UNIT - III ENGG. MATERIALS

End - Sem Exam = 18 Marks

* Question Paper Pattern :-

Unit - III (Engg. Materials)

Speciality Polymers — 9 Marks

Nanomaterials — 9 Marks

Only Theory Questions

Que. 1 (a) — 7 M (Speciality Polymers)

(b) — 6 M (Give Reasons)

1 Que. ↳ 2 Marks (Speciality Polymers)

2 Que. ↳ 4 Marks (Nanomaterials)

(c) — 5 M (Nanomaterials)

OR

Que. 2 (a) — 7 M (Nanomaterials)

(b) — 6 M (Give Reasons)

1 Que ↳ 2 Marks (Nanomaterials)

2 Que. ↳ 4 Marks (Sp. Polymers)

(c) — 5 M (Sp. Polymers)

* Reference book for Unit - III :-

(i) Engg. chem. by O. G. Palana

(ii) Polymer Science by V. R. Gowarikar

(iii)

* Course Objectives :-

To understand structure, properties & applications of speciality polymers & nanomaterials.

Index / Mind Map of Unit-III :-

[A] Speciality Polymers →

1) Engg. Thermoplastic
2) Biodegradable Polymers
3) Conducting Polymers
4) Electroluminiscent Poly.
5) Polymer Composites

} Def^n, Adv., Applications, Examples. One Detailed example - structure, Properties, Applications

[B] Nano-materials -

- Size
- Imp. Applications of nano-materials
- Classifica^n
- Imp. Properties
- Quantum Dots -
  - Def^n, Types, Properties, Applications.
- Graphene
- CNTs

* Prerequist -

→ Polymers - Def^n, Types, Examples, properties, Classif^n, Applications.

→ Nanomaterials -

- Def^n, Examples, Difference bet^n Macro &, Micro & Nano-materials, with examples. Analogies.

Engineering Thermoplastics :→

What are engg. thermoplastics?

These are high polymer resins that have better mechanical &/or thermal properties as compared to commodity plastics such as PVC, polystyrene, polyethylene, etc.

Advantages of Engg. Thermoplastics :

i) High Thermal stability.
ii) High Tensile strength
iii) High mechanical strength
iv) High impact strength
v) Light weight

Applications of Engg. Thermoplastics :

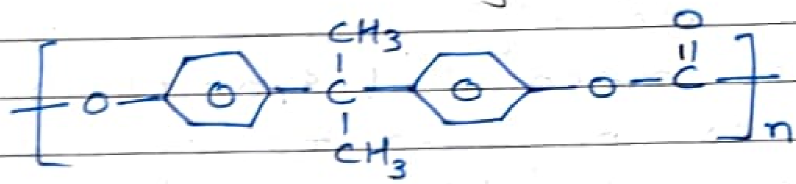
i) In automotive & aerospace
ii) In telecommunications, textiles,
iii) In computer components, satellite robots, etc.

Examples of Engg. Thermoplastics :

Polycarbonate, Polysulfones, Teflon, Acrylonitrile - Butadiene - Styrene (ABS) resin, etc.

Engineering Thermoplastic – Polycarbonate:
It consists of functional group –O–C(=O)–O–; Commonly known as 'Lexan or Merlon'.

Structure of Polycarbonate (PC) →



Properties :
i) High impact strength.
ii) Highly transparent plastic.
iii) Resistant to water & many organic compounds.
iv) Good heat resistance (useful upto 140°C)
v) High melting point (265°C).

Applications :
i) Electrical & electronic components (sockets, switches)
ii) Data storage – CD, DVDs.
iii) Optical applications – scuba googles, safety goggles, sunglasses, golf carts, etc.
iv) Construction material
v) Security components
vi) Hair drier bodies, camera, binacular bodies, toys, cooking utensil covers, etc.

Biodegradable Polymers –

These are the polymers which break down (decomposes) by bacteria, enzymes or fungi to result in natural byprducts such as harmless gases, water, inorganic salts, etc.

