ANALYSIS OF VARIOUS COMPONENTS IN DYE SENSITIZED SOLAR CELLS

Photocatalysis Assignment 1

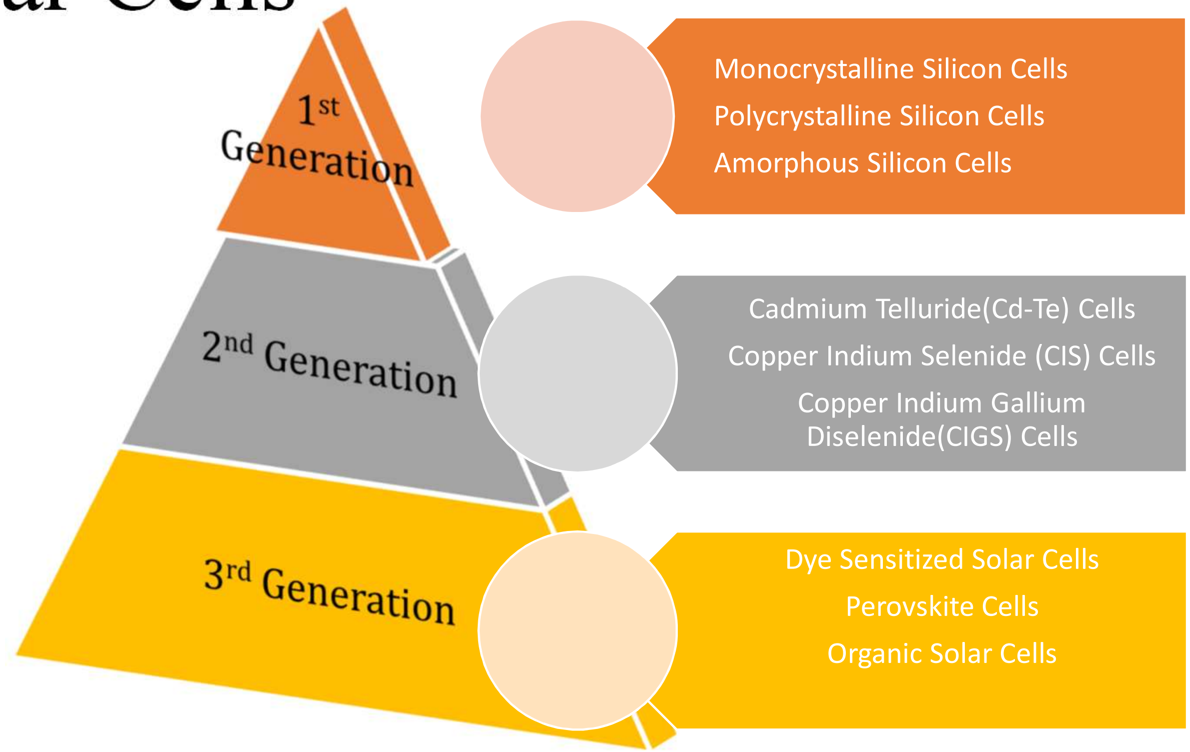
By,
Anjana Sa, ca21m003
Aditya Choudhury, ca21m002
Department of Chemical Engineering
IIT Madras

Solar Cells

- Solar Cells are devices that converts energy of sunlight to electricity by the process of photovoltaic. These are one of the best alternatives for conventional energy source.
- There different generations of solar cells based on the types of materials used.

i. **First Generation** solar cells are made from silicon, are currently the most efficient solar cells available for residential use and account for around 80+ percent of all the solar panels sold around the world. (p-n junctions photovoltaics)

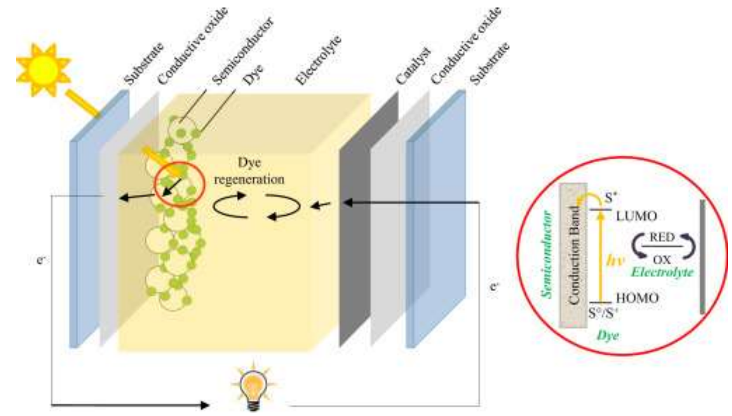
ii. **Second-generation** solar cells are usually called thin-film solar cells because when compared to crystalline silicon based cells they are made from layers of semiconductor materials only a few micrometers thick. The combination of using less material and lower cost manufacturing processes allow the manufacturers of solar panels made from this type of technology to produce and sell panels at a much lower cost. (thin film photovoltaics)

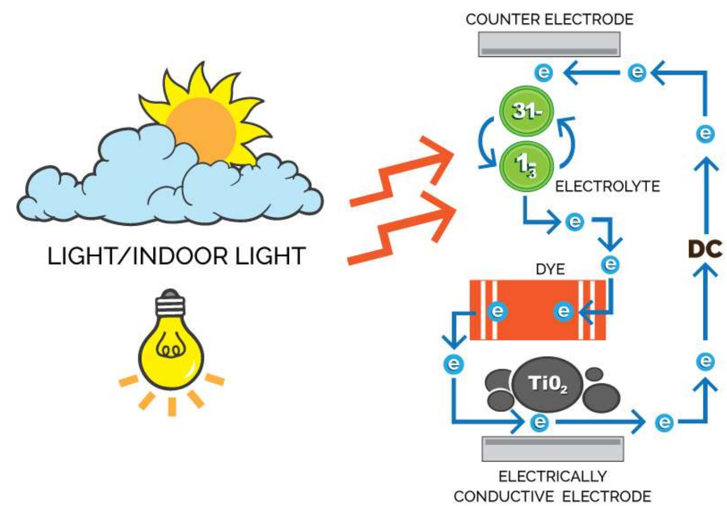


iii. **Third Generation** solar cells are being made from variety of new materials besides silicon, including nanotubes, silicon wires, solar inks using conventional printing press technologies, organic dyes, and conductive plastics.(multilayer thin film photovoltaics)

