

Module-2

Quantum Materials and Polymers

Quantum Dots: Introduction, size-dependent properties-quantum confinement effect, surface-to-volume ratio & band gap. Synthesis of Cd-Se Quantum dots by wet chemical method and its applications. Construction, working principle and applications of quantum dot sensitized solar cells (QDSSCs).

Polymer: Introduction, number average and weight average molecular weight of the polymers and numerical problems. Structure-properties relationship of polymers (Crystallinity, Strength, Elasticity and chemical resistivity]. Synthesis and properties of nylon-6,6 and its advantages in 3D printing applications. Synthesis and properties of chlorinated polyvinyl chloride (CPVC), and polymethyl methacrylate (PMMA) and their uses in device applications.

Conducting polymers- Introduction, synthesis of polyaniline, conduction mechanism and its engineering applications.

Introduction

Polymers are macromolecules that have high molecular mass built up by linkage together of a large number of small molecules called monomers. In Greek **Poly** means many, **mers** means units or parts. The molecular mass of polymers is high and ranges from 10,000 to 1,00,000.

Example: Polythene is a polymer formed by linkage of large number of ethylene.

Polymerization: The chemical process in which the monomers are converted into polymers is called **Polymerization**.

Degree of Polymerization: The number of times the unit is repeated in a homopolymer chain is referred to as the **degree of polymerization**. High polymers have high degree of polymerization.

Addition polymerization: It is a process in which unsaturated monomers, typically containing double or triple carbon-carbon bonds, repeatedly join together to form long polymer chains without the elimination of any byproducts.

- **Polyethylene** (from ethene)
- **Polypropylene** (from propene)
- **PVC** (polyvinyl chloride, from vinyl chloride)

Condensation polymerization: The polymerization process involves the reaction of bifunctional or multifunctional monomers, each containing two or more reactive groups such as –OH, –COOH, or –NH₂. During the formation of the polymer, small molecules like water, hydrochloric acid, or methanol are eliminated as byproducts.

- **Nylon** (e.g., Nylon-6,6 from hexamethylenediamine and adipic acid)

- **Terylene / PET** (from ethylene glycol and terephthalic acid)
- **Bakelite** (from phenol and formaldehyde)

Molecular weight of polymers:

The two main types of molecular mass are

- a) Number average molecular Weight
- b) Weight average molecular weight

Number average molecular Weight:

It is defined as the total mass (W) of all the molecules in a polymer sample divided by total number of molecules present.

$$M_n = \frac{n_1m_1 + n_2m_2 + n_3m_3 + n_4m_4 + \dots + n_im_i}{n_1 + n_2 + n_3 + n_4 + \dots + n_i}$$

Where n and M represent the number and molecular mass of each species respectively present in the polymer.

Weight average molecular weight:

It is various molecular species in proportion to their weights in the given material.

$$\bar{M}_w = \frac{w_1m_1 + w_2m_2 + w_3m_3 + w_4m_4 + \dots + w_im_i}{w_1 + w_2 + w_3 + w_4 + \dots + w_i}$$

Where w = nm

$$\bar{M}_w = \frac{n_1m_1 m_1 + n_2m_2 m_2 + n_3m_3 m_3 + n_4m_4 m_4 + \dots + n_im_i m_i}{n_1m_1 + n_2m_2 + n_3m_3 + n_4m_4 + \dots + n_im_i}$$

$$\bar{M}_w = \frac{n_1m_1^2 + n_2m_2^2 + n_3m_3^2 + n_4m_4^2 + \dots + n_im_i^2}{n_1m_1 + n_2m_2 + n_3m_3 + n_4m_4 + \dots + n_im_i}$$

$$\bar{M}_w = \frac{\sum n_im_i^2}{\sum n_im_i}$$

Numerical:

1. A polymer sample contains 1, 2, 3 and 4 molecules having molecular weight 1×10^5 , 2×10^5 , 3×10^5 and 4×10^5 respectively calculate the number average and weight average molecular weight of the polymer.