Need of biodegradable polymers –

Degradation of natural & synthetic polymers is done by thermal, mechanical or chemical processes which gives harmful products, environment pollution i.e. disposal of polymer waste has become a major issue. Hence, there is a very high need of biodegradation of polymers which reduce need of synthetic, non-biodegradable polymers, there by reducing its disposal problem & pollution.

Factors responsible for biodegradation of ~~polymer~~ polymers –

i) Microorganisms
ii) Environment
iii) Nature of polymer

Features of biodegradable polymers –

i) Amorphous polymers are more susceptible for biodegradation compared to crystalline polymers.
ii) Hydrophilic polymers are more suitable for biodegradation than hydrophobic.

iii) Generally, low mole. wt polymers undergo biodegradation to high mole. wt. polymers.

Classification of biodegradable polymers :

- → Natural eg. Cellulose, cotton, starch, protein, etc
- → Biosynthetic eg: PHBV (Poly hydroxy butyrate valarate)
- → Synthetic eg. Polyprolactone, Polylactic acid.

Applications of biodegradable polymers -

i) As packing material - disposable food service.

ii) Medical applications - controlled drug delivery, surgical implants & sutures

iii) Agricultural Applications - mulching, netting, twine, etc.

Limitations -

i) High cost.

ii) Specific conditions are reqd to decompose

iii) Manufacturing requires more energy.

Biodegradable Polymers -

- Polyhydroxybutyrate (PHB) -

$$\left[O - \overset{CH_3}{\overset{|}{CH}} - CH_2 - \overset{O}{\overset{\|}{C}} \right]_n$$

Properties of PHB -

It is brittle, water soluble, highly crystalline, non-toxic, high MP = 200°C, rapidly biodegradable.

- Polyhydroxyvalarate (PHV) -

$$\left[O - \overset{CH_2CH_3}{\overset{|}{CH}} - CH_2 - \overset{O}{\overset{\|}{C}} \right]_n$$

- PHBV - Polyhydroxy Butyrate - hydroxy Valarate (Biopol)

$$\left[O - \overset{CH_3}{\overset{|}{CH}} - CH_2 - \overset{O}{\overset{\|}{C}} - O - \overset{CH_2CH_3}{\overset{|}{CH}} - CH_2 - \overset{O}{\overset{\|}{C}} \right]_n$$

Biopol is the copolymer of 3-hydroxy butyric acid & 3-hydroxy valeric acid.

Preparation of Biopol -

$$\text{Glucose} \xrightarrow[\text{eutrophus}]{\text{acaligenes}} \begin{array}{c} \text{3-hydroxy butyric } \bar{a} \\ + \\ \text{3-hydroxy valeric } \bar{a} \end{array} \xrightarrow{\text{Polymerisn}} \begin{array}{c} \text{PHBV} \\ \text{(biopol)} \end{array}$$

Properties -

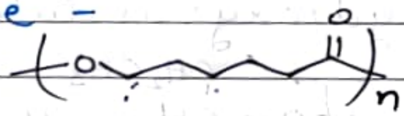
- Highly crystalline
- Flexible, good resistant to oil.
- Moisture resistant & impermeable.

Applications of PHBV →

i) In medical & veterinary applications (controlled drug delivery).
ii) In packaging - lamination, thin films, etc.
iii) In agriculture - fertilizers for plants.
iv) Useful for surgical, organ transplant.
v) Useful for ~~p~~ disposable personal hygiene.

Some other biodegradable polymers -

Polycaprolactone -



Polyglycolic acid -

$$H\left[O-CH_2-\underset{\underset{O}{\|}}{C}\right]_n OH$$

Polylactic acid -

$$H\left[O-\underset{H}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}-CH_2-\underset{\underset{O}{\|}}{C}\right]_n OH$$

Conducting Polymers -

Def^n - The polymers which conduct electricity due to delocalization of π electrons.

