



# POTENTIAL APPLICATION OF TITANIUM DIOXIDE IN SOLAR CELLS: A REVIEW

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**Abstract:** Titanium dioxide is widely studied due to its interesting properties such as wide band gap, crystalline nature, low cost, high refractive index and environment friendly. Titanium dioxide nanoparticles are suitable for many applications such as solar cells (anode material in solar cell), in batteries and also in antireflection coating. It affects the efficiency of solar cell & capacity in Li ion battery.

In the present work we discussed third-generation solar cells which are designed to achieve high power-conversion efficiency while being low-cost to produce. This review focuses on different types of third-generation solar cells such as dye-sensitized solar cells, Perovskite-based cells, and quantum dot solar cells. In these solar cells the TiO<sub>2</sub> is used as a photo anode due to its wide band gap, high refractive index and environment friendly nature. When TiO<sub>2</sub> is used as photo anode in DSSC then, its efficiency is increased up to 8.02%. Similarly, if TiO<sub>2</sub> is used as photo anode in QDSSC, its efficiency is increased up to 13.84%. TiO<sub>2</sub> used as an electron transport layer (ETL) in PSC, its efficiency reaches 13%. This also includes working principles and components of third generation solar cells. For Li-ion battery, TiO<sub>2</sub> has been used as an anode material due to its high structural stability, stable capacity and fast charge ability for lithium-ion insertion and desertion. This anode material avoids short circuit and battery explosion problem and also reduced the cost. TiO<sub>2</sub> enhances the performance of the third generation solar cells and Li-ion battery. Another application of TiO<sub>2</sub> is that it is used as an antireflective coating. TiO<sub>2</sub> as an antireflective coating reduces reflection and enhance light absorption.

**Key Words:** PSC - Perovskite Solar Cell, QDSSC- Quantum Dot Sensitized Solar Cell.

## 1. INTRODUCTION

Titanium dioxide is the oxide of titanium with a chemical formula of TiO<sub>2</sub> and was first discovered in 1791 from limonite (ore of titanium). Titanium dioxide (TiO<sub>2</sub>) attracted attention due to its wide band gap semiconductor (3-3.2 eV), large surface area, high catalytic activity, non toxicity and low cost [1]. TiO<sub>2</sub> belongs to the family of transition metal oxides. It is known to occur naturally in three crystalline phases: anatase, rutile and brookite (Figure.1.1). Comparing to these three structures, the rutile is more stable than the others. At temperatures above 550 °C, the anatase phase is transformed into the rutile phase. Anatase TiO<sub>2</sub> crystal structure comes within the tetragonal structure and it belongs to the space group I4<sub>1</sub>/amd. The anatase-phase unit cell contains four units of TiO<sub>2</sub> with 12 atoms. The three Ti atoms are each integrated with an O atom, they have an unattached structure in the same plane. It has one long bond and two short bonds. Rutile TiO<sub>2</sub> crystal structure also comes within the tetragonal structure and it belongs to the space group P4<sub>2</sub>/mnm. The rutile phase unit cell contains two units of TiO<sub>2</sub> with 6 atoms. The three Ti atoms are each integrated with an O atom; they have an unattached structure in the same plane. It has one long bond and two short bonds. Brookite TiO<sub>2</sub> crystal structure comes within the orthorhombic structure and it belongs to the space group Pbca. Its six Ti-O bonds also vary in length.

Figure 1.1 displays ball and stick models of the different tetragonal lattice systems for anatase, rutile and brookite. Moreover, rutile phase can be excited by both visible and ultraviolet (UV) light, whereas anatase is only excited by UV light and can be transformed into rutile at high temperatures. Brookite phase is not excited by UV light nevertheless its orthorhombic crystal system can be transformed into rutile by the use of heat. As shown in table 1, in case of the anatase tetragonal crystal structure, the lattice constants are, a = b = 3.78Å and c = 9.50Å. On the other hand the tetragonal structure of rutile has lattice constants are, a = b = 4.58Å, c = 2.95Å. The orthorhombic structure of brookite phase has lattice constants are, a = 5.43Å, b = 9.16Å, c = 5.13Å [1]. Because of its unique properties, titanium dioxide is widely used and is well known in nanoscience and nanotechnology. Nanoparticles (NPs) are generally defined as particles having at least one dimension smaller than 100 nm. Micro sized and Nano-size titanium dioxide is chemically identical because of its higher specific surface area; nano-powders may exhibit physical and chemical properties. Nano-sized TiO<sub>2</sub> in various forms is used widely in everyday life in a variety of products, such as in paints, household products, medications, cosmetics, sunscreens, pharmaceutical additives and food colorants, and many new applications are under development.

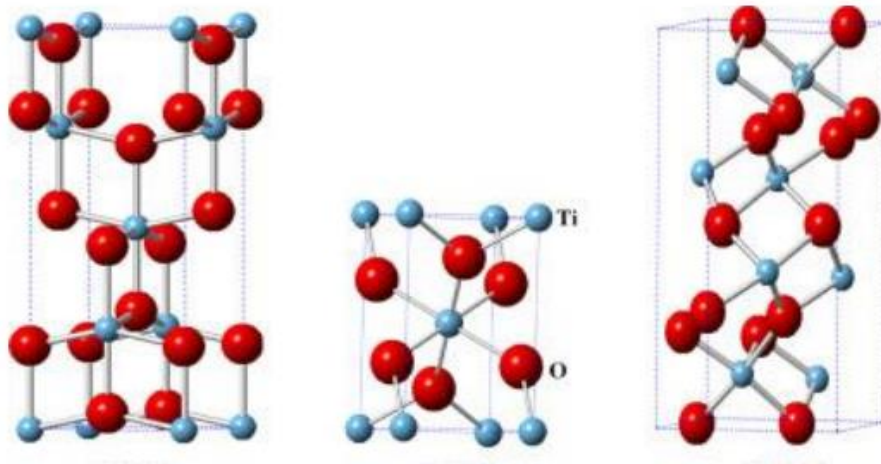


Figure 1.1: Crystal structures of Anatase, Rutile and Brookite [2].