Solution: Number of molecules $n_1=1$ $n_2=2$ $n_3=3$ $n_4=4$

Molecular weight of the polymer:

$$m_1 = 1 \times 10^5 \quad m_2 = 2 \times 10^5 \quad m_3 = 3 \times 10^5 \quad m_4 = 4 \times 10^5$$

$$\bar{M}_n = \frac{n_1 m_1 + n_2 m_2 + n_3 m_3 + n_4 m_4}{n_1 + n_2 + n_3 + n_4}$$

$$\bar{M} = \frac{(1 \times 1 \times 10^5) + (2 \times 2 \times 10^5) + (3 \times 3 \times 10^5) + (4 \times 4 \times 10^5)}{1 + 2 + 3 + 4}$$

$$\bar{M}_n = 3.0 \times 10^5$$

$$\bar{M}_w = \frac{n_1 m_1^2 + n_2 m_2^2 + n_3 m_3^2 + n_4 m_4^2}{n_1 m_1 + n_2 m_2 + n_3 m_3 + n_4 m_4}$$

$$\bar{M}_w = \frac{(1 \times (1 \times 10^5)^2) + (2 \times (2 \times 10^5)^2) + (3 \times (3 \times 10^5)^2) + (1 \times (4 \times 10^5)^2)}{(1 \times 1 \times 10^5) + (2 \times 2 \times 10^5) + (3 \times 3 \times 10^5) + (4 \times 4 \times 10^5)}$$

$$\bar{M}_w = 3.33 \times 10^5$$

2. A polymer polypropylene is found to have the following composition

- a) $R [\begin{array}{c} -CH_2 - CH - \\ : \\ CH_3 \end{array}]$ is 20% b) $R [\begin{array}{c} -CH_2 - CH - \\ : \\ CH_3 \end{array}]$ is 30%
- c) $R [\begin{array}{c} -CH_2 - CH - \\ : \\ CH_3 \end{array}]$ is 50%

is 50% calculate the \bar{M}_n and \bar{M}_w of polymer atomic mass of C=12, H=1 neglect the atomic mass of R.

Solution: Number of molecules $n_1=20$ $n_2=30$ $n_3=3$ $n_4=50$

Molecular weight of the polymer:

- a) $m_1 = (3 \times 12 + 6 \times 1) \times 400 = 16800$
 b) $m_2 = (3 \times 12 + 6 \times 1) \times 500 = 21000$
 c) $m_3 = (3 \times 12 + 6 \times 1) \times 600 = 25200$

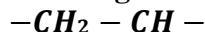
$$M_n = \frac{n_1m_1 + n_2m_2 + n_3m_3}{n_1 + n_2 + n_3}$$

$$M_n = \frac{(20 \times 16800) + (30 \times 21000) + (50 \times 25200)}{20 + 30 + 50} = 22260$$

$$\bar{M}^{\text{w}} = \frac{n_1 m_1^2 + n_2 m_2^2 + n_3 m_3^2}{n_1 m_1 + n_2 m_2 + n_3 m_3}$$

$$\bar{M}_w = \frac{[20 \times (16800)^2] + [30 \times (21000)^2] + [50 \times (25200)^2]}{(20 \times 16800) + (30 \times 21000) + (50 \times 25200)} = 22743.6$$

3. calculate the weight average molecular weight of PVC if degree of polymerization is 12250,



structure of repeating unit in PVC is : , molecular weight of repeating unit=62.5

Chlorophyll

g/mol.

Solution: Degree of polymerization = $\frac{\text{Average molecular weight of the polymer}}{\text{molecular weight of repeating unit}}$

Average molecular weight of the polymer

= *Degree of polymerization*

\times molecular weight of repeating unit

$$\text{Average molecular weight of the polymer} = 12250 \times 62.5 = 7.6 \times 10^5$$

4. A polymer sample contains 200 molecules of molecular mass 2000, 300 molecules of molecular mass 3000 and 500 molecules of molecular mass 5000. Calculate number average and weight average molecular weight of the polymer.

