waste prevention:** Design chemical synthesis of prevent generation of waste. (ZWT)
2. **Maximize atom economy:** Design synthesis so that the final product contains the maximum proportion of the starting material.

% Atom Economy = (Formula Wt. of Desired Product/ Formula Wt. of Reactant) x 100

1. **Design less hazardous chemical synthesis:** Design synthesis to use & generate substances with little or no toxicity to either humans or the environment. E.g. DDT (insecticide)-hazardous to human beings
2. Lindane (gamma isomer of BHC, insecticide)-not hazardous

4. Design safer Chemicals & products: Design chemical products that are fully effective yet have little or no toxicity OR which require less toxic route materials.

e.g. Preparation of Adipic Acid from benzene (carcinogenic)- not safe process/from glucose (enzymatically synthesized) - safe process

5. Use safer solvents & reaction conditions: Avoid using harmful solvents, separating agents. If you must use these chemicals, use them in minimum amount.

CH_2Cl_2, $CHCl_3$, CCl4 –not safer while water, supercritical CO_2- safer solvents

6. Increase energy efficiency: Run chemical reactions at room temperature and pressure whenever possible. E.g. use biocatalyst at ambient condition, use of microwave, use of refluxing conditions

7. Use renewable feed stocks: Use starting materials that are renewable rather than depletable.

8. Avoid chemical derivatives: Derivatives use additional reagents & generate waste. Therefore avoid using blocking or protecting groups.

9. Use catalysts, not stoichiometric reagents: Catalysts are effective in small amounts & can carry out a single reaction many times and therefore minimized waste generation. Stoichiometric reagents are used in excess and carry out a reaction only once.

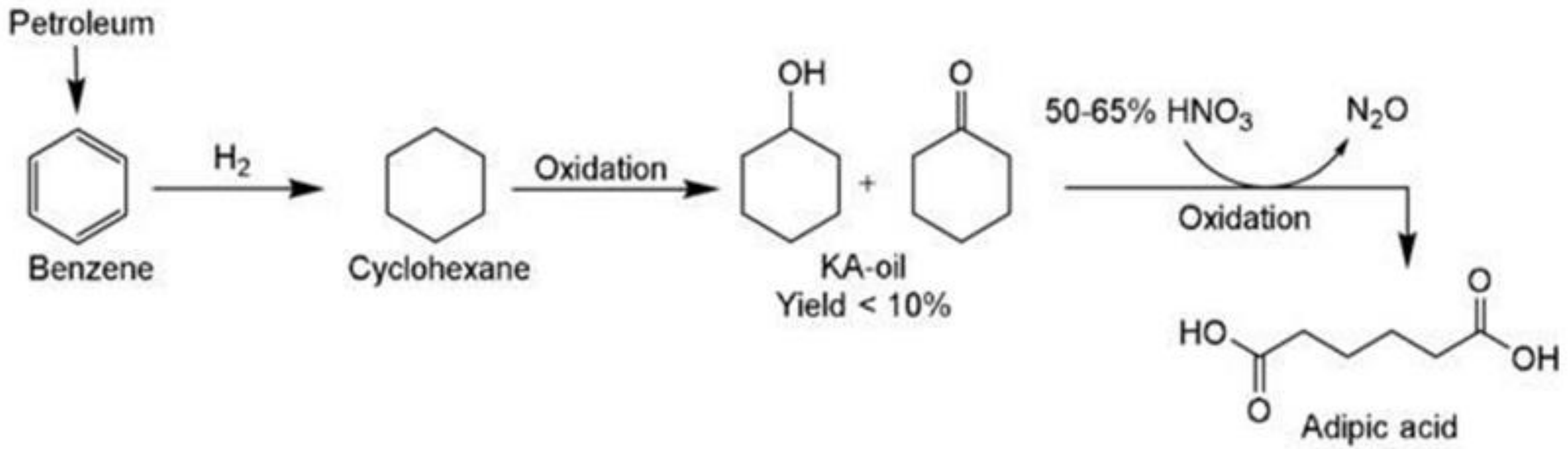
10. Design Chemicals & products to degrade after use: Design chemical products to break down to less harmful substances after use, so they do not accumulate in the environment.

11. Analyze in real time to prevent pollution: Real-time monitoring & control during synthesis minimizes & eliminates the formation of byproducts.

12. Minimize the potential for accidents: Design Chemicals to minimize the potential for Chemical accidents including explosions, fire releases to the environment.