Types of Conducting Polymers -

A] Intrinsically B] Extrinsically C] Doping

A] Intrinsically Conducting Polymers →

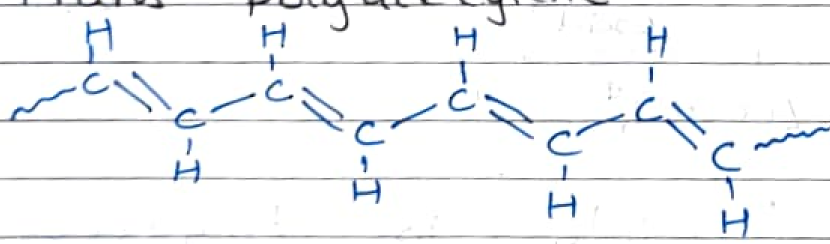
which conduct electricity of their own because of their structural features. i.e. through conjuga^n or delocalised $\bar{e}$ pair.

Structural Requirement -

- Linear, highly planar & possess conjug^n in the polymer chain.

e.g.

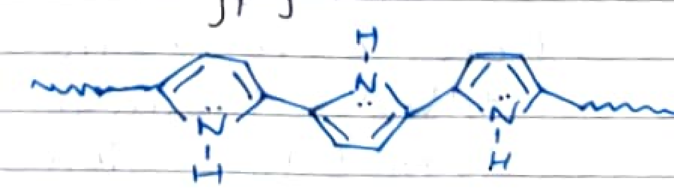
Trans - polyacetylene



Polyaniline

Polyparaphenylene -

Polypyrrole -



Polythiophene -

B] Doped Conducting Polymers –

Conductivity of intrinsically conducting polymers can be improved by creating +ve or –ve charge by doping on polymer chain.

Two types

P-Doping
- with Lewis acid
- Oxidation
- Removal of $\bar{e}$s
- +ve charge develops
- I_2, Br_2, $FeCl_3$, PF_6, AsF_5 → p-dopants

N-Doping
- with Lewis base
- Reduction
- Add^n of $\bar{e}$s
- –ve charge develops
- Li, Na metals; naphthyl amines – → n-dopants

$$(C_2H_2)_n + 2FeCl_3 \xrightarrow{Oxid^n} (C_2H_2)_n^+ + FeCl_4^- + FeCl_2$$

$$(C_2H_2)_n + Na \xrightarrow{Red^n} (C_2H_2)_n^{\ominus} Na^{\oplus}$$

$$2(C_2H_2)_n + 3I_2 \xrightarrow{Oxid^n} 2[(C_2H_2)_n^{\oplus} I_3^{\ominus}]$$

where $(C_2H_2)_n$ is Polyacetylene.

C] Extrinsically Conducting Polymers –

which conduct electricity when externally added ingredient in them.

Conductive element filled Polymer
e.g. metallic fibres, metal oxides, carbon black.

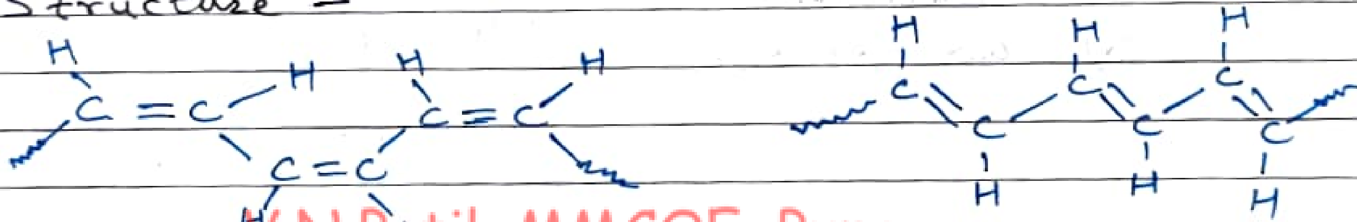
Blended conducting polymer
blending with conventional polymer physically or chemically

Applications of conducting polymers –

i) In solar cells.
ii) In optical display devices
iii) In molecular switches
iv) In electronic devices such as transistors, photodiodes & Ligh emitting diodes (LED).
v) In rechargable battery.

Conducting Polymer – Polyacetylene.

Structure –



Cis-polyacetylene Trans-polyacetylene.