Solution: Number of molecules $n_1=200$ $n_2=300$ $n_3=500$

Molecular weight of the polymer: $m_1 = 2000$ $m_2 = 3000$ $m_3 = 5000$

$$M_n = \frac{n_1m_1 + n_2m_2 + n_3m_3}{n_1 + n_2 + n_3}$$

$$M_n = \frac{(200 \times 2000) + (300 \times 3000) + (500 \times 5000)}{200 + 300 + 500} = 3800$$

$$\bar{M}^w = \frac{n_1 m_1^2 + n_2 m_2^2 + n_3 m_3^2}{n_1 m_1 + n_2 m_2 + n_3 m_3}$$

$$\overline{M}_w = \frac{[200 \times (2000)^2] + [300 \times (3000)^2] + [500 \times (5000)^2]}{(200 \times 2000) + (300 \times 3000) + (500 \times 5000)} = \frac{160 \times 10^8}{3.8 \times 10^6}$$

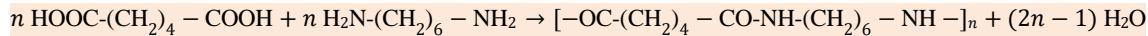
=4210.526

Assignment numerical:

1. A polymer has following composition 100 molecules of molecular mass 1000 g/mol, 2000 molecules of molecular mass 2000g/mol and 500 molecules of molecular mass 5000 g/mol. Calculate the number average and weight average molecular weight of the polymer. (June-2016)
2. In a polymer sample, 20% molecules have molecular mass 15000 g/mol, 45% molecules have molecular mass 25000 g/mol remaining molecules have molecular mass 27000 g/mol. Calculate the number average and weight average molecular weight of the polymer. (Dec 2015)
3. In a polymer sample, 20% of molecules have molecular mass 15000g/mol, 35% molecules have molecular mass 25000 g/mol and remaining molecules have molecular mass 20000 g/mol. Calculate the number and weight average molecular weights of the polymer.
4. A polymer sample contains 100,200,300 and 400 molecules having molecular mass 1000, 2000, 3000 and 4000 respectively. Calculate the number and weight average molecular weights of the polymer.
5. A polymer sample containing 50, 100 and 150 molecules having molar mass 1000, 2000 and 3000 respectively. Calculate the number and weight average molecular weights of polymer. **[Dec.2015/ Jan 2016]**
6. In a polymer sample, 20% of molecules have molecular mass 15000g/mol, 45% molecules have molecular mass 25000 g/mol and remaining molecules have molecular mass 27000 g/mol. Calculate the number and weight average molecular weights of the polymer. **[Dec.2015/ Jan 2016]**
7. A polymer sample contains 200 molecules of molecular mass 2000, and 200 molecules of molecular mass 40,000 g/mol. Calculate the number and weight average molecular weights of polymer.
8. A polymer sample contains 100 molecules of molecular mass 20,000 g/mol , 300 molecules of molecular mass 3000 and 500 molecules of molecular mass 5000. Calculate the number and weight average molecular weights of polymer. **[June/July- 2016]**

Nylon-6,6:

Nylon-6,6 is produced when equal amounts of adipic acid and hexamethylene diamine undergo polycondensation reaction with form an amide bond, releasing water as a byproduct.



Adipic acid

Hexamethylene diamine

Nylon 6,6

Properties of Nylon-6,6 (Simple Bullet Points):

- Very strong and can handle heavy loads.
- Hard to stretch or break.
- Does not wear out easily, even with movement.
- Can handle high heat (up to 255–265°C).
- Resists oils, greases, and many chemicals.
- Light in weight (lighter than many metals).
- Absorbs less moisture than other plastics.

Advantages in 3D Printing:

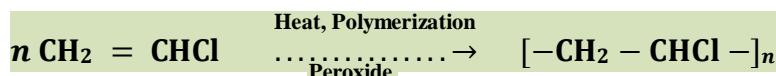
- Makes strong, flexible, and tough printed parts.
- Works well for prototypes and mechanical components.
- High melting point prevents warping in hot conditions.
- Durable, even with regular use.
- Resists damage from chemicals and oils—great for industrial parts.

Chlorinated Polyvinyl Chloride (CPVC):

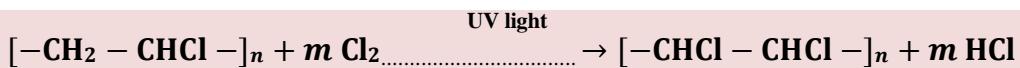
Synthesis of CPVC is carried out in two main steps as follows:

Step I: Preparation of PVC

Vinyl chloride monomers (VCM) undergo free-radical addition polymerization in the presence of a peroxide initiator under controlled heat and pressure to form polyvinyl chloride (PVC).