Table1: Structural characteristics of TiO<sub>2</sub> crystalline phases [3]

Properties	Rutile	Anatase	Brookite
Crystal structure	Tetragonal	Tetragonal	Orthorhombic
Space group	P4 <sub>2</sub> /mnm	I4 <sub>1</sub> /amd	Pbca
a(Å)	4.58	3.78	5.43
b(Å)	4.58	3.78	9.16
c(Å)	2.95	9.50	5.13
α (°)	90	90	90
β (°)	90	90	90
γ (°)	90	90	90
Band gap (eV)	3.0	3.2	2.96
Ti-O bond length(Å)	1.949(4) 1.980(2)	1.937(4) 1.965(2)	1.87~2.04
Density(g/cm <sup>3</sup> )	4.250	3.894	4.120

Usage of TiO<sub>2</sub> in solar cells has gained much attention due to the increasing performance of the cell [4]. Various types of semiconductors are used as photo anodes in solar cells like perovskite solar cell, dye-sensitized solar cell, metal oxide solar cell and quantum dot solar cell. But Titanium dioxide is an ideal semiconductor in the solar cell as it absorbs ultraviolet light and let only visible light pass through them.

As per our daily demands and in our day to day life, use of batteries increased in previous some years. Batteries are classified into two: rechargeable and non-rechargeable batteries. The rechargeable batteries are widely used. Lithium-ion batteries are one of the types of rechargeable battery. LIBs used graphite as anode material but because of several problems, titanium dioxide is now used as anode material.

Antireflective coatings can be made from various materials, like silicon dioxide or titanium dioxide. Multiple layers of different materials can also be combined to create more sophisticated coatings that provide improved antireflection across a broader range of wavelengths. These coatings are an important component in increasing the efficiency of solar cell.

## 1.1 Properties of Titanium Dioxide

### 1.1.1 Crystal Properties

TiO<sub>2</sub> exists in three polymorphic forms: anatase, rutile and brookite, based on the conditions of fabrication and post fabrication heat treatment. Both the anatase and rutile phases possess tetragonal crystal structures even though they do not belong to the same phase groups, while brookite has an orthorhombic structure. As shown in Figure 1.1, the distortion of anatase phase octahedral structure is slightly larger than that of rutile. With respect to solar cell application, anatase phase TiO<sub>2</sub> is chosen over other phases as a result of its low density, high electron mobility, and low dielectric constant. As a consequence of the anatase phase low density, it easily undergoes transition to the rutile phase at high temperatures. This observed transformation is not only temperature dependent but is also affected by some other factors such as doping concentration, initial phase and particle size [5].

### 1.1.2 Optical Properties

Several other structural parameters such as phase composition, band gap, crystalline quality, and particle size have been reported to influence the optical activities of TiO<sub>2</sub> nanoparticles. In pure TiO<sub>2</sub>, the anatase phase shows superior catalytic ability and electron mobility than rutile or brookite phases, a property that is beneficial for photovoltaic applications. The increased photo reactivity of the anatase phase has been linked to its low oxygen adoption capacity [5].

On exposure of TiO<sub>2</sub> nanoparticles to UV light, the electrons in their valence bands (VB) gain energy and as such undergo excitation to corresponding conduction bands (CBs), thus generating holes (h<sup>+</sup>) on those VBs (Figure 1.2). At this instance, the excited electrons (e<sup>-</sup>) are purely in 3d states, and due to dissimilar parity, the probability for e<sup>-</sup> transition is reduced, with attendant decrease in the e<sup>-</sup>/h<sup>+</sup> recombination. In this respect, the anatase phase is regarded as the active photocatalysis component that is also attributable to the generation of charge carriers (e<sup>-</sup> and h<sup>+</sup>) that arise from its ability to absorb UV light, which is in correspondence with its band gap. The rutile phase is generally regarded as a poor photo catalyst, due to the fact that the bulk recombination of h<sup>+</sup>

and  $e^-$  takes place. These  $h^+$  subsequently interact with the molecules of  $H_2O$ , thereby forming hydroxyl radicals ( $OH^\bullet$ ) that in synergy with the  $h^+$  effectively oxidize the organic compounds in their vicinity on the surface of the particles. Also, the  $e^-$  in the CB interact with air molecular oxygen following a reduction reaction process, thereby producing superoxide radical anions ( $O_2^{\bullet-}$ ). It is worthy to note that the charge couple ( $e^-/h^+$ ) redox potential of an ideal photo catalyst is expected to fall within the domain of its band gap. Additionally, the reduction activity of photoelectrons is determined by existence of energy level on the bottom of the CB of the photo catalyst, while the oxidation activity of photo generated  $h^+$  is a function of the energy level on top of the photo catalyst VB. Based on these properties,  $TiO_2$  nanoparticles are considered as near-ideal photocatalysis as their  $h^+$  are redox selective and strongly oxidized, dramatically increasing more research into nano-sized  $TiO_2$ -based photocatalysis.

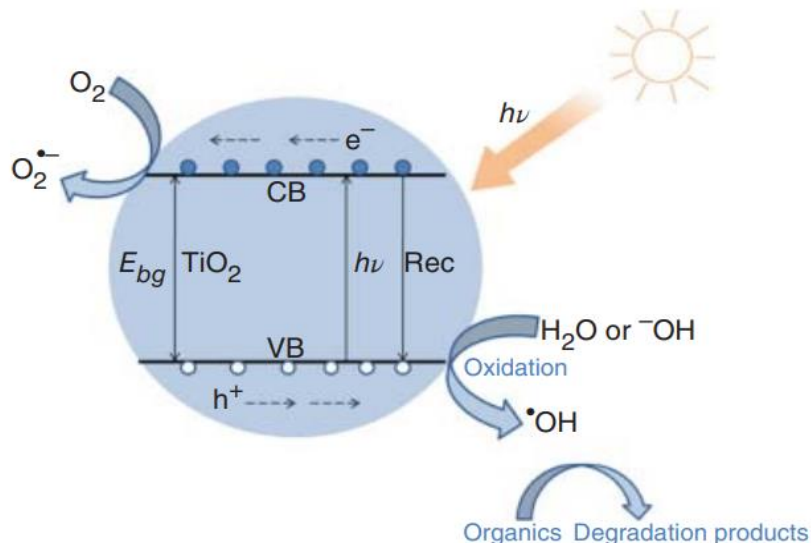


Figure 1.2: Illustration of general mechanism of  $TiO_2$  in solar photocatalysis process [5].

### 1.1.3 Electrochemical Properties

The chemical and physical properties of nano- $TiO_2$  are described by their electronic structure, size, shape, surface properties, and organization. The electronic properties of  $TiO_2$  nanoparticles have been reported as huge contributors to their particle and crystal-size distributions.  $TiO_2$  in its pure form is a wide band gap n-type semiconductor that possesses indirect energy band gaps of the rutile, anatase, and brookite phases of 3.02, 3.2, and 2.96 eV, respectively [5]. It has also been reported that rutile fermi level is lower than the anatase by  $\sim 0.1$  eV. Anatase has a smaller electron effective mass than rutile, resulting to an increase in mobility for the charge carriers in anatase, a characteristic that is highly favorable for optoelectronic devices production.