Preparation of Polyacetylene –

$$n\ HC \equiv CH \xrightarrow{\text{Zeigler Natta catalyst}} \left(CH = CH \right)_n$$

Zeigler Natta catalyst $\rightarrow Ti(OPr)_4\ Al(C_2H_5)_3$

$$\text{Cis-polyacetylene} \xrightarrow{\text{Heating}} \text{trans-polyacetylene}$$

Doping of Polyacetylene –

P-type
includes Br_2, I_2, Cl_2, etc.
Oxid^n

$$2(C_2H_2)_n + 3\ I_2 \longrightarrow 2\left[(C_2H_2)_n^{\oplus}\ I_3^{\ominus}\right]$$

N-type
includes Na, K
Reduction

$$(C_2H_2)_n + Na \longrightarrow (C_2H_2)_n^{\ominus}\ Na^{\oplus}$$

Properties of Polyacetylene -

- high density of 0.4 g/cm^3
- cis → flexible, coppery &
  trans → brittle, silvery
- insoluble in solvents

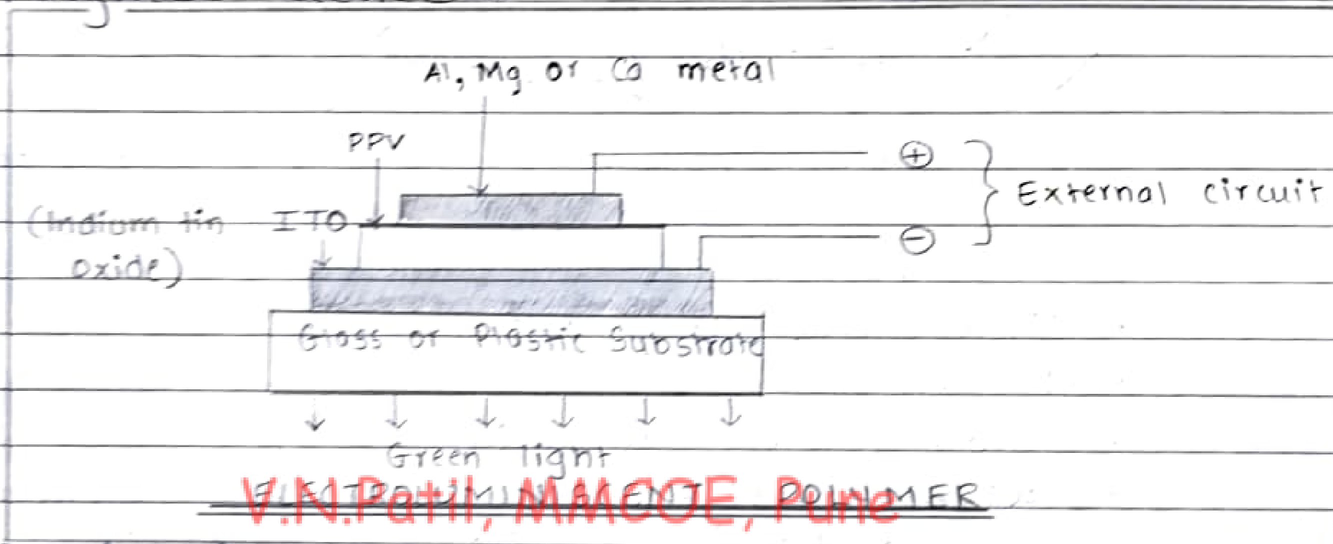
Applications of Polyacetylene -

i) In molecular switches
ii) Electric wiring
iii) electrode material in recharg able batteries
iv) as sensor

Electroluminiscent Polymers -

These are the polymers which emit light in presence of strong electric field.

Construction & Working of Electroluminiscent Polymer device -



Construction - It consists of transparent anode, hole transparent layer, emitter layer of polymer & a cathode Al, Mg alloy or Ca metal, stacked upon a glass or plastic support.