**Step II: Chlorination of PVC**

The obtained PVC is exposed to chlorine gas under UV irradiation, during hydrogen atoms in the PVC chain are replaced by chlorine atoms, leading to the formation of chlorinated polyvinyl chloride (CPVC).

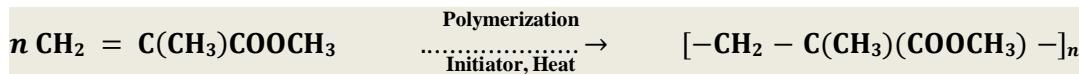
**Properties of CPVC:**

- CPVC is stronger and tougher than normal PVC.
- It has higher chlorine content, which makes it more rigid.
- CPVC can withstand higher temperatures (up to about 90–110 °C).
- It has good resistance to corrosion and many chemicals.
- CPVC is fire-retardant due to its high chlorine content.

- It shows good dimensional stability and does not warp easily.
- It is resistant to hot and cold water, so it is used in plumbing.
- CPVC has long service life and good mechanical strength.
- It can be easily processed by extrusion and molding.

Polymethyl methacrylate (PMMA) or Plexiglass

PMMA is synthesized by the free-radical bulk polymerization under an inert atmosphere using methyl methacrylate (MMA) monomers using initiators such as benzoyl peroxide or potassium persulfate and heat by addition polymerization.



PMMA in Device Applications

- **Optical devices:** Used in lenses, optical fibers, and light guides due to high transparency.
- **Display panels:** Utilized in LCD and LED screens for light transmission.
- **Medical devices:** Applied in intraocular lenses, bone cement, and dentures.
- **Solar cells:** As a transparent protective layer and encapsulant.
- **Microfluidic devices:** Due to easy machining and chemical resistance.
- **Automobile parts:** Headlight covers and indicator lamps because of clarity and weather resistance.
- **Protective shields:** Used as a glass substitute in safety windows and aquariums.

Conducting Polymers

Conducting polymers are obtained by doping an oxidizing or a reducing agent into organic polymers with conjugated backbone consisting of alternating double and single carbon – carbon bonds.

Conducting polymers are classified as extrinsic and intrinsic conducting polymers. Extrinsic conducting polymers are prepared by mixing polymers with conducting fillers like metal fibres, metal oxides, carbon black etc. In these polymers' conductivity is not due to matrix polymer but due to added conducting fillers. In intrinsic conducting polymers, conductivity is due to organic polymers themselves which start conducting upon doping with suitable agents.

The important doping methods are

- a) **Oxidative doping (p-type doping):** The polymer is treated with an oxidizing agent like iodine, aluminium chloride, perchloric acid etc. Oxidizing agent takes away electrons from π -back bone of the chain creating a hole. Thus, polymer becomes p-type conductor as it conducts by the movement of holes.
- b) **Reductive doping (n-type doping):** The polymer is treated with a reducing agent like sodium or lithium naphthalids. Reducing agents supply electrons to π -back bone of the chain. The polymer becomes n-type conductor as it conducts by free mobile electrons.

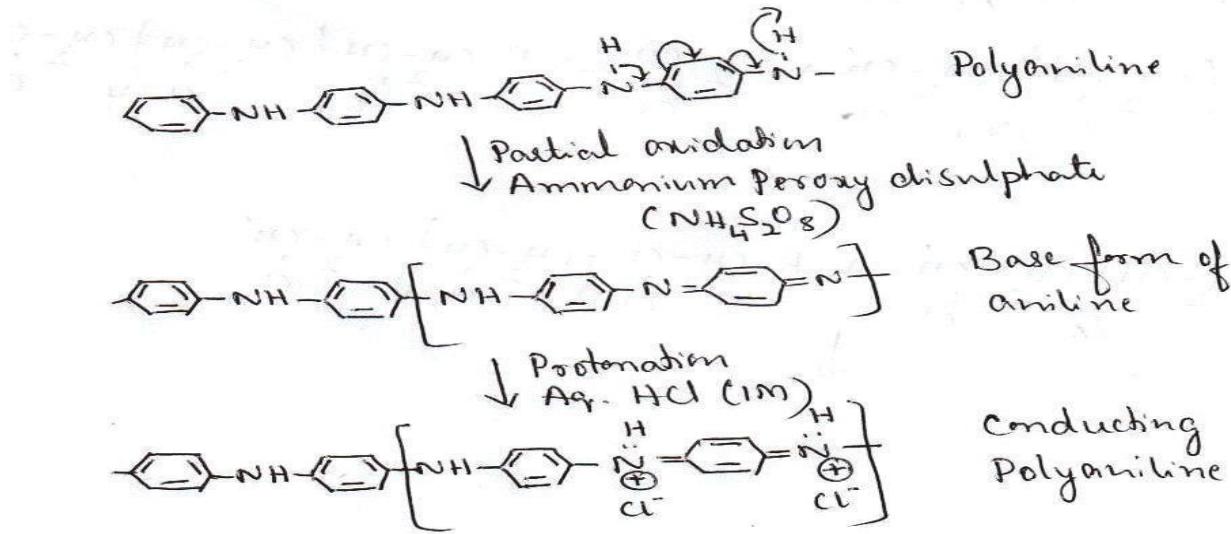
Synthesis of Polyaniline:

