

Module-2

Materials for Electronic Applications

Nanomaterials

Nanomaterials are materials whose length scale lies within the nanometric range (1-100 nm). Nano means dwarf.

Two principle factors cause the properties of nanomaterials to differ significantly from other materials: increased relative surface area and quantum effects.

Classification of Nanomaterials

Based on the number of dimensions which are not in the nano range.

1.Zero dimension (0-D)

All three dimensions are in the nanometric range. Eg: Nano particles

2.One dimension (1-D)

One of the dimensions is outside the nanometric range and other two are within the range.

Eg –nano wires, nano fibers and nano tubes.

3.Two dimension (2-D)

Two dimensions are outside nano range and one within the range.

eg –nano films, nano layers and nano coatings

4. Three dimensions (3-D)

All three dimensions are outside the nm range.

Eg-Bundles of nanowires and tubes, multilayered nano layers

Classification based on materials

- (a) **Carbon based nanomaterials** : Materials in which the nanocomponent is pure carbon eg: Carbon nano tubes(CNT), wires, spheres (Fullerenes) and graphene.
- (b) Metal based nanomaterials: These are materials made of metallic nanoparticles like gold, silver, metal oxides, etc. For example : Titanium dioxide (TiO_2)
- (c) Nanocomposites : Composite nanomaterials contain a mixture of simple nanoparticles or compounds such as nanosized clays within a bulk material. The nanoparticles give better physical, mechanical, and chemical properties to the initial bulk material.

- (d) Nano polymers or Dendrimers: These are nanosized polymers built from branched units. These are tree-like molecules with defined cavities. They can be functionalized at the surface and can hide molecules in their cavities. A direct application of dendrimers is for drug delivery.
- (e) Biological nanomaterials : These nanomaterials are of biological origin and are used for nanotechnological applications. The important features of these particles are i) self assembly properties and ii) specific molecular recognition. Self assembled nano particles can be used to release compounds under specific conditions and are used in drug delivery systems.
eg: DNA nano particles, nanostructured peptides.

Synthesis of Nanoparticles

1. Hydrolysis

Nanoparticles of metal oxides can be prepared by the hydrolysis of their alkoxide solutions under controlled conditions. Hydrothermal method and sol-gel method are of this type.

Sol-Gel method.

This method is based on the phase transformation of a sol into a gel . A sol is a colloidal system of nano solid particles dispersed in a liquid. A gel is a colloidal system in which liquid droplets are dispersed in solid nano particles. To remove impurities, the sol is transformed to a gel by changing the pH.

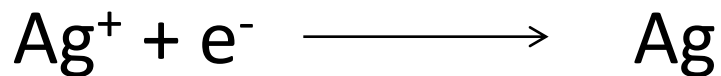


2. Chemical Reduction

Nanoparticles of gold and silver can be prepared by this method. This method can be divided into reduction using reducing agents and electro reduction.

Using reducing agents

Silver nanoparticles can be prepared by this method. 60 mL of 1mM AgNO₃ solution is taken in a beaker, covered and heated. On boiling the solution, 6mL of 10mM of trisodium citrate is added dropwise, about one drop per second. The beaker is then closed and kept for some time. Colour of solution changes to light golden. Cooled and solvent removed.



Properties of Nanomaterials

1. **Physical Properties:** Crystal structure of nanoparticles is same as bulk structure with different lattice parameters. The inter-atomic spacing decreases with size and this is due to long range electrostatic forces and the short range core-core repulsion. The melting point of nanoparticles decreases with size.
2. **Chemical Properties:** Properties of materials with nanometer dimensions are significantly different from those of atoms and bulk materials. This is mainly due to the nanometer size of the materials which render them: 1. large fraction of surface atoms, 2. high surface energy, 3. spatial confinement, 4. reduced imperfections, which do not exist in the corresponding bulk materials. Nanophase ceramics are of particular interest because they are more ductile at elevated temperature as compared to the coarse-grained ceramics.

Applications of Nanomaterials

1. Nano magnetic particles are used for magnetic refrigeration.
2. Nanosemiconductors are used in solar cells.
3. Carbon nanotubes are used for making paper batteries.
4. Have medical applications like treatment of tumours.
5. Used as gas sensors.
6. Nanotube based transistors are used for miniaturizing electronic devices.
7. Dyeing fabrics that never fades.

Carbon Nanotubes (CNTs)

- A carbon nanotube is a carbon allotrope that resembles a tube of carbon atoms. Carbon nanotubes are extremely robust and difficult to break, but they are still light.
- Two-dimensional graphite is folded or rolled into a cylindrical shape structure to create nanotubes. Inside, nanotubes are hollow. The nanotube has a diameter of 1-3 nanometers.
- Arc-discharge method, laser ablation, chemical vapor deposition method etc are the commonly used methods for the synthesis of CNTs.
- It is 10^5 times thinner than human hair.
- CNTs are at least 100 times stronger than steel. They conduct heat and electricity far better than copper.