## 1.2 Synthesis of $TiO_2$ nanoparticles by Different Methods

The various synthesis methods of  $TiO_2$  nanoparticles are shown in Figure 1.3.

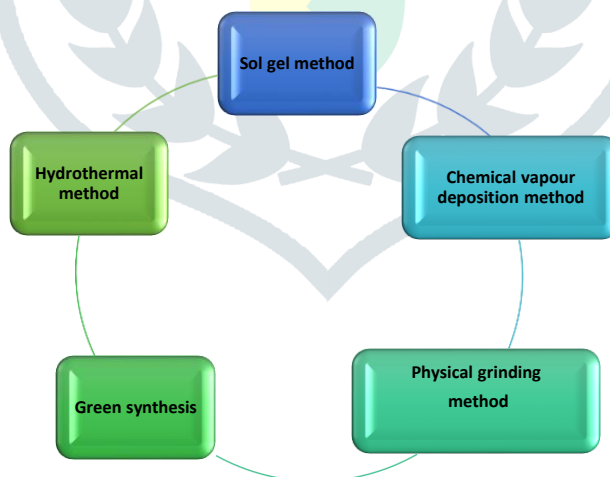


Figure 1.3: Different Methods of Synthesis Of  $TiO_2$  nanoparticles.

### 1.2.1 Physical grinding method

Physical grinding method is adopted for the size reduction of  $TiO_2$  powder. A quantity of  $TiO_2$  powder was put in a grinding machine which having high speed rotator. It was uniformly grinded and crushed well for 15 minutes with utmost precaution to avoid any contamination. At the end, the finely grinded powder was separated. Thus, the bulk  $TiO_2$  powder was made as nano-sized powder [6].

### 1.2.2 Sol-gel method

The sol-gel process is a wet chemical and cost effective method for the synthesis of various metal oxide nanoparticles. In this method, the molecular precursor (metal alkoxide) is dissolved in water or alcohol and converted to gel by heating and stirring by hydrolysis/alcoholysis. Since the gel obtained from the hydrolysis/alcoholysis process is wet, it should be dried using appropriate

methods. For example, if it is an alcoholic solution, the drying process is done by burning alcohol. After the drying stage, the produced gels are powdered and then calcined. The different stages of sol-gel method are shown in Figure 1.4.

For the preparation of TiO<sub>2</sub> nanoparticles via sol-gel process, ethanol was mixed with deionized water under constant stirring. Further, TTIP (titanium tetraisopropoxide) was mixed in the above solution under constant stirring while maintaining the temperature at 85 °C and gel was formed. After forming the gel, it was dried in the oven at temperature 60 °C. The calcination was performed for 3 h at 400 °C and the TiO<sub>2</sub> nanoparticles are obtained [7].

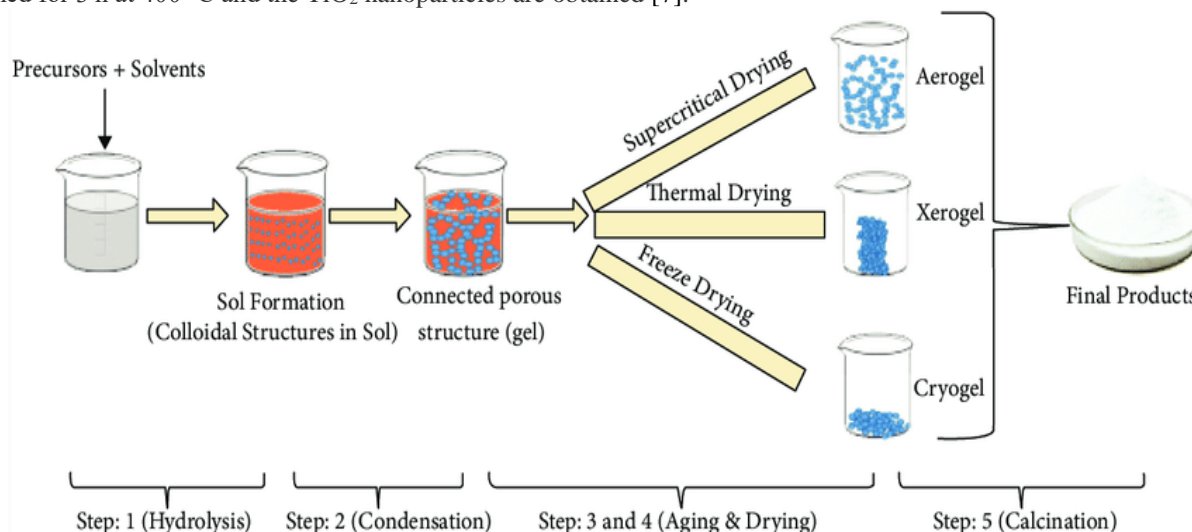


Figure 1.4: Different stages of Sol Gel process [8].

### 1.2.3 Green synthesis method

The green synthesis process is environmental friendly technique, because it uses the extracts of plant parts such as peels, leaves and flowers. It is a one of the best method as it does not require any high end equipments, hazardous chemicals and high temperatures. The TiO<sub>2</sub> nanoparticles is synthesized using orange fruit Peel extract [9]. Orange peel acts as reducing agent for synthesis of TiO<sub>2</sub> because it contains Citric acid as main source.

Orange peel was collected from the orange fruit, make it into small pieces, then orange peel was directly taken into the beaker and extracted with water for 2 hrs at 90°C. The extract was filtered by using filter paper. The filtrate was stored for the further synthesis of nanoparticles as shown in Figure 1.5. Dissolve titanium tetra isopropoxide in distilled water for synthesis of TiO<sub>2</sub> nanoparticles. Added extract drop wise under constant stirring up to achieve pH of solution became 7.

In this process formation of nanoparticles were occurred, separate this nanoparticles using filter paper and washed the materials with distilled water repeatedly to remove the by-products. The obtained wet nanoparticles were dried at 80°C for overnight. Finally particles were calcinated at 600°C for 3 hours for obtaining Rutile phase.