When n number of aniline molecules undergo oxidative polymerization in presence of dil HCl and ammonium persulfate to form polyaniline.



Mechanism of conduction in Polyaniline (PANI)

The synthesis of conducting polyaniline is an example of doping technique. In this technique current carrying species (-ve / +ve) are created by the protonation of imine nitrogen.



Polyaniline exists in several different oxidation states of which only emeraldine salt (Reduced form aniline) conducting.

Polyaniline is partially oxidized using a suitable oxidizing agent, into a base form of aniline which contains alternating reduced and oxidized forms of aniline polymer back bone.

Base form of aniline treated with aqueous HCl (1M), undergoes protonation of imine nitrogen atom, creating current carrying species (+ve) in the polymer backbone. These charges are compensated by the anions (Cl⁻) of the doping agent giving the corresponding salt.

Applications:

- **Conductive coatings** for electronics and textiles (antistatic applications).
- **Corrosion protection** on metals through protective coatings.
- **Chemical and biosensors** for detecting gases, humidity, and biomolecules.
- **Electrode material** in batteries, supercapacitors, and rechargeable devices.
- **Flexible electronics** such as OLEDs, wearable sensors, and smart textiles.
- **Electromagnetic interference (EMI) shielding** in electronic devices.
- **Environmental and biomedical applications**, including water purification and drug delivery.

Structure property relationship:

Crystallinity:

- **Linear polymers** have straight chains without side branches or large groups sticking out. This lets the chains pack closely and neatly, making them crystalline.
For example, **polyethylene** has a repeating unit: $-CH_2 - CH_2 - CH_2 - CH_2 -$, so the chain is straight, allowing the sections to line up easily.
- Polymers like **polyvinyl acetate** have branches:

These branches keep the chains from fitting closely, making them less crystalline.

- **Factors increasing crystallinity:**
 - Linear and regular chains, especially with polar groups, boost crystallinity.
 - Isotactic polymers, where all side groups are on the same side, are more crystalline than atactic polymers (random side groups).

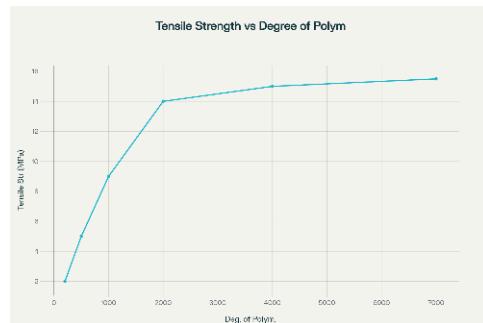
How Crystallinity Affects Properties

- High crystallinity makes polymers stronger, stiffer, opaquer, and less soluble in solvents.
- As crystalline increases, solubility decreases.

Tensile strength:

Tensile strength is the maximum stress that the material can withstand. Tensile strength of a polymer depends on the molecular weight. Tensile strength increases with molecular weight up to 2,000 and thereafter increase is negligible.

Low molecular weight polymers are soft and gummy, but high molecular mass polymers are tough and heat resistant. Cross-linked polymers are stronger than linear polymers and less than branched polymer.



Elasticity:

Elasticity is the ability of a polymer to stretch when a force is applied and to return to its original shape when the force is removed. This behavior occurs because the molecular chains uncoil during stretching and recoil when the force is released. Polymers exhibit elasticity as long as the chains do not separate from each other, preventing breakage during extended stretching.