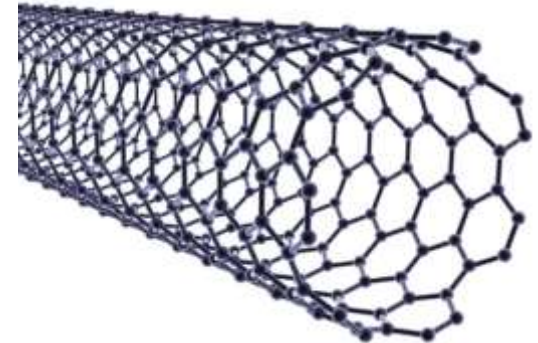
Classification of CNTs— There are two types of CNTs namely single-walled (SWCNT, one tube) and multi-walled (MWCNT, several concentric tubes).

SWCNT can be visualized as rolled-up tubular shell of graphene sheet. Based on rolling, SWCNTs are classified into armchair, zigzag and chair.

Armchair nanotubes: equal edge length.

Zigzag nanotubes: edges with zigzag lines.

Chair nanotubes: Unequal edge lengths and a helical structure.



MWCNT is a stack of graphene sheets rolled up into concentric cylinders. Three different types are Russian doll model, Parchment model and mixed model. In Russian doll model, sheets of graphene are arranged into concentric cylinders; in Parchment, single graphene sheet is rolled around itself and mixed model is a mixture of both models.

Carbon Nanotubes Properties

- Strength and hardness : They are the strongest and stiffest materials. High strength could be attributed to the covalent sp^2 bonds formed between the individual carbon atoms. They can withstand a pressure of upto 24 Gpa without deformation.
- Electrical conductivity: CNTs are electrically and thermally conductive and have a high tensile and mechanical strength. Electron travelling through a CNT behaves like a wave travelling through smooth channel-Ballistic transport.
- Thermal conductivity: All CNTs are very good thermal conductors along the tube but good insulators laterally to the tube axis-Ballistic conduction. The thermal stability is upto 2800°C in vacuum and about 750°C in air.

Carbon Nanotubes Applications

- Carbon nanotubes are utilized in energy storage. It is used for making paper batteries.
- CNT is used in solar cells , automotive parts, water filters, thin-film electronics, coatings, and electromagnetic shields.
- Because of their large surface area, CNTs have been successfully used in pharmacy and medicine to adsorb or conjugate a wide range of medicinal and diagnostic substances.
- CNT films are ideal for high reliability touch screens.
- CNT can operate as loud speaker.

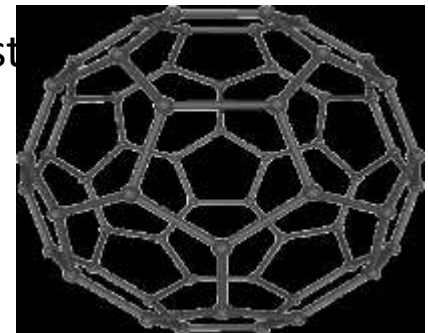
Fullerenes

These are the molecular form of very pure carbon. They are zero-dimensional, hollow, closed cage like structure of carbon atoms. Most abundant fullerene is buckminsterfullerene (buckymann, C₆₀). C₆₀ was developed by heating graphite rods in a helium atmosphere. They possess spherical structure of 60 carbon atoms. Fullerenes contain twelve five membered rings and twenty six membered rings and possess a perfect icosahedral geometry. This geometry is similar to that of a soccer football. In fullerene, each carbon atom is bonded to three other carbon atoms and is SP² hybridized.

The SP² hybridised carbon atoms, which are at their energy minimum in planar graphite, must be bent to form the closed sphere which produces angle strain. The electrophilic addition reduces angle strain by changing SP² hybridisation to SP³. This decreased bond angle from 120 to 109.5° allows the bonds to bend less when closing the sphere and thus the molecule becomes more stable.

Applications:

- They are used in drug delivery system and used as contrast agents in MRIs.
- They are used in electronic circuits.
- They are used as lubricant in ball bearings.
- They are used in water treatments and as sensors.
- They can be used to store hydrogen.
- They are used for making durable, high performance coatings that resist wear and corrosion.



Properties of Fullerenes

- The fullerenes are extremely strong molecules, able to resist high pressures. They are harder than steel and diamond.
- Fullerenes are normally electrical insulators, but when crystallized with alkali metals, the resultant compound can be superconducting .
- Fullerenes absorb strongly in the UV-Vis regions of the spectrum.
- Fullerene is ferromagnetic.
- It is soluble in organic solvents such as toluene, chlorobenzene, and 1,2,3-trichloropropane. The higher fullerenes have a variety of colours.

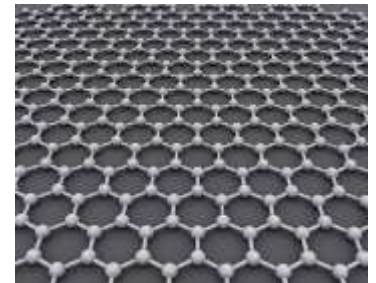
Graphene

Graphene is a one-atom-thick layer of carbon atoms arranged in a hexagonal lattice. It is the building-block of Graphite, but graphene is a remarkable substance on its own - with a multitude of astonishing properties which repeatedly earn it the title “Wonder material”.

The various methods for the synthesis of graphene are: Mechanical exfoliation method, chemical vapor deposition, thermal decomposition on SiC and graphene oxide reduction method.