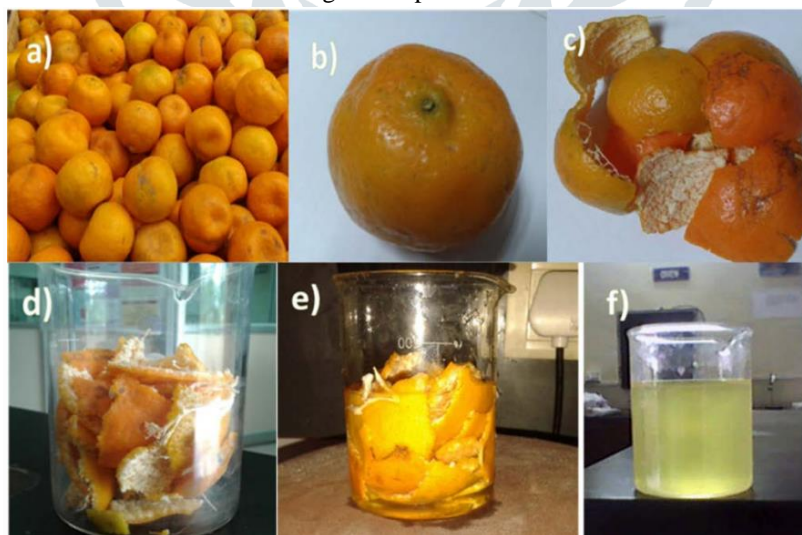


Figure 1.5: (a) Collection of orange fruits, (b) single orange fruit, (c) Orange fruit waste, (d) Cutted pieces of Separated petals, (e) while extracting, (f) Juice of orange peel extract [9].

### 1.3 XRD pattern of TiO<sub>2</sub> nanoparticles

The XRD analysis of the prepared sample of TiO<sub>2</sub> nanoparticles was done using a Bruker make diffractometer, Cu-K $\alpha$  X-rays of wavelength ( $\lambda$ )=1.5406 Å and data was taken for the 2 $\theta$  range of 10° to 70° with a step of 0.1972°. The X-ray diffraction pattern of the synthesized TiO<sub>2</sub> nanoparticles is shown in Figure 1.6. Varshney et al. reports that absence of spurious diffractions indicates the crystallographic purity. The 2 $\theta$  at peak 25.4° confirms the TiO<sub>2</sub> anatase structure. Strong diffraction peaks at 25° and 48° indicating

TiO<sub>2</sub> in the anatase phase. There is no any spurious diffraction peak found in the sample. The 2θ peaks at 25.27° and 48.01° confirm its anatase structure. The intensity of XRD peaks of the sample reflects that the formed nanoparticles are crystalline and broad diffraction peaks indicate very small size crystallite [6].

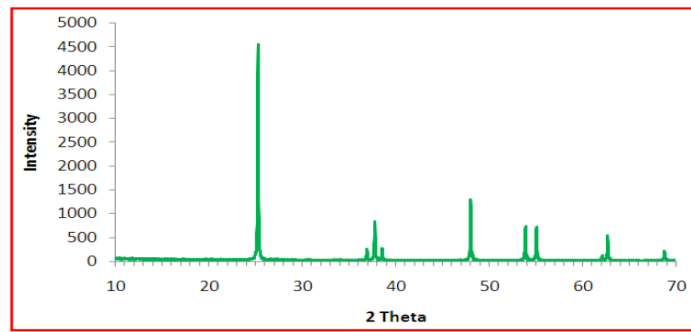


Figure 1.6: XRD pattern of TiO<sub>2</sub> nanoparticles [6].

## 2. PHOTOVOLTAIC CLASSIFICATION

Energy can neither be created nor be destroyed but can be converted from one form to another form. This is the law of conservation of energy. Nowadays, energy and environmental requirements had led to the widest challenges all over the world. The huge increase in global consumption has encouraged searching for alternative energy sources with threat that fossil energy resources may soon be depleted. Currently about 59% of world energy consumption comes from fossil fuels (natural gas, coal, oil). 9.6% comes from nuclear power & 31.4% from renewable energy.

Energy sources are classified into two types:

### Non-Renewable sources

They include coal, oil, natural gas & nuclear power. Today fossil fuels are used in power plants to produce electricity. They are not environment friendly & can have serious impact on our health. They also contribute to global warming. So we are looking for renewable energy sources.

### Renewable sources

Renewable energy is commonly characterized as an energy that originates from natural replenished resources. For example, wind, sun light, etc. It replaced traditional fuels in several areas such as electricity production & motor fuels etc. Solar cells are the one of the safest & cheapest way to produce electricity. The solar cell is an electrical device which directly converts solar energy into electricity. They also do not emit any green house gas or harmful material.

Solar cells are classified into different generations based on technology, methods & its evolution as shown in Figure 2.1.

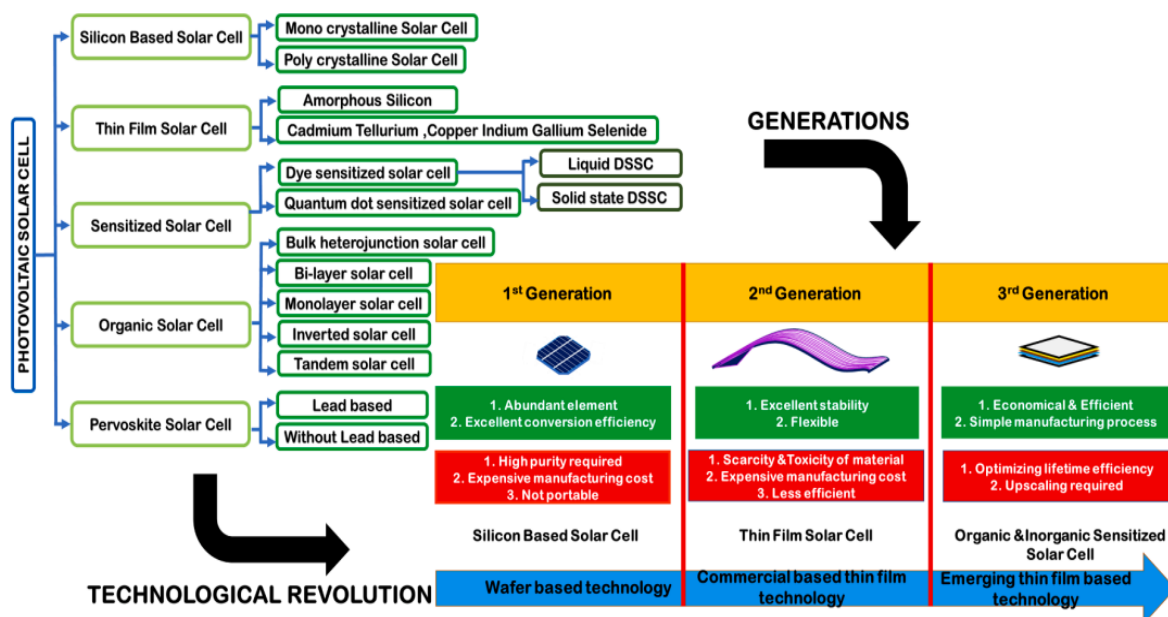


Figure 2.1: Photovoltaic classification and its generations explaining side and disadvantage side with physical appearance. (Green background showing advantages and red background showing disadvantages) [10].