Synthesis of Adipic acid- Conventional route:

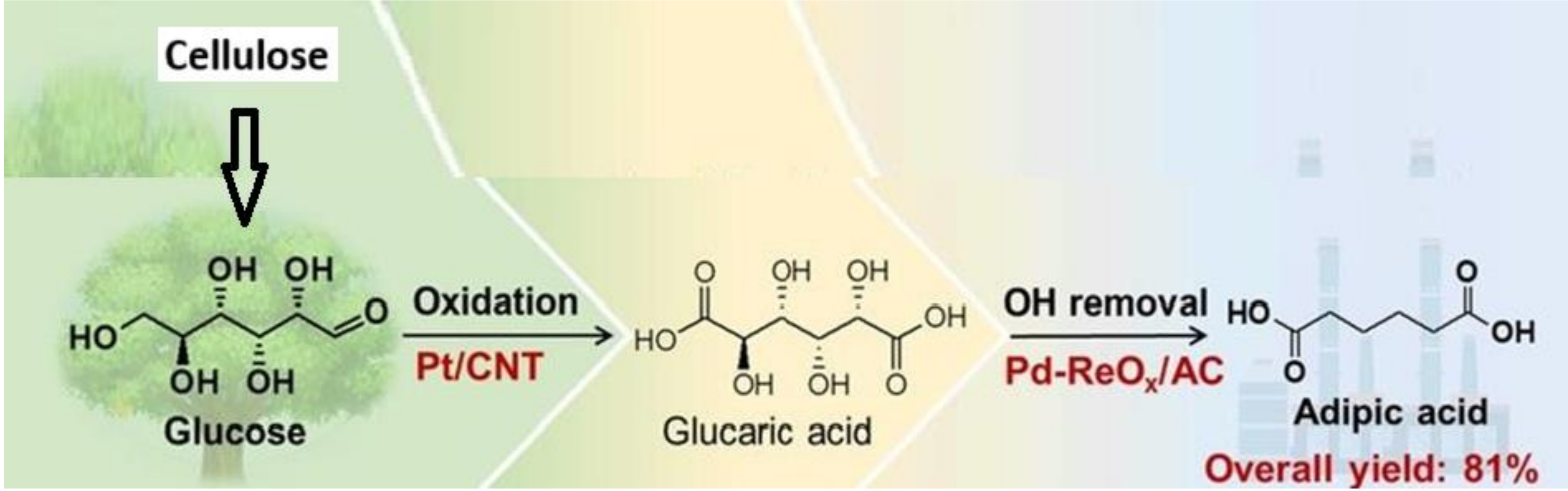
In conventional method adipic acid is prepared from benzene, which is extracted from Petroleum, a non-renewable Source. For oxidation, HNO3 is used, which releases N_2O and pollute air. Inhalation of N_2O causes breathing issues and throat etching.