Dye Sensitized Solar Cells

- Dye Sensitized solar cells (**DSSC)** belongs to the group of third generation thin film solar cells.
- It is based on a semiconductor formed between a photosensitized anode and an electrolyte.
- Also known as Grätzel Cells, it was originally co-invented by Brian O'Regan and Michael Grätzel in 1988 at U C Berkley. This work was later developed by these scientists at EPFL until 1991.
- DSSC have been extensively under research for more than two decades due to their simple preparation methodology, low toxicity and ease of production.
- However, there is lot of scope for the replacement of current DSSC material due to their high cost, less abundance, and long-term stability. Hence we need to focus our research to tackle these obstacles.





Working and Schematics of DSSC

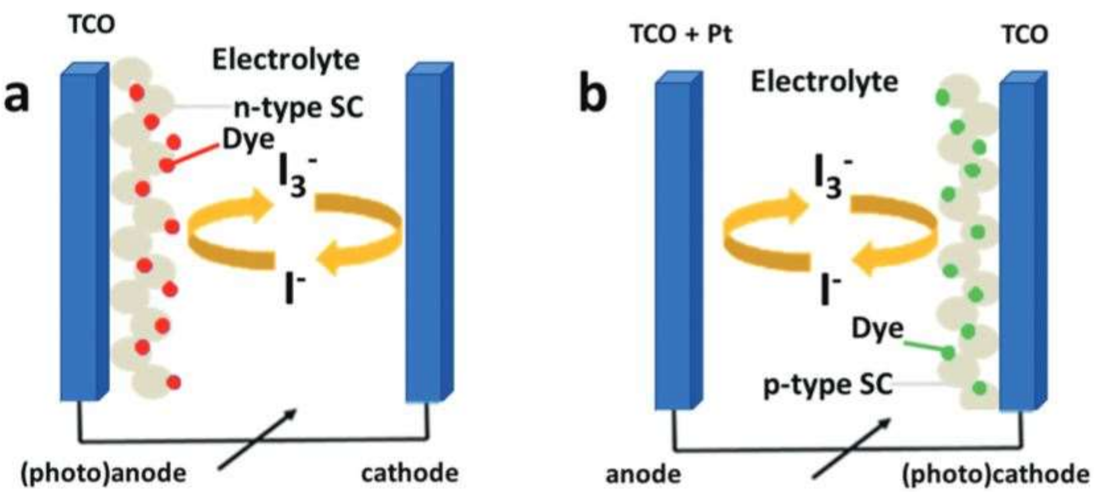
Dye Sensitized Solar Cells

There are 2 types of DSSCs

- n-type DSSC- charge movement is guaranteed by negative carriers (i.e. electrons).
- p-type DSSC- the charge movement is due to positive carriers(i.e. holes)

The major components (with examples) are

1. **Photoelectrodes/Working Electrodes**: for n-type it is a photoanode(TiO_2) and for p-type it is a photocathode(NiO). It is a mesoporous oxide layer.
2. **Photosensitizer(PS)/Dye:** porphyrin dye(p-type), Ru based dyes(n-type). It is a monomolecular layer adsorbed on the surface of the mesoporous oxide layer to harvest incident sunlight.
3. **Electrolyte:** usually an organic solvent containing a redox mediator, such as iodide/triiodide couple for the recovery of dye and the regeneration of electrolyte itself during operation
4. **Counter Electrode(CE):** Pt thin film on conducting substrate. Catalyzes the redox couple regeneration reaction and collect electrons from the external circuit.



The above figure is the schematic representation of DSSCs. The figure **a** is n-type and **b** is p-type.

Scientists involved in the field have deeply investigated the feasibility of a p-type DSSC. Unfortunately, the photoconversion efficiency of the "inverted" geometry/ p-type(inverted term is used to describe the direction) has never approached that of the conventional geometry (lower by one order of magnitude), despite the great efforts in tailoring photocathode materials and the development of dedicated sensitizers and redox couples. Hence for now, we will be focusing on describing about the n-type DSSC.

How DSSC Works?

The working principle of DSSCs involves 4 fundamental steps for the conversion of electromagnetic radiation coming from the sun into electrical energy. They are:

1. The initial step involves impingement of sunlight onto the dye which then undergoes photoexcitation.
2. Due to this excitation, electrons are generated. These electrons are then injected in the conduction band(CB) of the photoanode which then moves to the external circuit.
3. The electrolyte then supplies the electrons to the oxidized dye molecules for reduction, through the redox mediator (reactions of iodide and tri-iodide), so that the dye does not undergo decomposition.
4. At the cathode, the redox mediator in oxidized state (tri-iodide) eventually recovers an electron from the external load to complete the electronic circuit.

COMPONENTS

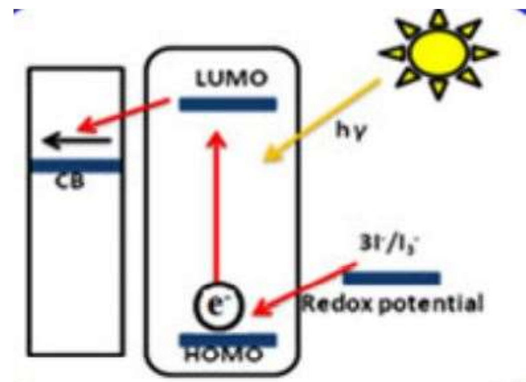
PHOTOSENSITIZERS/DYES

❖ Dye is the component of DSSC responsible for the maximum absorption of the incident light.