Elasticity can be enhanced by:

- Introducing cross-links at appropriate molecular positions to connect the chains,
- Avoiding bulky groups such as aromatic and cyclic structures in the repeating units, which hinder chain movement,
- Incorporating more non-polar groups in the chain to increase cohesion between chains, thereby reducing chain separation during stretching.

Chemical Resistivity:

- Chemical resistivity of a polymer refers to its ability to resist swelling, softening, dissolving, and loss of strength when exposed to solvents or chemicals.
- Polymers containing polar groups such as $-\text{OH}$ or $-\text{COOH}$ are typically dissolved by polar solvents like water or alcohols.
- Polymers with non-polar groups such as $-\text{CH}_3$ and C_6H_5 are not easily dissolved by polar solvents but dissolve readily in non-polar solvents like petrol, benzene, and carbon tetrachloride.

- Polymers with a higher degree of crystallinity exhibit greater chemical resistance than their amorphous counterparts.
- Chemical resistivity increases as the degree of cross-linking in the polymer structure increases.

Quantum dots (QDs):

Quantum dots (QDs) are nanoscale semiconductor particles typically ranging from 2 to 10 nanometres in size. Due to their quantum confinement effects, QDs exhibit unique optical and electronic properties, such as size-dependent light emission. These properties make them highly valuable in various applications including display technology, solar cells, biomedical imaging, and quantum computing. Their ability to emit specific wavelengths of light by simply changing their size makes them a versatile tool in nanotechnology and materials science.

Surface-to-Volume Ratio:

As quantum dots decrease in size, their surface-to-volume ratio increases significantly. A greater proportion of atoms are located on the surface, which can influence chemical reactivity, electronic states, and optical behaviour.

Band Gap Variation:

The band gap in quantum dots is not fixed, unlike in bulk semiconductors. Due to quantum confinement, reducing the size of the QD increases its band gap energy. This size-dependent tunability of the band gap allows precise control over the color of light absorbed or emitted by the QD, making them highly useful in applications such as LEDs, lasers, and biomedical imaging.

Quantum Confinement Effect:

quantum confinement effect when they are very small—around the size of a few nanometers. At this tiny scale, the movement of electrons and holes inside the QD is limited in all directions. This causes the energy levels to become separate, like steps, instead of being continuous. As the size of the QD gets smaller, the gap between energy levels (called the band gap) becomes larger. Because of this, small QDs give off blue light, while bigger ones give off red light. So, the color of light from a QD depends on its size.

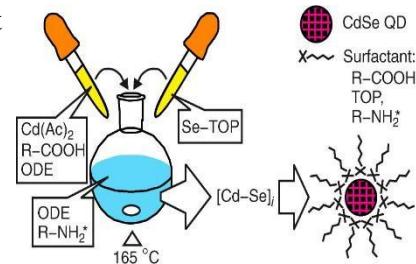
Synthesis of Cd-Se Quantum Dots by Wet Chemical Method

• Principle:

Cd-Se quantum dots (QDs) are semiconductor nanocrystals whose optical properties depend on particle size. They are synthesized by controlled wet chemical routes using cadmium and selenium precursors in the presence of stabilizers/capping agents.

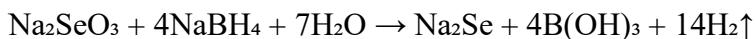
Selection of Precursors

- **Cadmium source:** CdCl_2 , $\text{Cd}(\text{CH}_3\text{COO})_2$, or $\text{Cd}(\text{NO}_3)_2$.



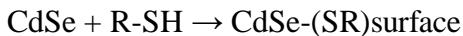


- **Selenium source:** Na₂Se, or Na₂SeO₃



- **Preparation of Reaction Medium:** Dissolve cadmium precursor in aqueous or organic solvent. Adjust pH to mildly alkaline if needed.

- **Addition of Stabilizer / Capping Agent:** Agents like mercaptoethanol, thioglycolic acid (TGA), or trioctylphosphine oxide (TOPO) are added. These prevent aggregation and control nanoparticle growth.



- **Nucleation and Growth:** Controlled heating (50–100 °C) with constant stirring. Selenium precursor is slowly introduced into the cadmium solution. Reaction is often carried out under inert atmosphere (nitrogen/argon) to prevent oxidation. Particle size (2–8 nm) is tuned by varying temperature, precursor ratio, and reaction time.