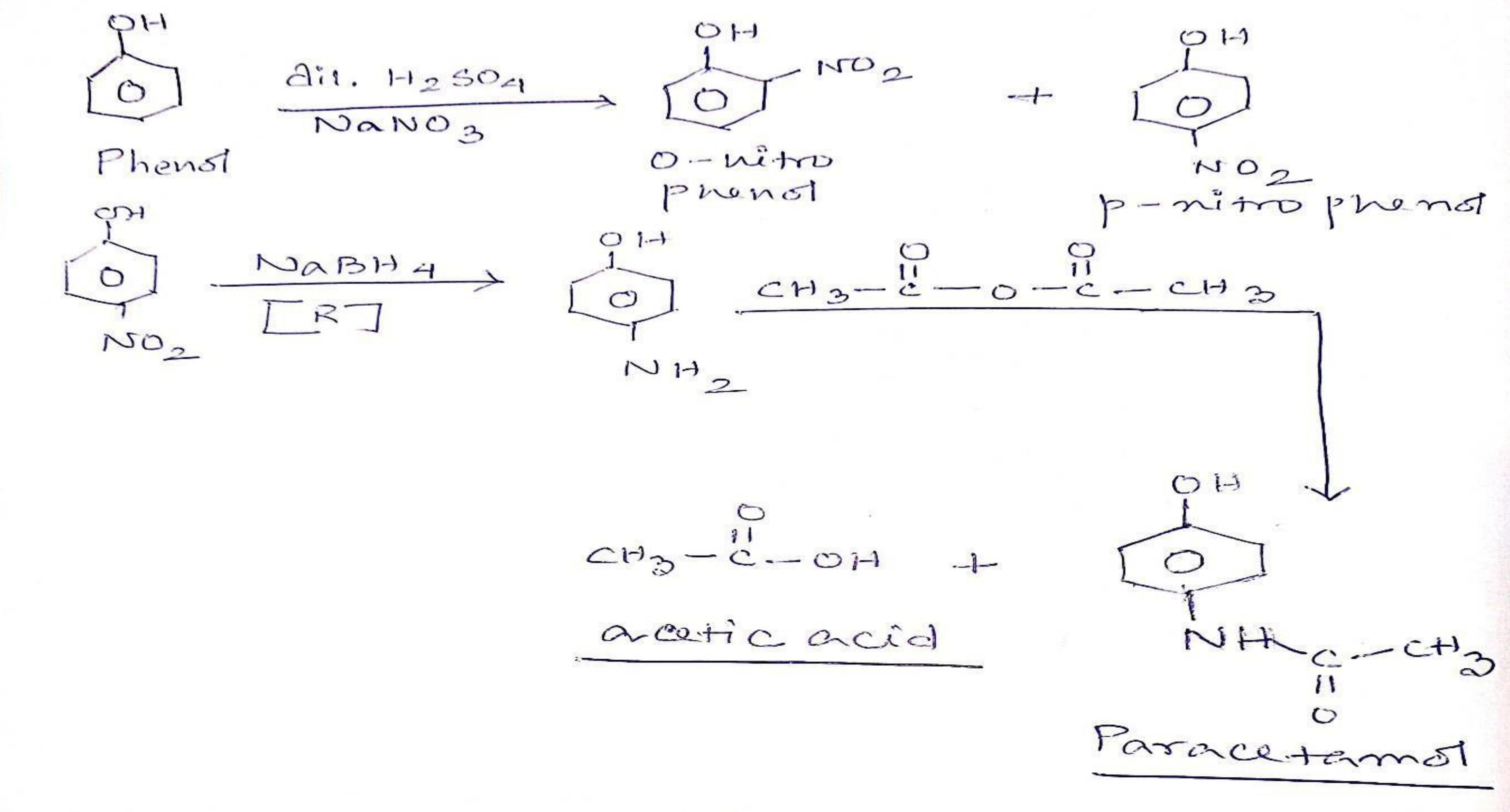
Synthesis of Adipic acid- Green route :

- **In this method, cellulose derived glucose converted into adipic acid via glucaric acid.**
- **CNT support Pt nanoparticles are efficiently oxide glucose to glucaric acid.**
- **Pd- Rhenium oxide composite effectively remove hydroxyl group.**

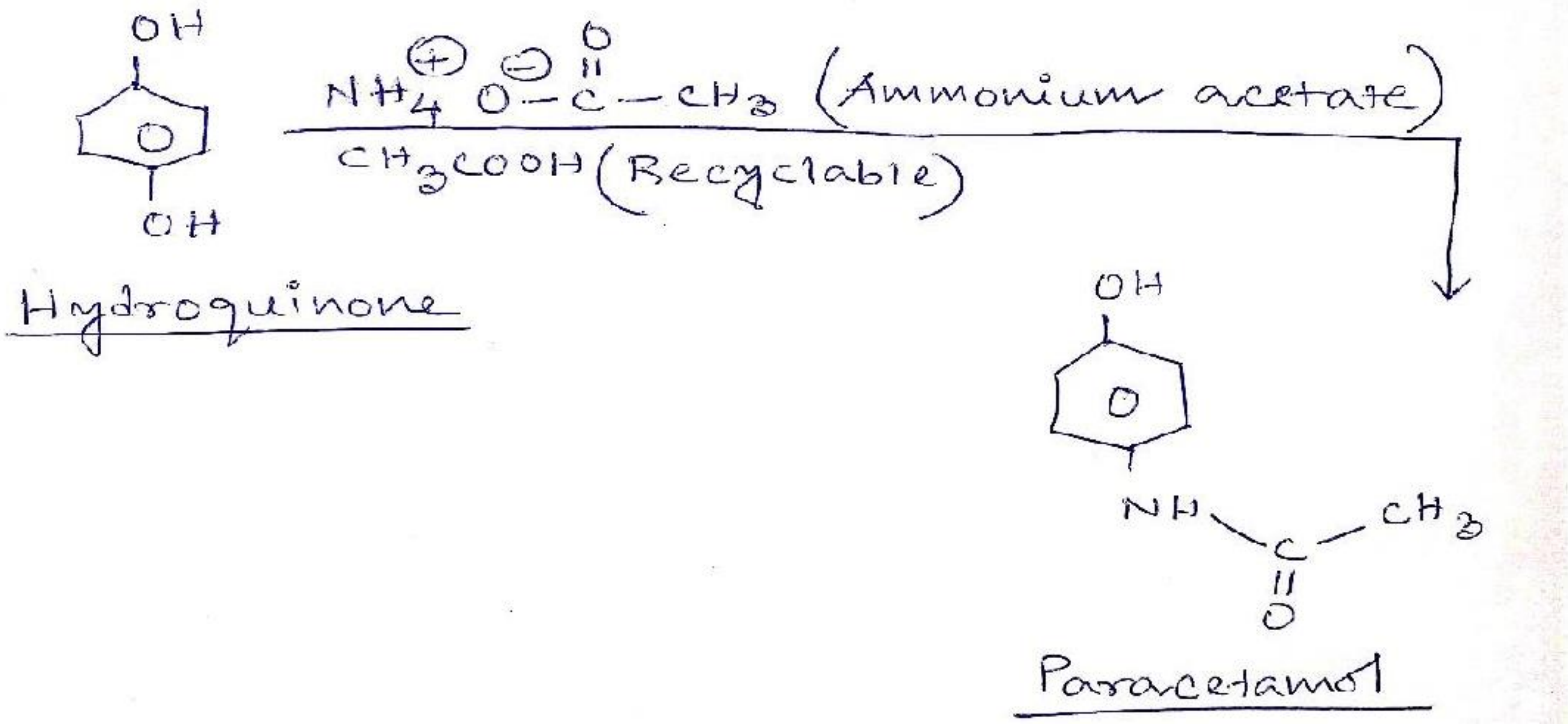
Synthesis of Adipic acid- Green route :