❖ The role of a sensitizer in DSSC is as a molecular electron pump.

❖ It helps in absorbing the visible light, pumping an electron into the conduction band of TiO2 layer, accepting an electron from the redox couple, and then repeating the cycle.

❖ A sensitizer should possess certain peculiar characteristics such as



1. The absorption spectra of the dye should cover ultraviolet-visible (UV-vis) and near-infrared region (NIR) regions.
2. The dye should have high stability in the oxidized, ground, and excited states
3. The dye should have suitable redox potential. The highest occupied molecular orbital (HOMO) should be located far from the conduction band of photoanode. The lowest unoccupied molecular orbital (LUMO) should be placed as close and higher than the conduction band.
4. They should have good efficiency in the charge injection (transfer of electrons to photoanode) and regeneration processes(electron transfer from electrolyte).

RUTHENIUM COMPLEX DYES

Ruthenium complex dyes are considered to be the most successful sensitizers because:

i. Ru(II) metal's octahedral geometrical structure tolerates extending of specific ligands in a controlled manner.

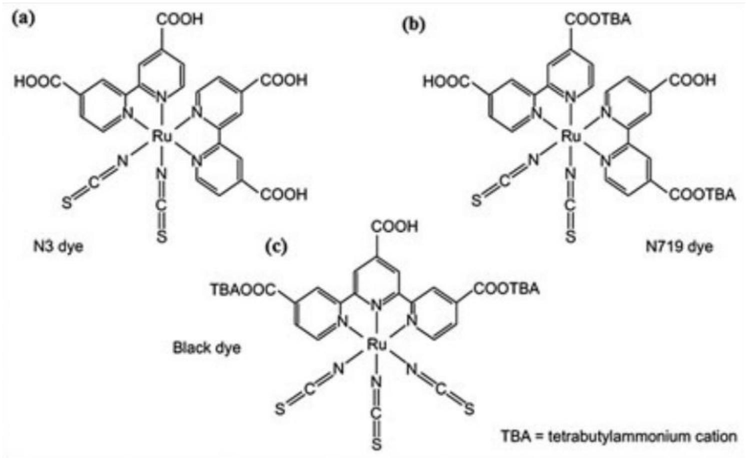
ii. We can tune the photophysical, photochemical and electrochemical properties of Ru(II) complexes.

iii. It possesses stable and accessible oxidation states from I to IV.

iv. They have good solubility in many solvents.

v. They have higher absorption in the visible range.

vi. They possess excellent electron injection, and efficient metal to ligand charge transfer.

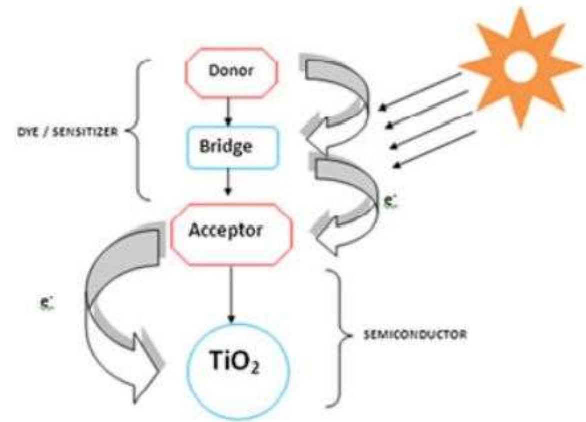


Examples of Ru based dyes

DISADVANTAGES OF RU BASED DYES

- Even though Ru based dyes are capable of yielding conversion efficiencies greater than 10%, their preparation normally requires multi-step procedures and time-consuming chromatographic methods.
- Ru metals are very rare and hence are costly.
- They are very toxic in nature due to its carcinogenic property.
- They have lo molar extinction coefficients and are restricted near infrared absorption.

Because of these disadvantages, research into Ru free dyes are being conducted. A good replacement for Ru dyes are Organic Dyes



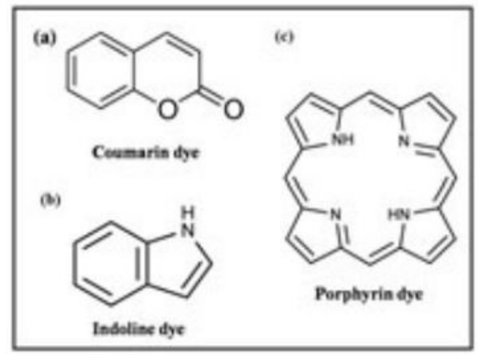
ORGANIC DYES

- These sensitizers consists of conjugated organic molecules.
- The molecular framework of these molecules consists of 3 major parts: Donors, Linkers and Acceptors.
- Linkers are usually π-conjugated system that link electron-donating (D) and electron-accepting (A) groups by bridges, the so-called D-π-A sensitizers.

ADVANTAGES OF ORGANIC DYES

Organic dyes have found to have many advantages over Ru dyes. They are:

1. They have high molar extinction coefficient
2. Based on the level of conjugation, the absorption range of these molecules can be tuned.
3. These are free from expensive and toxic metals
4. These have high stability under elevated temperatures
5. They are stable under prolonged illumination

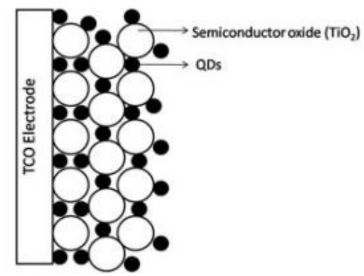


DISADVANTAGES

- The best conversion efficiency reached is still less than that of ruthenium dyes.
- Synthesis of these molecules and often be complex with low yield.
- During synthesis, costly metals are often used making it expensive.
- They can sometimes form aggregates on photoanodes making less efficient.