Graphene's properties

- Graphene is the thinnest material known to man at one atom thick, and also incredibly strong - about 200 times stronger than steel. On top of that, graphene is an excellent conductor of heat and electricity and has interesting light absorption abilities. It is truly a material that could change the world, with unlimited potential for integration in almost any industry.
- Graphene has extremely high electrical current density (a million times that of copper) and intrinsic mobility (100 times that of silicon). Graphene has a lower resistivity than any other known material at room temperature, including silver. There are also some methods to turn it into a superconductor (it can carry electricity with 100% efficiency).
- Graphene is the perfect thermal conductor - it features record thermal conductivity higher than that of carbon nanotubes, graphite and diamond (over 5,000 W/m/K). Graphene conducts heat in all directions - it is an isotropic conductor.
- Graphene is extremely thin, but it is still a visible material, and is used to make very efficient solar cells.



Applications of Graphene

- The use of graphene in the manufacturing of rechargeable batteries could be a great leap towards energy efficiency. This material would prevent devices overheating, so they would be tougher and lighter.
- The use of graphene in construction promises to improve the insulation of buildings. It helps to make it more resistant to corrosion, dampness, and fire, and therefore tougher and more sustainable.
- In health sector, making bones and muscles that would be introduced through surgical operations uses graphene implants.
- Smaller, lighter, tougher, and more efficient devices could be manufactured with the application of graphene in electronics.
- Graphene based membranes can purify water in a more efficient way and is also used in air filters.

Carbon quantum Dots

Quantum dots (QDs) are zero-dimensional small carbon nano particle. It consists of semiconductor particles with a few nanometres in size (2-10 nm). Their optical and electronic properties that differ from those of larger particles via quantum mechanical effects. These are also known as **semiconductor nanocrystals**.

It can be synthesised by two main methods: top—down and bottom-up. The top-down involves breaking large carbon structures to small CQDs through chemical oxidation. The bottom-up involves building CQDs from small carbon molecules through hydrothermal synthesis.

Properties of QDs

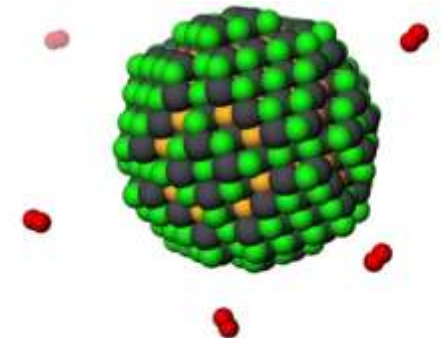
When a quantum dot is illuminated by UV light, an electron in the quantum dot can be excited to a state of higher energy. In the case of a semiconducting quantum dot, this process corresponds to the transition of an electron from the valence band to the conductance band. The excited electron can drop back into the valence band releasing its energy as light.

Quantum dots have properties intermediate between bulk semiconductors and discrete atoms or molecules. Their optoelectronic properties change as a function of both size and shape. Larger QDs (5-6 nm) diameter emit longer wavelength λ , with orange or red colour. On the other hand, smaller QDs (2-3 nm) emit shorter wavelength λ , resulting blue and Green colour. QDs are 20 times brighter and 100 times more stable more than traditional fluorescent reporters.

Applications of QDs

QDs are used in:

- single-electron transistors, solar cells, and LEDs,.
- lasers, single-photon sources, and second-harmonic generation,.
- CQDs can be used to improve photocatalytic degradation of organic pollutants and dyes in water.
- quantum computing, cell biology research, microscopy, and medical imaging.



POLYMERS

Polymers are molecules with large molecular masses formed by linkage of small repeating units called monomers.

Fire Retardant Polymers : Halogenated and Non-halogenated

Halogenated FRs Examples (More efficient)

- Polybrominated Diphenyl Ethers (PBDEs)
- Polybrominated styrene
- Hexabromocyclododecane (HBCDD)
- Tris and other halogenated trialkylphosphates
- PolyFR (GreenCrest)

Non-halogenated FRs Example (greener type)

- Polyimides,
- Polybenzoxazoles (PBOs),
- Polyamides,
- Polyurethanes
- Polybenzthiazoles (PBTs)

CONDUCTING POLYMERS

A polymer which can conduct electricity is termed as conducting polymer.