### 2.1 Dye Sensitized Solar Cells

One of the most exciting technological advancements in the world of solar cells is the DSSC. It functions as a cell that mimics the method used by plant cells to produce energy. The electron moment produced by the combined influence of the photon energy & the chemical reaction is a photo-electrochemical cell. The DSSC has the potential to be an energy source in the future because it is

less expensive than traditional solar photovoltaic's. The photoanode, sensitizer, electrolyte and counter electrode are the essential elements of DSSC. The photo anode is developed using semiconductor nanostructures. On the transparent conductive glass, a variety of nanostructures including nanorods, nanotubes and nanowires have been created.

### History of dye sensitized solar cells

Dye sensitized solar cells were first published in 1972, in which zinc oxide was used as photoanode and was sensitized by using chlorophyll. It was demonstrated that the generation of electricity by exciting the dye (chlorophyll) molecules using photons and the electrons were moved to the external circuit through the semiconductor. But its efficiency was low. In 1991 Swiss scientist Professor Gratzel used the mesoporous  $\text{TiO}_2$  electrodes alongside with the Ruthenium-based natural organic dyes showed an efficiency of over 7% [11]. After going through numerous improvement phases, DSSC technologies have achieved 14.2% power conversion efficiency (PEC) in 2020, which was surpassed in 2022 by Ren et al. who reported a figure of 15.2% [23].

#### 2.1.1 Components of Dye-Sensitized Solar Cell

The various components of DSSC are shown in Figure 2.2.

##### Transparent conductive oxide (TCO)

TCO is a wide band gap n-type semiconductor with a high free electron concentration. As Fluorine doped Tin oxide (FTO) and Tin doped Indium oxide (ITO) have good electrical conductivity, high transparency and low material expenses they are most well-known TCO.

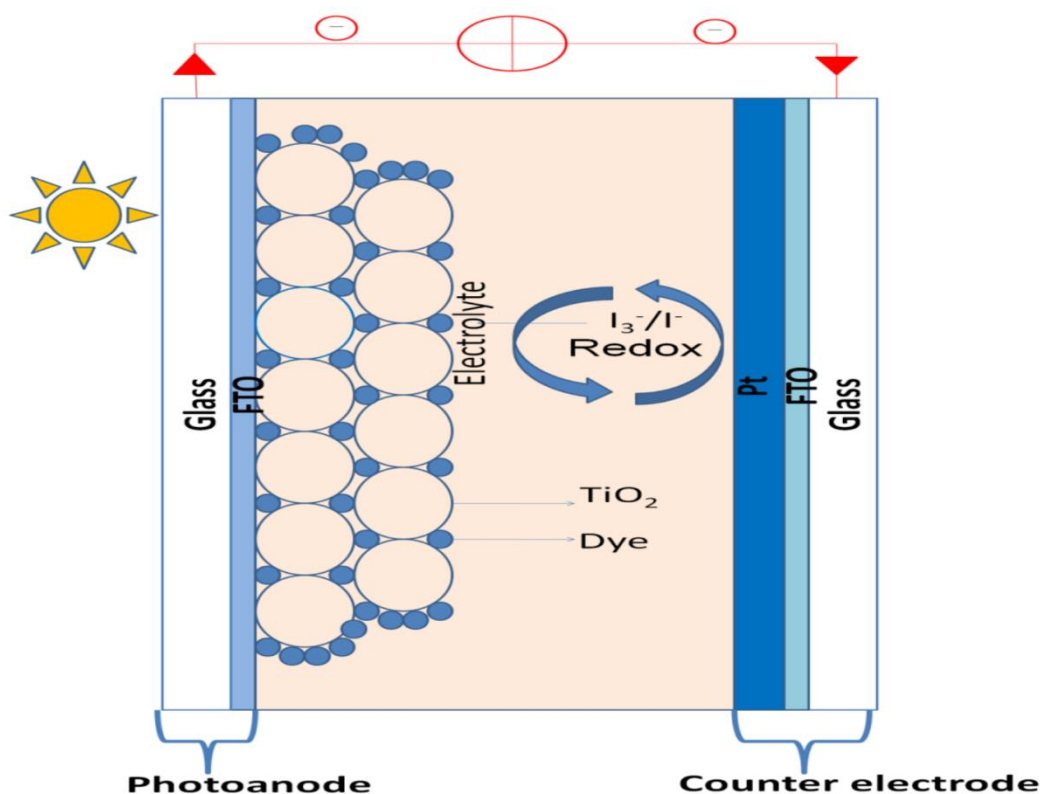


Figure 2.2: Schematic diagram of dye-sensitized solar cell [11].

##### (a) Indium doped Tin oxide (ITO)

ITO has been one of the most widely used TCO because of its high diffusion and high conductivity. However, when the material is placed at a temperature over  $300^{\circ}\text{C}$ , its conductivity decreases. This is caused by the decrease in oxygen vacancies in the decrease of electric carriers. Furthermore, the cost and toxicity of the material cause the researchers to find a better alternative.

##### (b) Fluorine doped Tin oxide (FTO)

FTO is another type of TCO that is widely used especially in solar cells. This is because of good stability at high temperatures and its less cost compared to ITO [11].

##### Photoanode

The photoanode is made up of semiconductor nanoparticles placed on transparent conducting glass that has been dye sensitized. For the photoanode, numerous semiconductor oxides such as  $\text{ZnO}$ ,  $\text{SnO}_2$  and  $\text{TiO}_2$  are used as a material. Among these semiconductor oxides,  $\text{TiO}_2$  has received more attention due to its wide band gap, availability, low cost, and lack of toxicity. Also, its conduction band edge lies somewhat marginally below than the excited state energy level of numerous dyes. This is a condition for efficient electron injection [23].

The semiconductor plays a vital role in a DSSC, since it acts as a substrate for the absorption of dye and receives electrons from the dye. The dye, upon photo-excitation, introduces the electron into the semiconductor conduction band, where it is further

transferred to the counter electrode, completing the circuit. TiO<sub>2</sub> nanoparticles are frequently utilized because of their excellent dispersion and crystallinity. Anatase, brookite and rutile are the three most stable polymorphs of TiO<sub>2</sub>; the complex synthesis process of the brookite makes it the least common among the mentioned polymorphs of TiO<sub>2</sub>. The solar energy conversion performance of anatase and rutile to some extent is the same; however, anatase is favored over rutile due to its superior charge transport, larger specific area and higher electron Fermi level. In addition, anatase has a band gap of 3.2 eV compared to 3.0 eV for rutile, resulting in greater conduction band energies for the anatase form. Researchers are working hard to create different nanostructures for anatase such as nanorods, nanofibers and nanowires using different synthesis techniques including hydrothermal, physical vapor deposition and chemical vapor deposition. Screen printing, doctor blade and spin coating are the different techniques used for coating TiO<sub>2</sub> on the conducting glass substrate.