QUANTUM DOT SENSITIZERS

- Quantum Dots(QDs) are inorganic nanoparticles that are semiconductors have..
- Because of their properties, these nanoparticle can be used as sensitizers in DSSCs.
- These QDs are either adsorbed on photoanode from the colloidal solution or can be produced *in situ.*
- They have shown interesting properties like shift of excitonic peak to higher energy, blue shift in absorption band edge and below picosecond radiative rates of optical.
- Examples are CdS, CdSe



Schematic of (QD) sensitized DSSC photoanode.
TCO: transparent conducting oxide.

Advantages of QDs

- They possess excellent property of tunable size/shape-dependent energy bandgaps
- QDs have high optical absorption coefficients (α = ~100,000 cm^{-1})
- They have large dipole moments which leads to faster electron injection.
- They also have multiple exciton generation characteristics.

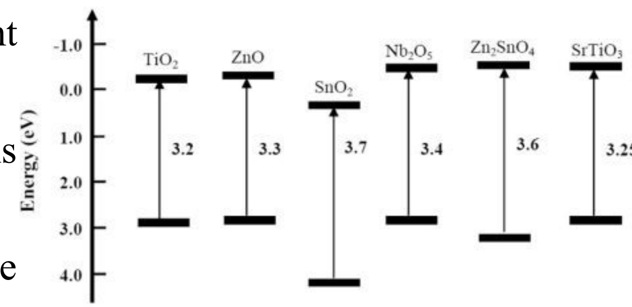
Disadvantatges

- Their efficiency is low(below 7%).
- They have higher rate of charge recombination.

COMPONENTS

WORKING ELECTRODE- PHOTOANODE

- A Photoanode is generally wide band gap semiconducting metal oxides (like TiO_2, SnO_2, ZnO, NbO_5 and $SrTiO_3$) that are coated over transparent conducting substrates.
- The metal oxide absorbs dye molecules, collects the photo-excited electrons and conducts photo-electrons from dye to the conducting substrates.
- The band gap, composition and morphology of metal oxides as well as the thickness of metal oxide layers influence the charge collection, transportation and light harvesting properties.



Examples of photoanodes and their band gaps

For an efficient photoanode, it should

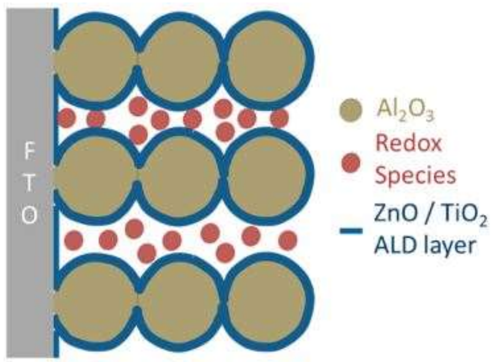
1. possess high surface area to enhance dye loading for effective light harvesting.
2. be transparent to visible light for minimizing the loss of incident photon.
3. hold the conduction band sufficiently below the lowest unoccupied molecular orbitals (LUMOs) of the dye to allow adequate injection of photo-generated electrons.
4. have high electron mobility for efficient electron transport,
5. not be active to the redox electrolyte to reduce electron recombination rate.
6. contain defects or hydroxyl groups or some other groups to attach dye molecules onto its surface.

TiO_2 AND ZnO PHOTOANODE

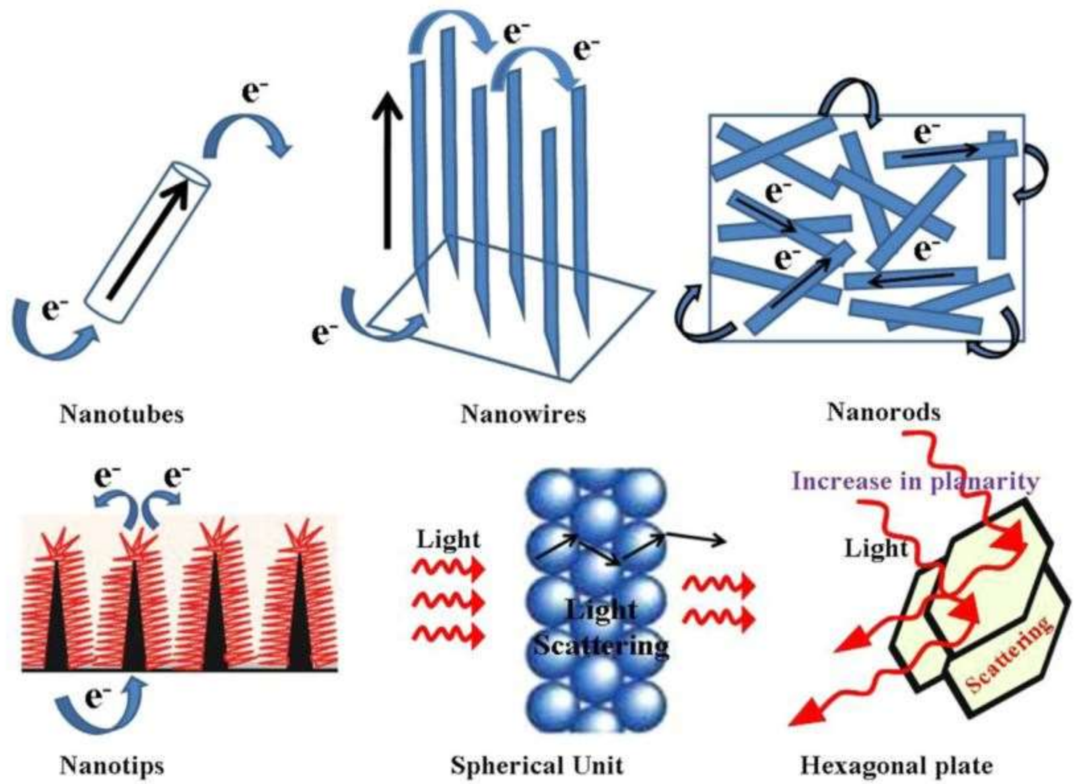
- TiO_2 mainly exists in 2 allotropes. They are Rutile and Anatase.
- Experimentally it has been observed that anatase has higher energy band gap(3.2eV) compared to that of rutile(3.0 eV) making it a better photoanode.
- ZnO also exists in 2 allotropes. They are Wurtzite and Zincblende.
- At ambient conditions, wurtzite allotrope is more stable and thus more common and easy to for research purposes
- Nanoparticle anatase TiO_2 is currently the material of choice for DSSCs as it has shown the highest efficiency of 12%
- Various properties such as electron mobility, stability, bandgap of both TiO_2 and ZnO has been tuned by varying