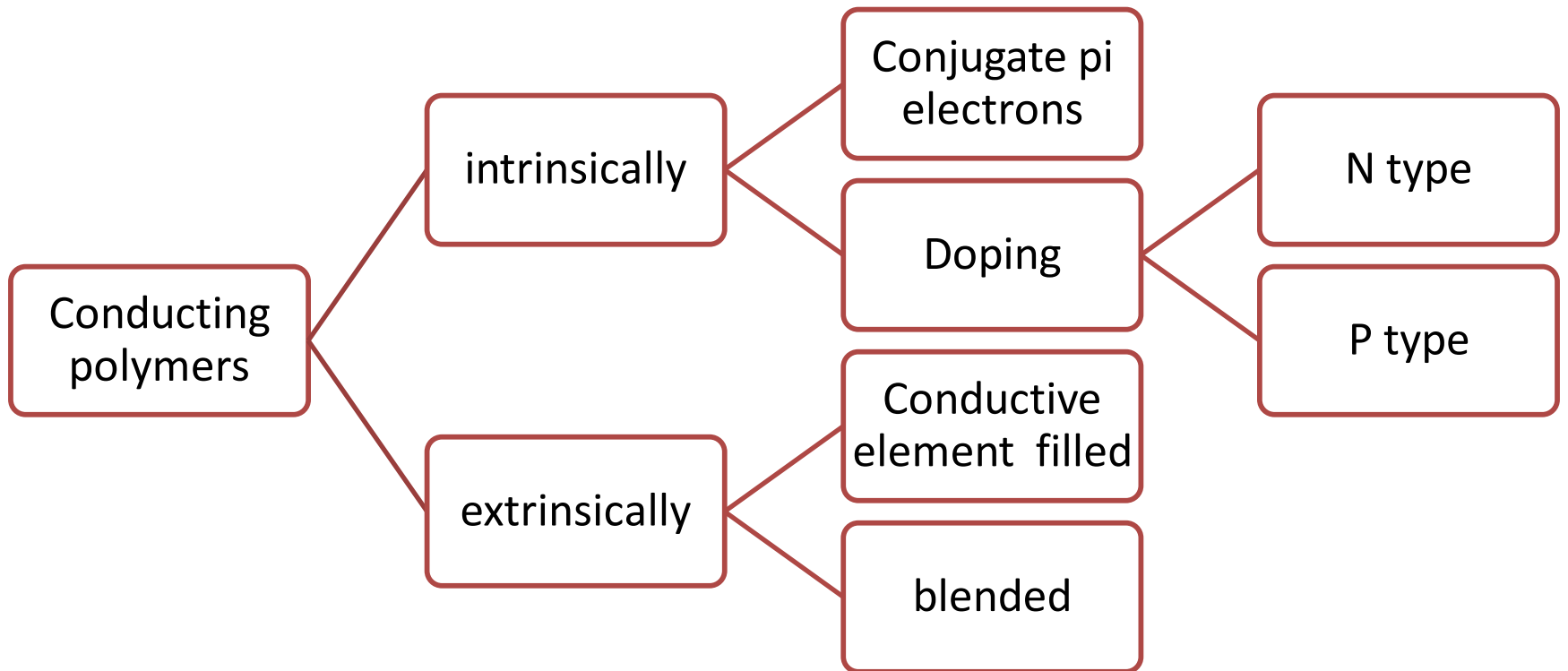
Eg –poly acetylene

Classification :

Two types

1. Intrinsically conducting

2. Extrinsically conducting



Intrinsically Conducting

Here, conductivity is due to conjugation in structure.

1. Conjugated pi electron conducting polymers

Characterised by the presence of conjugated double bonds along the backbone of the polymer.

Electrical conduction would occur when electron from valence band are excited to conduction band either thermally or photolytically.

Eg – polyacetylene.

2. Doped conducting polymers

Conductivities of polymers can be increased by creating positive or negative charge on polymer back bone by oxidation or reduction. This process is referred to as Doping

Doping is of two types

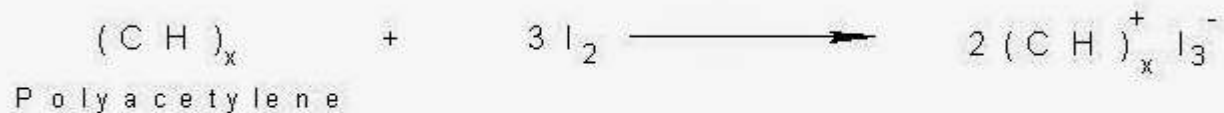
1. p-doping

In this **some electrons are removed** and the holes so created can move along the molecule. It is done by oxidation process

Eg of p-dopant (Lewis acid) are BF_3 , FeCl_3

The polymer is treated with a Lewis acid.

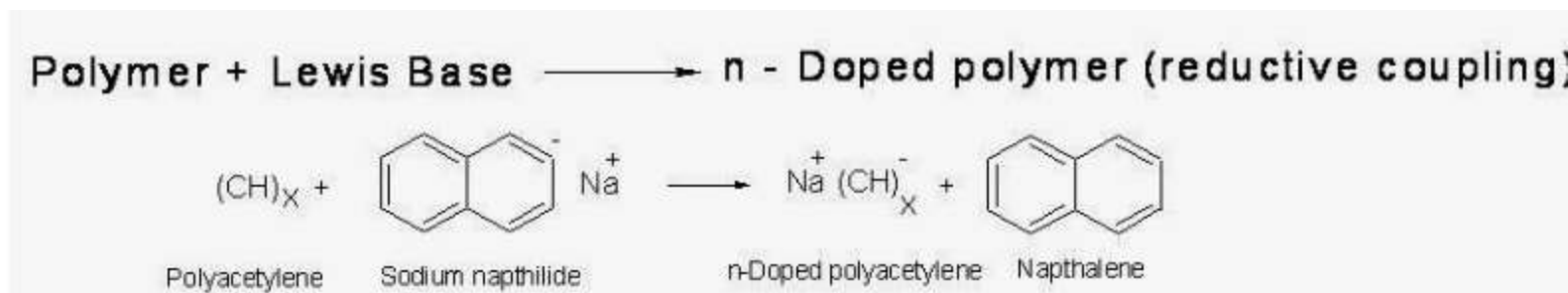
Polymer + Lewis Acid \longrightarrow p - Doped polymer (oxidative coupling)



2. n-doping

Here **some electrons are introduced** into the polymer . Usually this is achieved by reduction.