### Dye materials

The dye in a DSSC plays a very important role- that is, to absorb solar energy and converts it into electrical energy [23]. By keeping the role of a dye in DSSC in mind, some key conditions are required for a dye to be considered efficient, namely:

- (i) It should be capable of maximum absorption from the visible region and near infrared region.
- (ii) It should have excellent binding with anode material.
- (iii) The anode material conduction band must be low compared to the LUMO (Lowest Unoccupied Molecular Orbital) of a dye.
- (iv) The anode material conduction band must be high compared to the HOMO (Highest Occupied Molecular Orbital) of a dye.
- (v) The anchored groups strongly bond the dye with the photoanode surface. The most common anchoring group is a carboxylic acid (-COOH), which shows good stability.

Premetallized, natural and metal-free synthetic organic are the three different types of dye sensitizers. Figure 2.3 shows the various types of dyes. Among the mentioned sensitizers, premetallized sensitizers exhibit the highest efficiency and greatest stability. However, manufacturing these dyes is difficult, costly and harmful to the environment. Metal-free synthetic organic sensitizers such as premetallized sensitizers required a complicated production procedure. On the other hand, natural dyes can easily be extracted from leaves, fruits and stem etc. Premetallized and metal-free synthetic organic dye-based DSSCs have high efficiency compared to natural dye based DSSCs. But natural dyes do not need any complex preparation process and are cheap, non-toxic and environment friendly.

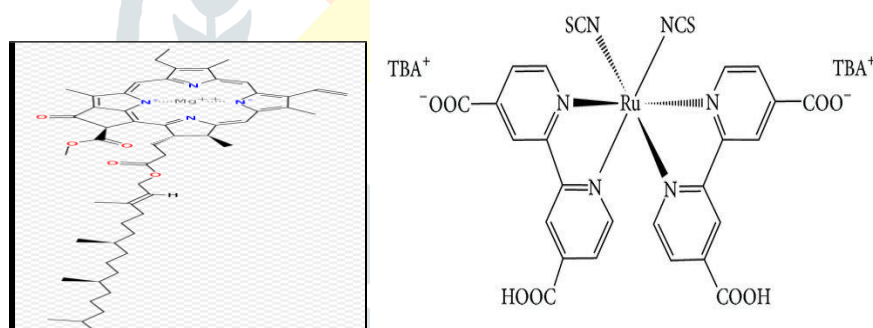


Figure 2.3: (a) Chlorophyll a dye [24]

(b) Z907 dye [25].

### Electrolyte

The material which is filled in between the working electrode and counter electrode is electrolyte. The aim behind the electrolyte is to give electrons to the oxidized sensitizer to forestall and the excited electrons are recovered by the sensitizer. It should be a transparent material that permits light to pass through it simultaneously has good conductivity and fast redox reactions. The liquid iodide/triiodide redox couple is commonly used as an electrolyte this is dissolve in some organic solvents. The organic solvent is the significant material that gives the iodide/triiodide ion dissolution and diffusion environment [11].

For excellent properties of the redox couple was vital for the DSSC electrolyte. The dye molecule that lost one electron in the titanium dioxide is now oxidized, which means there are fewer electrons than there were before. The dye wants to regain its initial state. So, it needs to get an electron. It receives this electron from the iodine electrolyte and the dye returns to ground state. This makes the iodine before becoming oxidized. When the initially lost electrons arrive at the counter electrode, it returns the electron to the electrolyte.

### Counter Electrode

The counter electrode in DSSC should give higher conductivity because it must give liquid electrolyte electrons to finish the redox reaction, in a brief timeframe for lifetime stability and forestalling the electron recovers. Presently the most widely used material is Platinum. Platinum has high electron mobility which can quickly regenerate the electrolyte [11]. Moreover, utilizing gold as the counter electrode found that the electrolyte corrodes gold. Platinum, on the other hand is more stable against electrolyte corrosion properties.

### 2.1.2 Working of DSSC

The working of the DSSC can be illustrated by the energy level representation given in Figure 2.4. The red arrow indicates the path of electrons which generated by the dye excitation. The recombination paths are indicated by black dotted arrows [11].

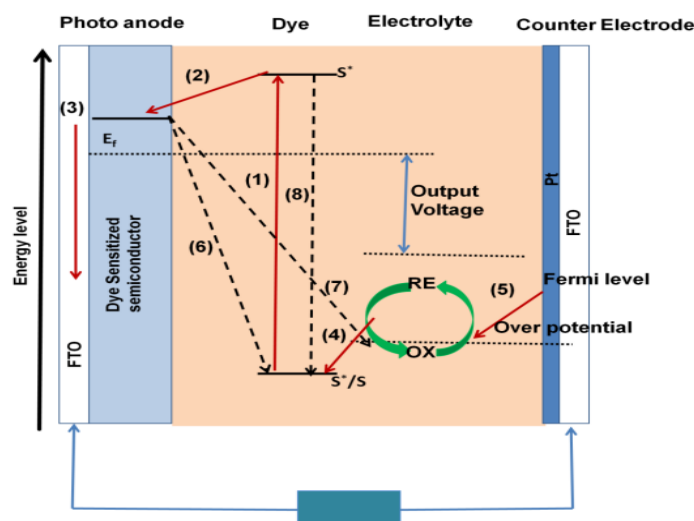


Figure 2.4: Energy level diagram of the dye-sensitized solar cells [11].

Here in the equation the light sensitizer is represented as S, and the excitation of sensitizer is represented as S\*, electron is represented as e<sup>-</sup> and electrolyte is represented as E. The processes are:

- (1) The dye absorbs the incoming photons and it goes to the excited state, where it elevates an electron from the valence to the conduction band and is denoted by equation 1.1



- (2) As the electron is produced by dye returning to the ground state, it transfers to the conduction band of TiO<sub>2</sub>, which oxidized the dye. This is denoted by equation 1.2



- (3) The electron is also transferred from TiO<sub>2</sub> to the outer circuit via the conducting substrate and to the surface of counter electrode to which the electrolyte is compensated.