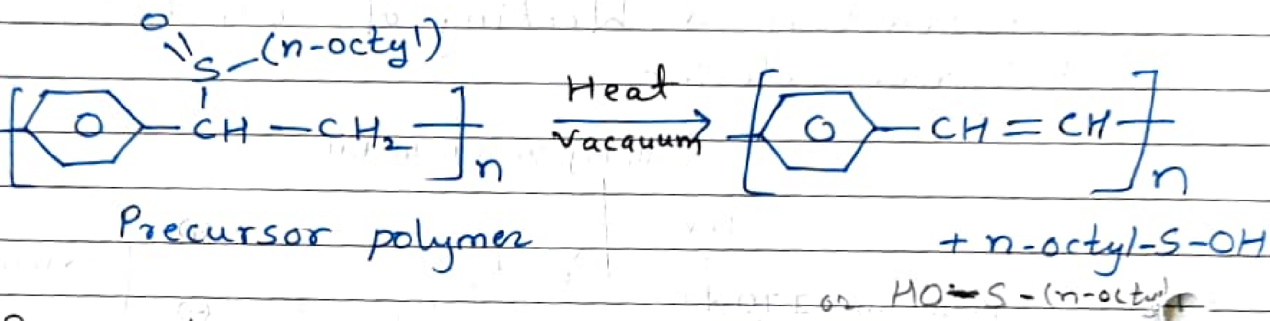
Working - Electrons & holes are injected from cathode & anode respectively into polymer. These ē & holes recombine in the polymer emitter layer, to excite luminiscence (emission of light), during returning to ground state.

Commonly used anode - ITO (Indium Tin Oxide).

Applications of ELP → TV screens, mobile display, LED devices.

Example of Electroluminescent Polymers –
PPV (Polyphenylene Vinylene) →

Structure –



Properties –

- Insoluble in water
- Pure & high mole. wt.
- Diamagnetic material
- Gives bright Yellow – Green fluorescence
- Low intrinsic electrical conductivity which increases upon doping.

Applications –

- Used in Organic Light Emitting Diode (OLED).
- In organic solar cells, sensors, etc.
- In photovoltaic cells
- Flat panel displays
- Theatre, hall decorⁿ
- Electroluminiscent Night lamps.

B] Nanomaterials :→

$1\ nm = 10^{-9}\ mtrs.$

Importance / Applications of Nanomaterials:

i) Nanophase Ceramics are more ductile at elevated temp. & can be used in macroscopic semiconductor process.

ii) Nanostructured Semiconductors has special optical properties.
eg. Luminiscence in Si powder. Hence, used in IR optoelectronic devices.

iii) Nanosized metallic powder used in production of gas tight material, dense parts & porous coatings. Cold welding property is used in Metal-Metal bonding used in electronic instruments.

iv) Magnetic nanocomposites are used for ferro fluids (Mechanical force transfer), magnetic refrigeration.

v) Nano ZnO is superior UV blocking material used in sunscreen lotions.

vi) Nano metal clusters - in catalytic applications based on their activity, selectivity, electro catalysis.

vii) Nanostructured MnO_2 - for rechargable batteries of cars.

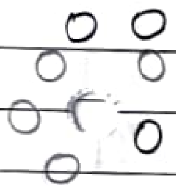
viii) Nano silicon films - in solar cells, due to their higher transparancy.

ix) Nano TiO_2 - in dye sensitized solar cells.

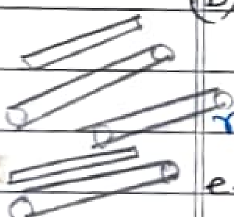
Classification of nanomaterial based on Dimensions :-

Zero-D   One-D   Two-D   Three-D

No dimensions are larger than 100 nm.

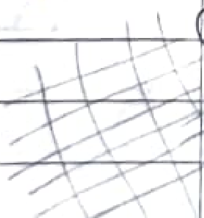


(a) Zero-Dimensional → all dimensions are measured within nano-scale range.
e.g. Quantum dots, hollow spheres like fullerene
Use – LEDs, solar cells, lasers, etc.