1. the size of the nanoparticle
2. by changing the shape of nanoparticles from spheres to rods.
3. by changing its arrangement from 1 dimensions(e.g. nanowires) to 2d(nanosheets) to 3d (nanorods with branching) structure.
4. Addition of dopants by suitable cations or anions will modify the band gap which in turn modulate the electrical properties of the anode.

Block diagram of the photoanode.



Screenprinted mesoporous alumina nanoparticles (green) are coated with different thicknesses of ZnO or TiO_2 overlayer (blue) by atomic layer deposition techniques. The brown dots represent the redox species in the electrolyte.



Schematic of electron transfer pathways and light propagating route in different nanostructures as photoanode

Advantages of TiO_2

a) Nanowires: Enhanced dye absorption. Efficiency= 7.11%

b) Nanosheets: High porosity. Efficiency= 5.77%

c) Electrospining materials: Better light harvesting nature. Efficiency= 10.3%

d) Nanosheets/nanoparticles: Effective light absorption of nanosheets and light absorption of nanoparticles. Efficiency= 7%

e) TiO_2 is advantageous in terms of electron recombination, as it is relatively inert to single-electron redox mediators.

Disadvantage:

Slower electron mobility

Advantages of ZnO

a) Nanowires: Sufficient interaction of dye with incident light. Efficiency= 2.63%

b) Nanosheets: Higher surface area and strong reflection quality. Efficiency= 1.82%

c) Nanodendrite/nanoparticle: Quasi-single-crystalline 3D framework helps in fast electron transport. Efficiency= 3.74%

d) ZnO is favorable for the systems demanding faster electron transport because of faster recombination rate

Disadvantages:

a. Lower efficiency

b. Expensive compared to TiO_2

COMPONENTS

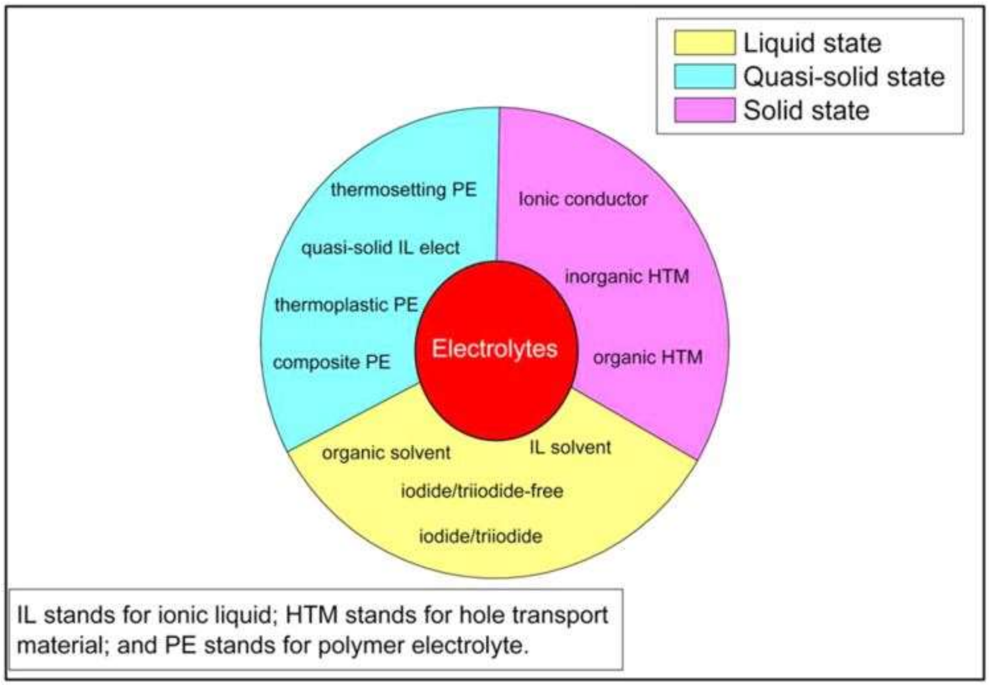
ELECTROLYTE

The electrolyte is one of the most crucial components in DSSCs as it is responsible for the inner charge carrier transport between electrodes and continuously regenerates the dye and itself during DSSC operation.

The following properties should be present in an electrolyte:

1. Redox couple should be able to regenerate the oxidized dye efficiently.
2. Should have long-term chemical, thermal, and electrochemical stability.
3. Should be non-corrosive with DSSC components.
4. Should be able to permit fast diffusion of charge carriers, enhance conductivity, and create effective contact between the working and counter electrodes.
5. Absorption spectra of an electrolyte should not overlap with the absorption spectra of a dye.