- **Separation and Purification:** The quantum dots are precipitated, centrifuged, and washed with solvents. Excess unreacted species and surfactants are removed.
- **Final Product:** Stable colloidal Cd-Se quantum dots with size-dependent photoluminescence (emission colours ranging from blue to red).

Applications:

- Optoelectronics: Used in light-emitting diodes (QLED displays), lasers, and photovoltaic cells.
- Biological Imaging: Serve as fluorescent probes due to tunable emission and high photostability.
- Solar Cells: Improve efficiency of quantum dot-sensitized solar cells (QDSSCs).
- Sensors: Employed in chemical and biosensors for detecting heavy metals, biomolecules, and pH changes.
- Photocatalysis: Useful in degradation of pollutants and water splitting for hydrogen production.
- Medical Applications: Potential use in targeted drug delivery and cancer therapy (though toxicity issues exist due to Cd).
- Quantum Computing: Investigated for qubit development due to discrete energy levels.

Quantum Dot Sensitized Solar Cells (QDSSC):

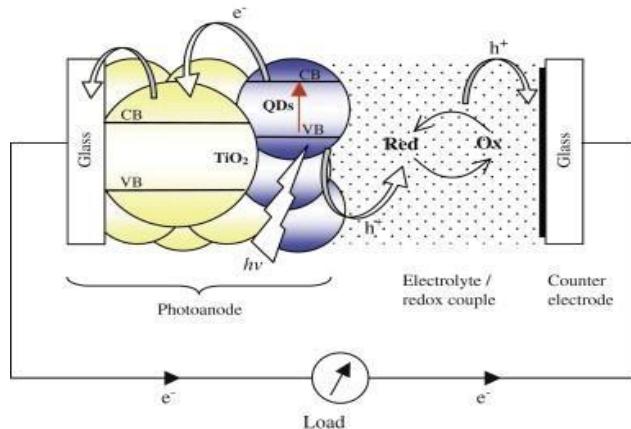
Introduction

- Quantum dots (QDs) are often referred to as *artificial atoms*.
- They are semiconductor nanocrystals, only a few nanometers in size, with unique optical and electronic properties distinct from bulk materials.
- A **Quantum Dot Solar Cell (QDSC)** is a photovoltaic device that uses QDs as the primary light-absorbing material.
- QDs can replace conventional bulky materials such as silicon or copper indium gallium selenide.
- Their band gap can be tuned by simply altering the size of the dots, making them highly adaptable across a wide range of energy levels.

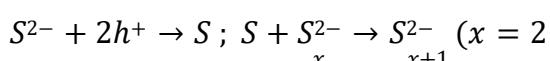
Construction

- **Photoanode:** A conducting glass substrate is coated with a semiconductor layer (commonly TiO_2). The outer surface is then sensitized with QDs.
- **Electrolyte:** A redox electrolyte, usually polysulfide, acts as a hole conductor and facilitates charge transfer.
- **Cathode electrode:** It helps regenerate the electrolyte and completes the circuit.

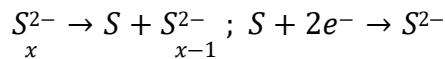
Working Principle



1. QDs absorb sunlight and electrons are excited from the valence band to the conduction band.
2. The excited electrons are transferred to the semiconductor layer, leaving holes behind on the QD surface.
3. The electrolyte captures these holes and undergoes reduction reactions:



4. Electrons move from the photoanode to the cathode through the external circuit, producing current.
5. At the cathode, the electrolyte is regenerated by gaining electrons:



Advantages

- High power-to-weight ratio with excellent efficiency.
- Low power consumption during operation.
- Cost-effective with improved electrical performance.
- Flexible in use, enabling applications not limited to rooftops but also windows and other transparent surfaces.

Disadvantages

- Cadmium selenide (CdSe)-based QDs are highly toxic and require a stable polymer shell for safe use.
- Cadmium and selenium ions are cytotoxic, raising environmental and health concerns.

Applications

- Biological labelling and imaging.
- Detection systems and fluorescence resonance energy transfer donors.
- Used in LEDs, photodetectors, photoconductors, and photovoltaic devices.
- Biomedical and environmental applications.
- Catalysis and chemical reactions.