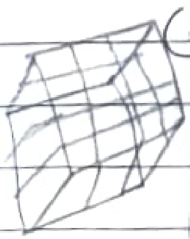


(b) One-Dimensional → Two of the three dimensions are measured within nano scale range.

e.g. Nanorods, nanotubes (~~CNN~~ ~~CNTs~~), nanoribbons nanobelts, etc.
Use – Fabrication of electronic, optoelectronic & EEDs (Electronic emission diodes), etc.



(c) Two-Dimensional → Only one out of three dimensions are measured within nanoscale range.
e.g. CNTs, nanoplates, nanoprisms, nanodiscs, etc.
Use – sensors, display devices, etc.



(d) Three-Dimensional → All three dimensions are not measured within nanoscale range.
e.g. (~~bl~~ (bulk nanomaterials)
e.g. bundles of nanowires, nanocoils, nanopillars, etc.
Use → in electronic circuits, drug delivery system, etc.

Important properties of nanomaterials →

a) Optical Properties -
It depends upon size, shape, surface characteristics, interaction with the surrounding environment.
Used in optical detector, laser, sensor, display, solar cells, biomedicine, etc.

b) Electrical Properties -
These are different from their bulk materials. As the diameter of nanomaterials decreases, electrical conductivity increases.

c) Mechanical Properties -
It is influenced by porosity, grain size & filler used.
e.g. Polymers filled with nanoparticles increases their mech. properties.

d) Magnetic Properties -
~~eg.~~ It can be increased by capping bulk material with nanoparticles.
e.g. Pd, Pt (original non-magnetic), but its ferromagnetism is acquired by capping.

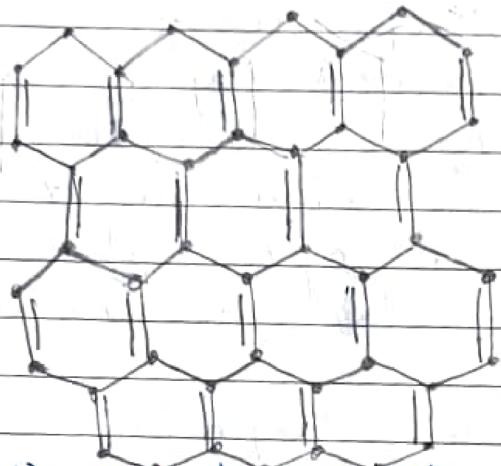
Carbon based Nanomaterials -
Graphene -
Structure - i) It is two dimensional crystalline material. ~~2-Dimensional structure~~
ii) It possess sp^2 hybridisation
iii) It is a single layer of carbon packed in hexagonal (honey-comb) lattice structure

iv) C-C bond length 0.142 nm.
v) Dist. betn 2 layers is 3.4 A°.

Page: 3-18
Date: / /

Diagram :-

sp² hybridization



2-D Structure

C-C bond length 0.142 nm

honycomb lattice

Properties :→ i) 200 times stronger than steel.
ii) Good conductor of heat & electricity.
iii) High stiffness & toughness.
iv) It shows a large & non-linear dimagnetism.

Preparation :-
i) It is produced by abrasion of pencil drawing.
ii) Flakes of graphene are obtained by exfoliation technique using adhesive.
iii) Impure graphene is obtained by heating Na metal with ethanol for 3 days.

Applications :-
i) As energy storage material
ii) As filtration material
iii) As sensor for gas detection.
iv) In catalysis for fuel cells.
v) In making polymer composites.
vi) In smart phones, LEDs, solar panels (due to transparent & flexible conductor).

Carbon Nanotubes :→ (CNTs)

These are considered as allotropes of carbon with cylindrical form made of graphene sheets.

It is imagined by folding of a graphene sheet in single or multiple layers.

Types of CNT →

SWCNT (Single walled CNT)

These are single surface CNT into cylindrical form

3 types of SWCNT –

Zigzag – shows metallic or semiconductor nature.
Achiral in nature

Arm chair – shows metallic nature
Achiral in nature

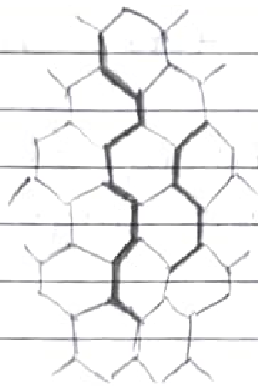
Helical or chiral – shows semiconductor in nature.
Chiral in nature.