Eg for n-dopant(Lewis base)are Li, Naphthalide etc.



Extrinsically conductive polymers

Conducting polymers whose conductivity is due to the presence of externally added ingredients.

1. Conductive element filled polymer.

The filling elements can be carbon black, metallic fibres etc.

2. Blended conducting polymers

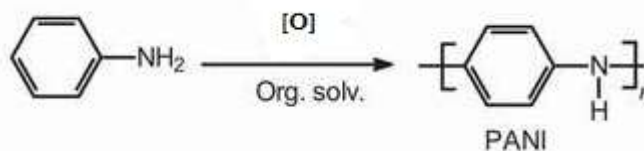
Obtained by blending conducting polymers with conventional polymers. They possess better properties.

POLYANILINE

It is the oxidative product of aniline under acidic conditions –also known as aniline black.

Synthesis

- An aqueous solution of ammonium persulphate is added slowly to a solution of aniline dissolved in dil. Hydrochloric acid at a temp. of 5°C. under agitation.
- After an hour a precipitate is formed, which can be removed by filtration.
- The polymer thus obtained is washed with ammonium hydroxide and dried.



Polyaniline -Properties

- 1.Stable in air.
- 2.Soluble in organic solvents
- 3.Magnetic behaviour –exhibits high spin density and ferromagnetic spin interaction
- 4.Change colour in different oxidation states –can be used in sensors.
- 5.More noble than copper- used in printed circuit board manufacturing
- 6.Dopped poly aniline is a good conductor.Originally it is a semiconductor

Applications of polyaniline

- 1.As electrode material for rechargeable batteries.
- 2.In the dissipation of static electric charges in metallic containers.
- 3.As shield in complex electronic circuits and em radiations
- 4.In biosensors to control solar energy absorption.

4. Polypyrrole

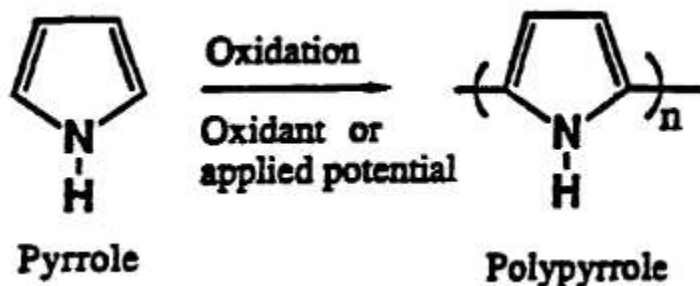
Preparation

a) Electrochemical method:

By the electrolysis of pyrrole in aqueous acetonitrile solution using platinum electrodes and tetra ethyl ammonium boron tetrafluoride as the supporting electrolyte. The polymer will be precipitated as a blue black film on the anode.

b) Chemical polymerization

It can be carried out in a beaker by mixing 0.1 M aqueous solution of pyrrole and 0.1 M ammonium persulphate in 1 : 1 ratio for 3 hrs. The polymer precipitates out.



Properties

1. Polypyrrole has excellent electrical, thermal and mechanical properties.
2. It has good environmental stability and high conductivity.
3. Ppy is an insulator while its oxidative derivatives are good electrical conductors

Applications of Polypyrrole

- 1.Used mostly in biosensors and immunosensors
- 2.Better mechanical match with live tissue, hence applied in biomedical field.
- 3.Has applications in tissue engineering.
- 4.Employed in dye sensitised solar cells

OLED (organic light emitting diode)

This is a light emitting diode (LED) in which the emissive layer is a film of organic compound which emits light in response to an electric current.

There are two types of organic layers – those based on small molecules and those employing conducting polymers.(conjugated polymers)

Construction of an OLED

A typical OLED is composed of a layer of organic material situated between two electrodes , the anode and cathode, all deposited on a substrate.

Parts of OLED

Substrate:

A clear plastic or glass that supports OLED is called substrate.

Anode:

When current passes through the OLED, it removes electrons and adds holes. Usually used anode is ITO (Indium Titanium Oxide)

Hole Transport Layer (HTL)

It is the conducting layer made of conducting polymer like polyaniline. It helps for the transport of holes from the anode through the OLED.