Synthesis of Paracetamol- Conventional route:



Synthesis of Paracetamol- Green route:



Acetic and other by-products are recyclable & re-usable. This method is metal-free, additive - free &, high has high yield (>95%) and high selectivity.

Environmental impact of green chemistry on society or benefits:

Environment:

1. **Green chemicals either degrade to harmless products or are recovered for further.**

2. **Plants and animals suffer less harm from toxic chemicals in the environment.**

3. **Lower chance for global warming, ozone depletion & smog formation.**

4. **Less chemical disruption of eco-systems.**

Environmental impact of green chemistry on society or benefits:

Human health:

1. **Higher yields for Chemical reactions, consuming smaller amounts of precursor to obtain the same amount of product.**

2. Fewer synthetic steps, faster manufacturing of products, increasing plant capacity saving energy & water

3. Reduced use of petroleum products, slowing their depletion.

Environmental impact of green chemistry on society or benefits:

Human health:

4. **Reduced generation of waste, eliminating costly disposals methods of the hazardous chemicals**
5. **Increased consumerism by displaying a safer products label.**

Assignment

Q1: What is Molecular orbital theory? Draw M.O. diagram of O_2 & NO molecule. Calculate bond order & explain its magnetic behavior. ***AKTU, Sem II 2017-18, 2021-22, 2022-23***

Q2: What are liquid crystals? Distinguish between Nematic and Smectic liquid crystal & applications of liquid crystals. ***AKTU, Sem I 2017-18, Sem I 2018-19,2019-20, 2022-23***

Q3: Describe the structure and applications of Graphite and Fullerenes. Explain the reasons for electrical and lubricating properties of Graphite. ***AKTU, Sem I 2019-20, 2021-22 , 2022-23***

Assignment

Q4: What are the Carbon Nano Tubes? Discuss the applications of nanomaterials. **AKTU, Sem II 2017-18, 2022-23**

Q5: Write down the 12 principles of green Chemistry. Explain the Synthesis of Adipic acid & Paracetamol from conventional method as well as green route.

Dr. A.P. J. K. TECHNICAL UNIVERSITY, LUCKNOW(UP) B.Tech. (SEM.I) THEORY EXAMINATION, 2022-23 ENGINEERING CHEMISTRY(BAS102)

Paper ID: 22014   Max.Marks:70

SECTION A

1. **Attempt *all* questions in brief.   2 x 7 = 14**

(a)On the basis of MO theory calculate the bond order of NO. Will NO be paramagnetic or diamagnetic?

(b)What are Chiral Drugs? Give examples of Chiral Drugs.

(c)Give important applications of electrochemical series.

THANK YOU

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