MWCNT (Multiwalled CNT)

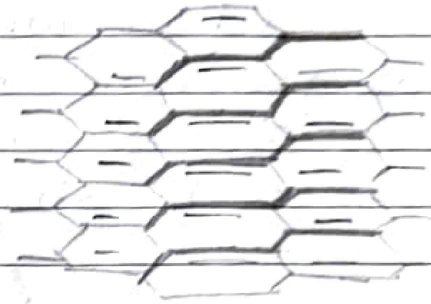
These are multi-surface CNTs into cylindrical form.

It consists of two or more number of rolled-up concentric layers of graphene.

1] Zigzag SWCNT.



2] Armchair SWCNT :



3] Chiral /Helical SWCNT.

Properties of CNT :-

- CNTs have high thermal conductivity.
- —— " —— tensile strength.
- CNTs are the strongest, flexible and stiffest material.
- CNTs are one dimenstional structures, All carbon atoms in CNTs are sp^2 hybridized
- CNTs possess high electrical conductivity.

Applications of CNTs →

- CNTs are used to trap smaller sized ions from a solution.
- To store H_2 gas.
- As a catalyst for certain reactions.
- In drug delivery systems.
- In air & water filtration.
- In fibres & fabrics - combat jackets to provide protection from bullets.
- For energy storage.
- In ceramics.

Synthesis or Preparation of CNTs →

- Carbon arc discharge
- Laser ablation
- Chemical vap. deposition

Chemical Vapour Deposition Method :-

$$\text{Hydrocarbon} \xrightarrow[\text{press. } 0.1 - 1 \text{ torr},\ 1000^\circ C \text{ temp.}]{Fe/Co/Ni/Pt} \text{cracking} \ (\text{C - black}) \longrightarrow \text{SWCNT} + \text{MWCNT}$$

This method is useful to obtain CNTs (SWCNTs & MWCNTs) on large scale.

A hydrocarbon gas (CH_4, C_6H_6, etc.) is cracked with the help of catalyst Fe/Co/Ni/Pt to produce carbon black.

Quantum Dots :→

Def^n - These are the semiconductor nanoparticles which has unique optical & transport properties.

Types of Q.D. →

Gr. III & Gr. V Semic. Q.D.	Gr. II & Gr. VI Semic. Q.D.	Silicon (Si) Q.D.
Gr. III elements - B, Al, Ga, In & Gr. V elements - N, P, As, Sb, Bi	Gr. II elements - Zn, Cd Gr. VI elements - O, S, Se, Te	Made up of Si element, has great potential
e.g. GaAs (Gallium Arsenide) - as a Light source in optical data processing	CdSe (cadmium selenide), ZnO - due to fluorescence properties used in electronics, bio-medicine	used as a component of optical chip, sensors, etc.

Properties of Q.D. :→

- Q.D. have properties intermediate bet^n bulk semiconductors & discrete atoms or molecules.
- Many semiconductor substances can be used as q.d.
- Commonly used semiconductor materials for making Q.D. are Si, CdS, CdSe, InAs
- Q.D. shows fluorescence because of gap between V.B. & C.B.
- Q.D. show colour glow when illuminated (incident) by UV light.

Applications of Q.D. →

i) Biological Applications –
- medical imaging, biosensors, tumour targetting, diagnostics.

ii) Optical Applications –
- Light Emitting Diodes (LEDs), solid state lighting, QD-LED, QD-WLED (white), etc.
- QDPs (Q.D. Photodetectors) in integrated circuits, spectroscopy, etc.
- In hybrid solar cells (CuInSeS QD)
QD solar cells
These are more cost effective than Si solar cells.

iii) In TV or computer displays.

iv) In communications devices (to produce miniature lazers).
(small)