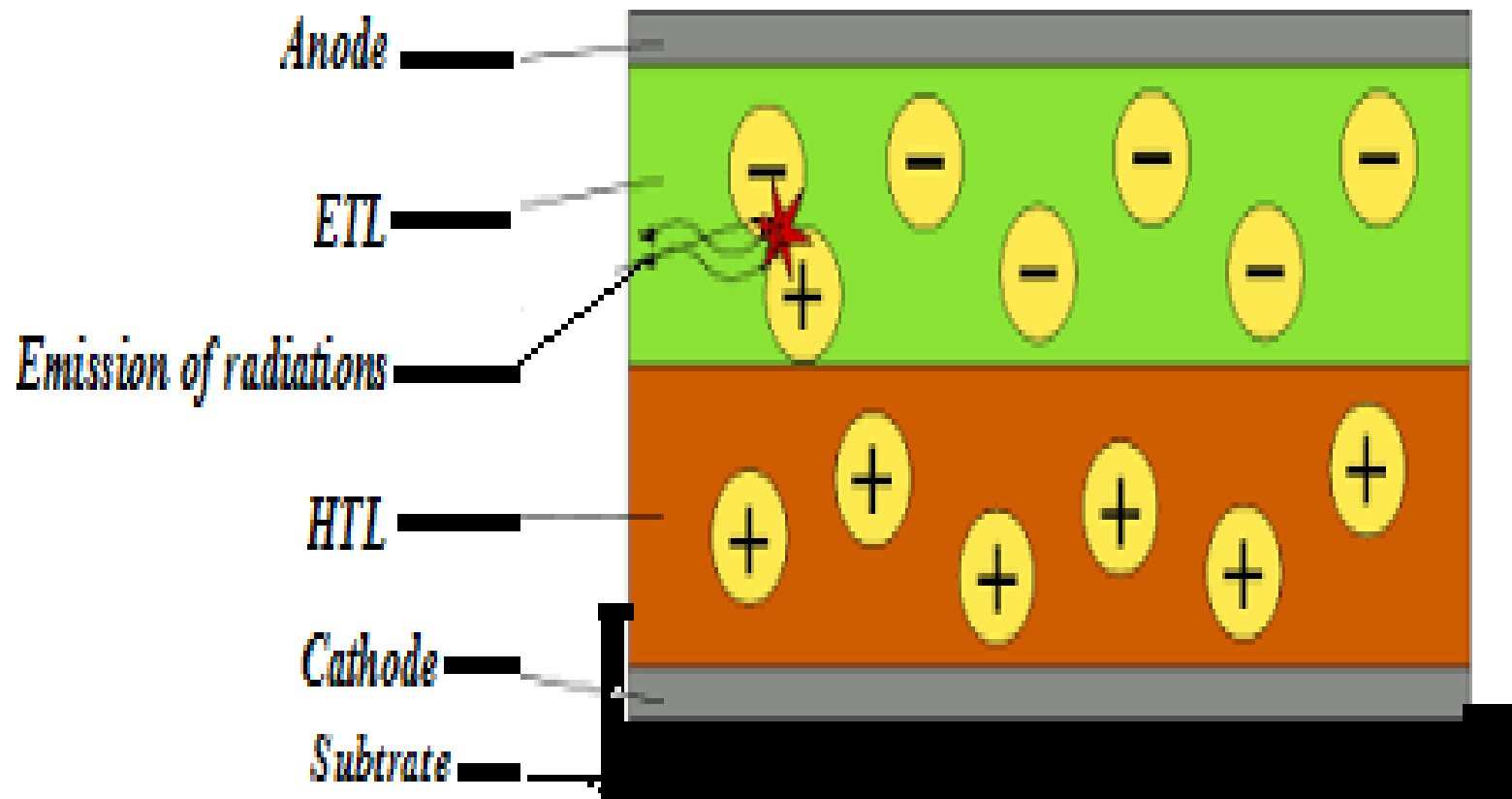
Electron Transport Layer (ETL)

It is the emissive layer made of polyfluorene. Light is produced in the ETL. It helps for the transport of electrons from the cathode through the OLED.

Cathode:

It ejects electrons when current flows through the OLED. Al or Ca is used as cathode.

Schematic bilayer of OLED



Working of OLED

- The organic molecules are electrically conductive as a result of delocalisation of pi electrons.
- A voltage is attached across anode and cathode.
- The cathode receives electrons and anode loses them.
- The added electrons make an n-type emissive layer. The p-type conductive layer becomes positively charged with positive holes.
- When a hole meets an electron, they cancel out and a burst of energy is released in the form of light. This is called recombination.
- OLED produces light as long as the current flows.

Applications of OLED

1. Manufacture of OLED is economical and efficient than LCD.
2. Contrast ratio of OLED is very high. Hence applied in HD TV
3. No backlight is produced by this device.
4. Refresh rate is greater than LCD display
5. Response time is less than 0.01 ms.

Dye-Sensitized Solar Cells (DSSC)

- A **dye-sensitized solar cell (DSSC)** is a low-cost solar cell belonging to the group of thin film solar cells. It is based on a semiconductor formed between a photo-sensitized anode and an electrolyte, a *photoelectrochemical* system.

Construction of DSSC

The DSSC cell generally consists of a set of layers of different components, including transparent conductive oxide layer (TCO), semiconducting metal oxide nanoparticles (usually TiO_2), dye-sensitizer (organic or metallo-dye), electrolyte (Iridium or Cobalt complexes), and counter electrode (Platinum).

Parts of DSSC

- **TCO glass substrate**

DSSCs are generally fabricated with using the substrates which are transparent as well as conductive. Thin film of Indium Tin oxide (ITO) acts as TCO.

- **Nano Semiconducting Metal Oxide Electrode**

Semiconducting metal oxides with wide band gaps such as TiO_2 , ZnO , and SnO_2 are used in the DSSCs. TiO_2 nanoparticles are the best choice due to their non-toxic nature, cost-effectiveness and easy availability.