- (4) The oxidized dye gets regenerated by the redox electrolyte. It is represented by equation 1.3



- (5) The electrolyte compensation takes place at the counter electrode. It is represented by equation 1.4



- (6) It is also possible for recombination electrons to oxidized dye, and this is denoted by the equation 1.5



- (7) The recombination of electrons with an oxidized electrolyte is represented by equation 1.6



- (8) The transfer of electrons back to ground state by non radiative transfer is denoted by equation 1.7



Now, the effect of Photoanode on the efficiency of DSSC is summarized in table 2.

Table 2. The effect of Photoanode on the efficiency of DSSC.

Photoanode	Dye	Electrolyte	Counter Electrode	η (%)	Reference
TiO <sub>2</sub>	Ru(II) complex HD-2 with SA1	I <sup>-</sup> /I <sup>3-</sup>	Pt	8.02	[23]
TiO <sub>2</sub> doped with graphene	N3 dye	I/I <sub>2</sub>	Pt	7.50	[12]
TiO <sub>2</sub> doped with Au	N3 dye	I/I <sub>2</sub>	Pt	7.04	[12]
TiO <sub>2</sub> nanowires doped with Sn	N719 dye	I <sup>-</sup> /I <sup>3-</sup>	Pt	8.75	[13]
TiO <sub>2</sub> -ZnO nanofibres	N719- Ru dye	I <sup>-</sup> /I <sup>3-</sup>	Pt	6.33	[14]



## 2.2 Perovskite Solar Cell

A perovskite solar cell is a type of solar cell which includes a perovskite absorber, most commonly a hybrid organic –inorganic lead or tin halide – based material, as the light harvesting active layer, which produces electricity from sunlight. Perovskite absorber materials such as methyl ammonium or form amidinium lead halide are extremely cheap to produce & simple to manufacture [26]. Their high efficiencies & cheap production costs make perovskite solar cells are extremely commercially attractive option. The first ever perovskite material-based solar cell had an efficiency of 3.8%, introduced by Kojima et al. in 2009. After extensive research efforts, the latest recorded PCE of 25.7% was achieved by Ulsan National Institute of Science and Technology (UNIST). Perovskite solar cells junction efficiently is a number of somewhat different architecture depending either on the role of the perovskite material in the device or the nature of the top & bottom electrode. Device in which positive charges are extracted by the transparent bottom electrode (anode) can predominantly be divided into sensitized, where the perovskite junctions mainly as lighter absorber & charge transport occurs in other materials, electron & hole transport occurs in the bulk of the perovskite itself. Similar to the sensitization in dye-sensitized solar cell (DSSC), the perovskite materials coated onto a charge-conducting meso-porous scaffold, most commonly TiO<sub>2</sub> as light absorber. The photo-generated electrons are transferred from the perovskite layer to the meso-porous sensitized layer through which they are transported to the electrode and extracted onto the circuit. Different components of the perovskite solar cell shown in Figure 2.5.

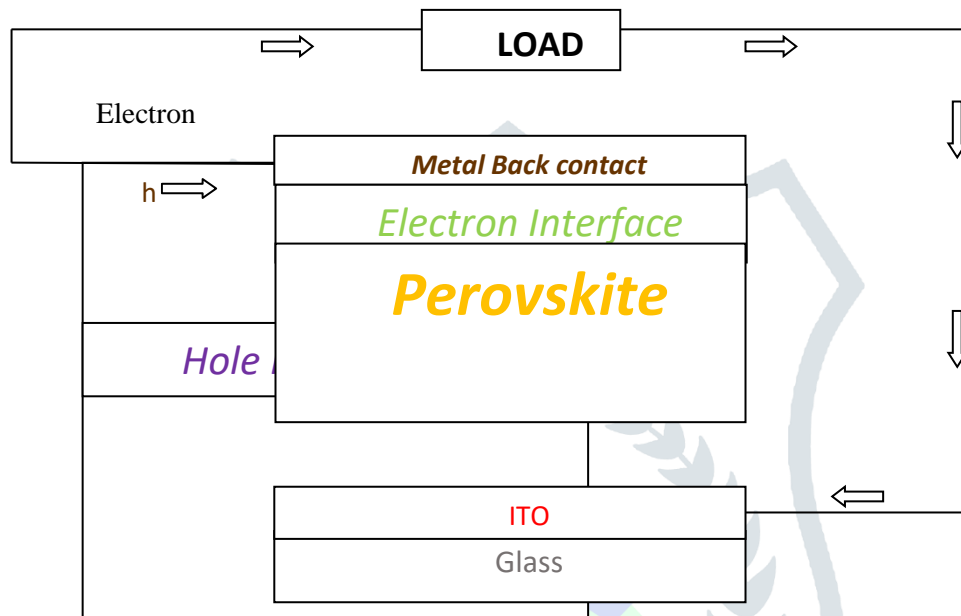


Figure 2.5: Schematic Diagram Of Perovskite Solar Cell.[26]

### 2.2.1 Components of Perovskite Solar Cell

#### Compact Metal Oxide Blocking Layer

The role of the metal oxide layer in perovskite solar cell is to prevent or rather slow down, the recombination between the electrons injected into the conductive oxide layer & the holes in the perovskite. The blocking layer should be thin pin-hole-free & compact with as uniform as possible. Simultaneously, it blocks the holes flow so it is also called as blocking layer. The deposition of the blocking layer is carried out on the conductive glass substrate. It should possess the continuous, compact n-type contact & suitable for electron selectivity. TiO<sub>2</sub> is the mostly use as blocking layer material in perovskite solar cell. The TiO<sub>2</sub> can be deposited by spray pyrolysis, atomic layer deposition or by the sintering of a spin-coated method [26].

#### The Mesoscopic Scaffold

On the top of blocking layer is usually deposited a thin meso-porous film. The meso-porous scaffold layer contains nano-particles of a metal oxide acts as a way for electrons to be collected before they recombine. The TiO<sub>2</sub> meso-porous layer was used in a configuration similar to that if DSSC's, where the perovskite sensitizer was sandwiched in the gaps between the particles. Today's a thin meso-porous film of about 100nm gives highest performances devices. Today's most efficient perovskite solar cell still use a meso-scopic scaffold, hence the role of the porous network of the electron transporting layer cannot be overlooked [27].

#### The perovskite Absorber

The perovskite layer acts as photoactive in the visible region of the solar spectrum. It absorbing all the visible radiation (photons) & generating free charge carrier. Perovskite & related cubic & tetragonal perovskite & direct band gap semiconductor. The pure perovskite has a band gap range from 1.57 to 2.2eV & its absorption coefficient ( $10^2$  to  $10^5\text{cm}^{-1}$ ) is high throughout the visible spectrum & part of the infrared, similarly to most other direct band gap semiconductors used in photovoltaic [26]. Depositing perovskite layers with high diffusion lengths is another key aspect in obtaining high power conversion efficiencies.. Most organic inorganic perovskite are deposited from solution & cannot withstand prolonged heating treatments. Initially perovskite was deposited by preparing concentrations of the precursor materials (metal halide & CH<sub>3</sub>NH<sub>3</sub>I or CsI) in a polar solvent, such as N-butyrolactone(GBL) , N-dimethylformamide (DMP) or dimethylsulfoxide(DMSO).