Classifications of Electrolyte



The electrolytes in DSSCs are broadly classified on the basis of their physical states, compositions, and formation mechanisms. They are **liquid state**, **quasi-solid state** and **solid state**

Factors affecting the transport mechanism

- In the electrochemical circuit of DSSCs, the electrons transport through TiO_2 crystalline film and the holes transport through the electrolytes or hole conductors.
- In this sense, electrolytes or hole conductors are hole-transport mediators. The basic function of electrolytes or hole conductors is the regeneration of dye and itself in DSSCs.
- Thus in order to understand how various electrolytes affect the efficiency of solar cells, we must analyze the factors that affect the movement of the charge carriers.

1. Rate of transport of the charge carriers.
2. the size of the redox species.
3. the viscosity of the solvent.
4. the concentration of the redox mediator.
5. the distance between the electrodes.

LIQUID ELECTROLYTES

- In 1991, using a very rudimentary liquid electrolyte consisting of an organic solvent and a dissolved iodide/triiodide redox couple without extra additives, *O'Regan* and *Gratzel* pioneered an efficient DSSC with an efficiency of 7.1−7.9%.
- They are composed of 3 parts- solvents, ionic conductor(redox couple), and additives.

a. Solvent: The solvent is a basic component in liquid electrolyte, and it gives an environment for the dissolution and diffusion of ionic conductor. Examples- Acetonitrile, ethylene carbonate

b. Ionic Conductor: They undergo redox reactions in order to regenerate the dye. They are then regenerated by the counter electrode. These ions transport charge carriers. Examples- I^-/ I_3^- , $SCN^-/(SCN)_3^-$

c. Additives: The redox couple potential, semiconductor surface state, shift of the conduction band edge, recombination kinetics, as well as the photovoltaic parameters of DSSCs can be improved by adding a small amount of additives. Examples 4-tert-butylpyridine, Li^+

- The liquid electrolytes possess some important features-

1. easy preparation
2. high conductivity
3. low viscosity
4. good interfacial wetting between electrolytes and electrodes and thus high conversion efficiency

- Today, liquid electrolytes are still the most widely utilized transport medium for DSSCs and have produced the highest efficiency of 13% for traditional DSSCs.

DISADVANTAGES:

a. The long-term instability caused by the leakage and volatilization of organic solvents limits its practical application.
b. They can undergo photo-degradation and desorption of dye
c. Can cause corrosion of counter electrode
d. They are ineffective in sealing of the cells for long-term applications

QUASI-SOLID STATE ELECTROLYTES

- Quasi-solid state or semisolid state is a special state of a substance between solid and liquid states.
- Quasi-solid-state electrolyte is a macromolecular or supramolecular nano aggregate system characterized by a remarkable ionic conductivity, usually higher than 10^{-7} S·cm^{-1} , for DSSCs, usually higher than 10^{-3} S·cm^{-1}
- Quasi-solid-state electrolytes always possess, simultaneously, both the cohesive property of solid and the diffusive property of liquid.
- There are three methods often used for preparing quasi-solid electrolyte.

i. liquid electrolytes are solidified by organic polymer gelators to form thermoplastic polymer electrolytes or thermosetting polymer electrolytes.

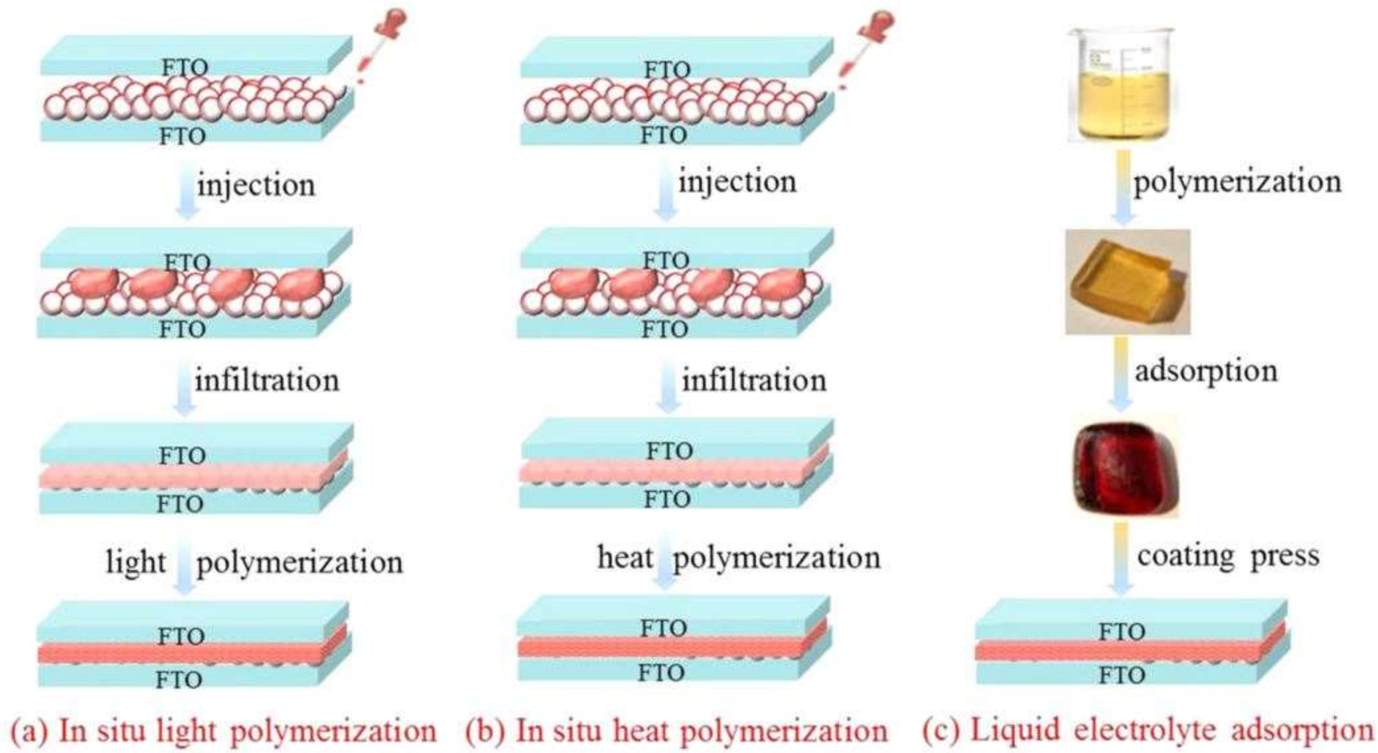
ii. liquid electrolytes are solidified by inorganic gelators, such as SiO_2, nanoclay powder, to form composite polymer electrolytes.