- **Dyes/Sensitizers**

Dyes or sensitizers aid in the light harvesting and hence govern the photoelectric conversion efficiency of the solar cell. The dye-sensitised metal oxide acts as the anode. Ruthenium –based complexes and organic dyes are commonly used.

- **Electrolyte/Redox Mediator**

Liquid electrolytes based on the iodide/triiodide redox couple are found to be more successful electrolytes. Electrolyte should have good contact with the dye-sensitised metal oxide semiconductor and the counter electrode.

- **Counter Electrode/Cathode**

Platinum and graphite-based materials have been extensively used as counter electrodes in DSSC applications. It facilitates the reduction of the oxidized dye molecules and completes the electrical circuit.

Working Mechanism of DSSC

- Working mechanism of DSSCs is slightly different from the conventional solar cells. It involves the following steps.
- Step 1: Dye molecules coated on the metal oxide semiconductor absorb wide spectrum of the sunlight. And upon absorption of sunlight the electrons of dye molecule get excited.

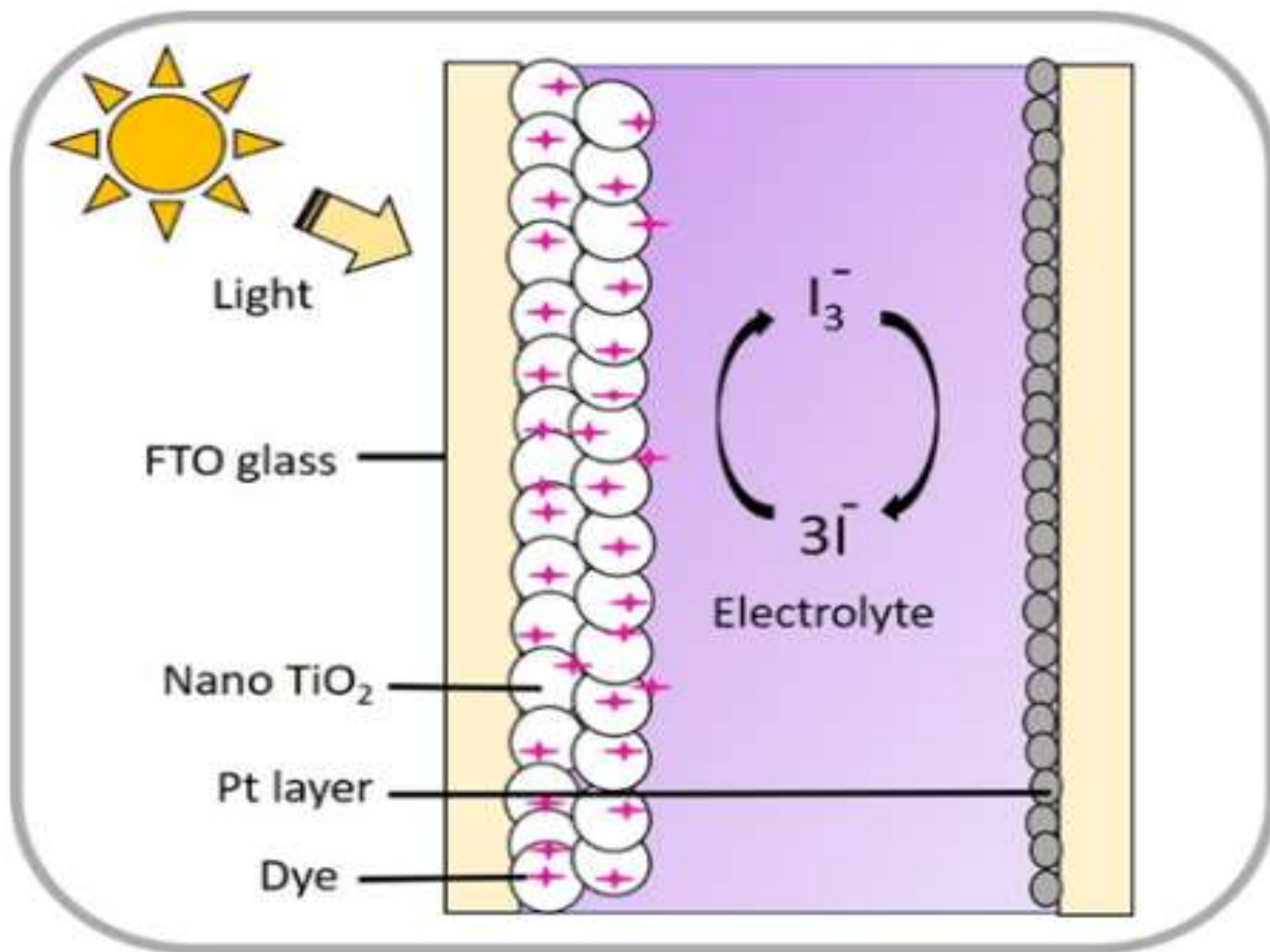
Step 2: The excited electrons of the dye molecule are injected into the conduction band of the metal oxide semiconductor.

Step 3: These electrons will diffuse through metal oxide and finally reach counter electrode through the circuit.

Step 4: The oxidized dye molecules will get the electrons from the redox mediator/electrolyte and come back to their original (reduced) form.

Step 5: The oxidized electrolyte species diffuse towards the counter electrode and get reduced.