iii. ionic liquid electrolytes are solidified by organic polymer or inorganic gelators to form quasi-solid ionic liquid electrolytes.

- An important example is :PEG/PC/KI+I_2. (PEG= Polyethylene glycol, PC= Propylene carbonate, KI= Potassium Iodide). These together form the quasi-solid state electrolyte for DSSCs

For method (a) and (b), 1st the mixture of monomer, ionic conductor(iodide/triiodide) and solvent are taken and added to the fabricated dye and photoanode. Then light(for a) or heat(for b) is applied so that in situ polymerization occurs to form quasi-solid electrolyte(gel structures)

Problem with in situ light polymerization is the presence of I_2. I_2 is a free radical inhibitor even at low concentration. Therefore, the design of light sources and the choice of components are crucial.



The above figure shows different ways of preparing and fabricating a polymer based quasi-solid electrolyte

FTO- Fluorine doped tin oxide.
This is used as anode substrate

ADVANTAGES

- quasi-solid-state electrolytes show better long-term stability than liquid electrolytes.
- They have the merits of liquid electrolytes including high ionic conductivity and excellent interfacial contact property.
- Highest efficiency reached is 10%

DISADVANTAGES

- DSSCs efficiencies of general quasi-solid state electrolytes are lower than that of DSSCs with liquid electrolytes.
- This is due to the inferior mass-transfer rates of the redox couples in the highly viscous medium and high electron transfer resistance at the electrolyte/electrode interfaces owing to imperfect wetting of electrode pores with the electrolyte.
- Even though they are more stable compared to liquid electrolytes, they still contain solvents and are generally thermodynamically unstable.

SOLID-STATE TRANSPORT MATERIAL

- Instead of an electrolyte a transport material is used to transport the charge carrier.
- The solid transport material can be made from ionic conductors , inorganic hole transport material or organic transport material. The inorganic and organic hole transport material will work as a p-type DSSC.

ADVANTAGES

Solid-state conductors can basically meet long-term stability requirements for DSSCs

DISADVANTAGES

DSSCs efficiencies for solid state electrolytes are lower, which is due to poor electrolyte/electrode interfacial contacts.

COMPONENTS

COUNTER ELECTRODE (CE)

•The counter electrode, collects electrons from the external circuit and catalyzes the redox reduction in the electrolyte, which has a significant influence on the photovoltaic performance, long-term stability and cost of the devices.

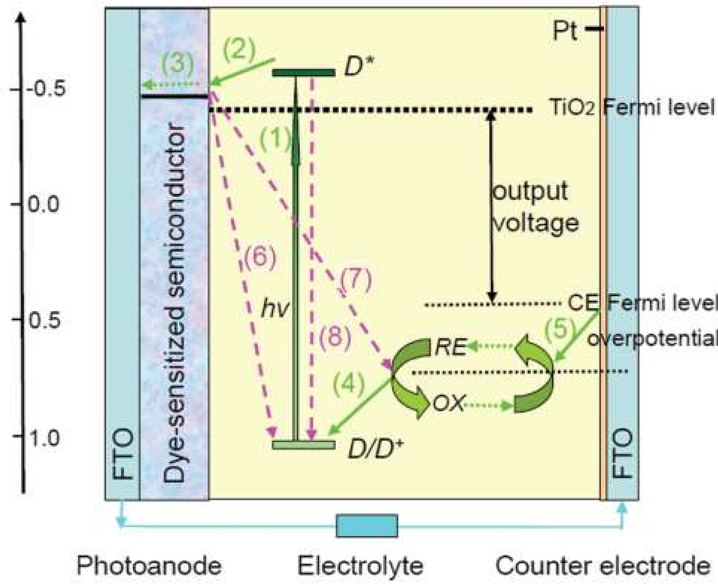
•In DSSCs, the CE undertakes three functions:

I. As a catalyst, it promotes the completion of process, which is the reduction of the oxidized redox couple by acceptance of electrons at the surface of the CE, and the reduction of the oxidized dye by collection of electrons via ionic transport materials in solid state DSSCs .

II. As a positive electrode of primary cells, it collects electrons from the external circuit and transmits them into the cell. Thus the ultimate function of the CE is to return the electrons from the external load back into the "circulation" within the cell.

III. As a mirror, it reflects the unabsorbed light from the cell back to the cell to enhance utilization of sunlight.

- According to these basic functions, an optimal CE should possess the following qualities as required: high catalytic activity, high conductivity, high reflectivity, low-cost, high surface area, porous nature, optimum thickness, chemical, electrochemical and mechanical stability, chemical corrosion resistance, energy level that matches the potential of the redox couple electrolyte, good adhesivity with TCO, etc.