And this cycle continues to produce the current. It is important to note that, the overall performance a DSSC depends on the energy levels of these four components: the ground state (HOMO – Highest Occupied Molecular Orbital) and excited state of the dye molecules (LUMO – Lowest Unoccupied Molecular Orbital), the band-gap of the metal oxide semiconductor and the redox potential of the electrolyte.



Applications of DSSC

- DSSCs can be used in interior applications due to their color and transparency.
- DSSCs' transparency makes them suitable for integration into building materials, turning windows and facades into transparent solar panels.
- DSSCs can be integrated into Internet of Things (IoT) devices, smart textiles, and electronic sensors to provide sustainable power sources.
- DSSCs can be used in Portable power systems, backpacks and bags.
- Thin, lightweight, and conformable DSSC modules can be incorporated into various surfaces, such as clothing and flexible electronic devices, enabling the creation of wearable and portable solar-powered systems.

Materials used in Quantum computing

Quantum computing is an emerging computer technology that uses the principle of quantum theory for computation. Quantum computers harness properties such as superposition, entanglement, and quantum interface for computing.

- **Superconductors:** Materials like niobium and aluminum are commonly used in superconducting qubits. Superconducting circuits operate at extremely low temperatures and exhibit zero electrical resistance, which helps in maintaining quantum coherence.
- Hexagonal boron nitride can be stacked to serve as the insulating layer in the capacitors used in superconductors.
- **Semiconductors:** Silicon, indium arsenide (InAs) and gallium arsenide (GaAs) are used to produce single photons.

Quantum computing requires very low temperatures to avoid decoherence to prevent error rates.

Super capacitors

Supercapacitors, also known as ultra capacitors or electric double-layer capacitors (EDLCs), are energy storage devices that bridge the gap between traditional capacitors and batteries. They offer high power density and fast charge/discharge cycles, making them useful in applications requiring rapid energy release and absorption.

- Key Features are High Capacitance, Fast Charge and Discharge, Long Cycle Life, and Low Energy Density.

Differences between battery and capacitors

Battery	Capacitors
Electrical energy is stored as chemical energy	Electrical energy stored as electric field.
Low life cycle	Very large life cycle
Energy density very high	Energy density is low
Lower power density	Higher power density
High internal resistance	Very low internal resistance

- **Working Principle:** Supercapacitors often use **EDLC technology**, where energy is stored through the electrostatic separation of charges in an electric double layer at the interface between an electrode and an electrolyte. Some supercapacitors use **pseudocapacitive materials**, where energy is stored through fast, reversible electrochemical reactions.
- **Electrodes:**
 - Typically made from high-surface-area materials like activated carbon, graphene, or carbon nanotubes.
- **Electrolytes:**
 - Can be aqueous or non-aqueous electrolytes. Generally a solvent mixed with conductive salts acts as the solid electrolyte and sulphuric acid or KOH solution acts as the liquid electrolyte. Each type affects the performance and stability of the supercapacitor.
- **Separator:**
 - A porous membrane that prevents electrical contact between the electrodes while allowing ion movement.
- **Collector:**
 - Carbon fibre, metal like Al, Pt, Cu, etc are used as collectors.

Advantages of supercapacitors

- Long cycle time and higher service life
- High efficiency and power density
- Low resistance
- Small sizes and environmental friendly.

Disadvantages:

- High self discharge rate
- Amount of energy stored per unit weight is low.
- Low voltage limits.

Applications of supercapacitors

- **Energy Storage:** In renewable energy systems to smooth out fluctuations and provide quick bursts of power.
- **Consumer Electronics:** For backup power and power stabilization in devices like smartphones and cameras.
- **Automotive:** To assist in regenerative braking systems and provide additional power for acceleration.

Spintronics

- Spintronics (spin transport electronics) is a field of electronics that utilizes the intrinsic spin of electrons, in addition to their charge, to store and process information. Unlike conventional electronics, which rely solely on the charge of electrons, spintronics leverages the magnetic moment associated with electron spin to achieve various functionalities.
- Spin orientations last longer than charge based informations, making them suitable for memory storage, magnetic sensors, and quantum computing.
- Spintronics make use of magnetoresistance effects for sensing and storing informations. Giant magnetoresistance (GMR) is a phenomenon where a material's electrical resistance changes drastically with applied magnetic field.
- GMR spin-valve sensors improved the capacity of hard disc drive by more than hundred-fold times.
- A spin polarised current can be generated in a very simple way by passing the current through a ferroelectric material. Spintronics materials should retain ferromagnetism at practical temperatures.
- Metal oxides of MgO , Al_2O_3 , graphene based materials are examples of spintronics materials.

Advantages of spintronics

- **Non-volatility:** Spintronic devices like MRAM retain data even when power is turned off.
- **High Speed and Low Power Consumption**
- **Enhanced Functionality** such as magnetic sensing and advanced data storage.

Applications of spintronics

- **Data Storage:** MRAM and other spintronic devices are used in computer memory and storage systems.
- **Magnetic Sensors:** Employed in various sensors for detecting magnetic fields, used in applications ranging from automotive to industrial.
- **Quantum Computing:** Spintronics is being explored for quantum computing due to its potential for manipulating quantum states.