Fundamental processes and constituent components of dyesensitized solar cells.

Types of Counter Electrode

Platinum counter electrodes:

- Platinum has been the most preferred counter electrode active material for DSSCs owing to high electrical conductivity, catalytic activity towards triiodide reduction, and high reflecting properties.
- The DSSCs with PCEs over 12% mostly use Pt as CE.

Advantage:

- Pt is a preferred CE active material for DSSCs by virtue of its excellent conductivity and catalytic activities for electrolyte regeneration, as well as good stability.

Disadvantage:

- Future large solar conversion systems producing electric power in the terawatt scale will prefer materials that are abundantly available. platinum is expensive and scarce in nature.
- Pt might not be stable over prolonged periods of time in the electrolyte containing I^-/I_3^- redox couples as may undergo oxidation and dissolution forming PtI_4 or H_2PtI_6.
- Pt is not an effective CE active material for redox couples such as cobalt-complexes, and polysulfide electrolytes used in DSSCs, owing to the energy match between counter electrodes and electrolytes.

Carbon counter electrodes:

- Several carbonaceous materials such as graphene, carbon nanotubes, carbon nanofibers, activated carbon, graphite, and carbon black have been successfully employed as counter electrodes.
- The highest PCE (14.3%) of DSSCs is based on the FTO/Au/GNP (graphene-nanoplatelet).

Advantages:

- Low cost, high surface area, high catalytic activity, high electrical conductivity, high thermal stability, good corrosion resistance towards iodine, high reactivity for triiodide reduction.

Disadvantages:

- Most of the performances of DSSCs based on carbon CEs are slightly lower than those assembled with Pt CEs, which may come from various resistances associated with carbon CEs, such as contact resistance to the TCO substrate, bulk resistance through the thicker carbon CE, and diffusion resistance in the pores of CE.
- Relatively low conductivity and catalytic activity compared to the Pt electrode.
- Carbon CE requires a large dosage to attain the targeted catalytic activity, and suffers from poor adhesion to the substrate.

Polymer counter electrodes:

- Conductive polymers are organic polymers that conduct electricity. Such compounds may have metallic conductivity or can be semiconductors.
- Most conductive polymers are derivatives of polyacetylene, polyaniline, polypyrrole or polythiophenes. The molecular structure feature of these polymers is conjugated double bonds for conduction.
- Conductive polymers are potential candidates used as Pt-free CE materials in DSSCs due to their facile synthesis, porous structure, electrical conductivity, low cost, abundance, and favorable catalytic properties.

Advantages:

- Conductive polymers are flexible, transparent, easily processed, and can be put into mass production easily.
- The properties of conductive polymers can be tuned easily.
- They show reasonable performance with respect to Pt counterparts.

Disadvantages:

- PEDOT (poly(3,4-ethylenedioxythiophene)) exhibits the best performance among conductive polymers, but its cost is comparable to that of Pt.
- PPy based CEs are cheaper but the performance is slightly inferior to that of PEDOT.

Transition metal compound counter electrodes:

- Transition metal compounds (TMCs), such as carbides and nitrides, have electronic structures similar to noble metal Pt, with interstitial phases or interstitial compounds, and they show Pt-like behavior.
- Some metal compounds including carbides, nitrides, chalcogenides, oxides, phosphides, and so on have been applied in DSSCs as CEs to replace expensive Pt CE

Advantages:

- Transition metal compounds have become a hot research area for CEs of DSSCs in recent years owing to their material diversity, low cost and Pt-like catalytic activity.
- They can be prepared by simple synthesis and can be easily modified.

Disadvantages:

- The performance of the TMC-based DSSC is relatively lower than that of the devices with other Pt-free CE materials, which might be explained by its poor conductivity for TMCs and the unreliable electron transportation between the TMC nanoparticles and conducting substrates.

ADVANTAGES OF DSSCS:

- Dye sensitized solar cells are the most efficient third-generation solar technology available & is greatly used in applications like rooftop solar collectors. The power production efficiency is around 11%, as compared to thin-film technology cells which are between 5% and 13%, and traditional commercial silicon panels which operate between 12% and 15%.
- In a silicon solar cell, it acts both as a source of electrons as well as an electric field provider, whereas in a DSSC, the semiconductor is used mainly for charge transport & the photo electrons are supplied by a different source(dye).
- DSSCs work even in low-light conditions. Hence they are very popular under cloudy weather conditions and non-direct sunlight, where traditional cells would be a failure. The cutoff in DSSC is so low they have been proposed for indoor usage, to collect energy for small devices from the lights in houses.
- A traditional solar cell is encased in glass with a metal at back for increasing its strength. Such setup may cause a decrease in its efficiency, as the cells heat up internally. However DSSCs are built up with only a thin layer of conductive plastic on the front side to allow radiation of heat much easily & quickly and therefore operate at low internal temperatures. Also the cell's mechanical structure is such that it indirectly leads to higher efficiencies in higher temperatures.

DISADVANTAGES OF DSSCS:

- DSSCs are not considered as an option, for large-scale deployments where higher-cost higher-efficiency cells are more viable. DSCC is not manufactured in commercial scale yet. The sharp cut in silicon solar panel costs have led other types of solar technology like Solar Thermal and Thin Film Technology taking a back seat.
- One of the major concerns in a dye sensitized solar cell design is the use of the liquid electrolyte, which is not very stable at varying temperatures. The electrolyte can freeze at low temperatures cutting power production and causing physical damage. Sealing the panels becomes a difficult task, when the liquid expands at higher temperatures.
- Another major drawback is the electrolyte solution, which contains volatile organic solvents and must be carefully sealed. Replacing the liquid electrolyte with a solid has been a major ongoing field of research.

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