### The Hole transporting Layer

In a perovskite solar cell, the HTM is responsible for transporting holes & blocking electrons. The imperfect crystal passivation & undesirable interfacial behaviour in perovskite solar cells causes the loss of converted photon energy by the surface recombination. To avoid such losses it is needed to minimizing the interface losses by interface modification between the active layers. So the hole transport materials (HTM) in perovskite layer also play an important role for their efficient perovskite solar cells. Many materials have been researched for their use as HTM in perovskite solar cells. Some of them are inorganic p-type semiconductors such as NiO, WO<sub>3</sub>& MoO<sub>3</sub>. The most commonly used HTMs are solution-processable p-type organic materials, either molecular or polymeric. Recently, Copper thiocyanate (CuSCN), has emerged as an attractive HTM candidate because they are highly stable & transparent across the whole visible spectrum[27].

### Back-Contact

Traditional thin film perovskite solar cells are back-contacted with a metallic layer. The material is usually gold, but silver is also widely used for its lower cost & higher reflectivity.

### 2.2.2 Perovskite Crystal Structure

Generally, perovskite refers to a calcium titanium oxide minerals species composed to calcium titanate, with the chemical formula of CaTiO<sub>3</sub>. The minerals was discovered in the Ural Mountain of Russia in 1839 & is named after Russian mineralogist Lev Perovski [26]. Later on the word 'Perovskite' was barrowed to describe any material with the same type of crystal structure as calcium titanium oxide(CaTiO<sub>3</sub>), known as the perovskite structure as shown Figure 2.6. It is described by the formula ABX<sub>3</sub>, where A & B are cations of different sizes (A is larger than B) & X is an anion that bonds to both.

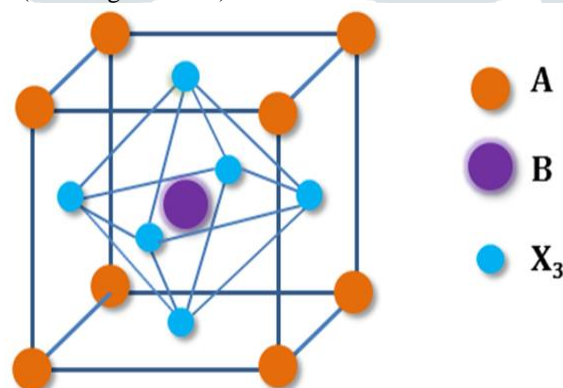


Figure 2.6: Perovskite Crystal Structure [26]

### 2.2.3 Working of Perovskite Solar Cell

The working of the PSC can be illustrated by the energy level representation given in Figure 2.7. For efficient solar cell, materials should possess following four features. Firstly, the materials possess lower exciton binding energy excellent photoelectric properties & high optical absorption coefficients (upto 10<sup>4</sup>cm<sup>-1</sup>). Second one is perovskite have to absorb light as an absorbing layer. Thirdly, the material possess a large dielectric constant & electrons & holes can be transmitted simultaneously & the transmission distance is upto 100nm or more & even more than one micrometer. These features lead to high open-circuit voltage (V<sub>dc</sub>)& a short-circuit current density (J<sub>sc</sub>) if the materials are employed in solar cell devices. Sunlight falls on the perovskite layer then it will absorb photons to generate excitons (electron-hole pair). Generated excitons from free carrier to generate a current due to the difference in the excitons binding energy of the perovskite materials or can recombine into excitons. Low carrier recombination probabilities of the perovskite materials & the higher carrier mobility make the perovskite with long diffusion distance & lifetime of the carrier. The longer diffusion length & lifetime of charge carrier are the major source of the excellent performance of perovskite solar cells. Generated free electrons & holes are collected by electron transparent material (ETM) & a hole transparent material (HTM).Electrons are transferred from the perovskite material to ETM layers & finally collected by FTO. At the same time, the holes are transferred to the HTM layers are collected by the metal electrode. Finally the FTO & metal electrode are connected and the photocurrent is generated in the outer circuit.

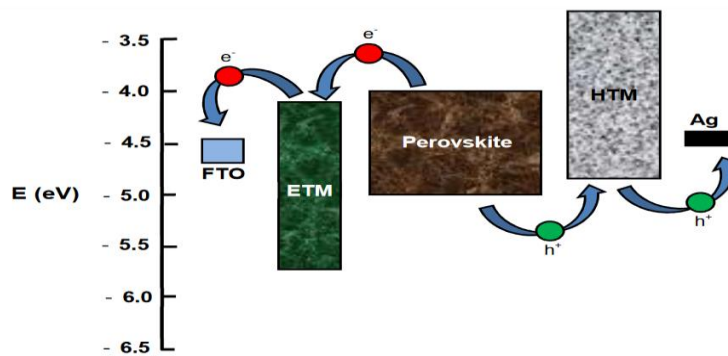


Figure 2.7: Energy Band Diagram of Perovskite Solar Cell [26].

Now, the effect of ETL on the efficiency of PSCs is summarized in table 3.

Table 3. The effect of ETL on the efficiency of PSCs.

Metal	ETL	Perovskite	HTL	$\eta$ (%)	Reference
Au	TiO <sub>2</sub> doped with Sn (tin)	MAPbI <sub>3</sub>	Spiro-OMeTAD	17.14	[15]
Au	TiO <sub>2</sub> doped with Li	FAPbI <sub>3</sub>	Spiro-OMeTAD	24.68	[16]
Au	TiO <sub>2</sub> doped with SnO <sub>2</sub>	MAPbBr <sub>3</sub>	Poly-triarylamine (PTAA)	19.80	[17]
Au	TiO <sub>2</sub> doped with Nb	MAPbI <sub>3</sub>	Spiro-OMeTAD	13.4	[18]

### 2.3 Quantum Dot Sensitized Solar Cell

A quantum dot is a semiconductor nanoparticle with a diameter of few nanometers typically 2 to 10nm, exhibiting electrical and optical characteristics. A quantum dot solar cell (QDSC) is a type of solar cell in which quantum dots are used as light absorbing material. Quantum dot sensitized solar cells have many advantages over other solar cells such as low production cost, optical band gap. They can be adjusted by varying their sizes, due to quantum confinement effects and possibility for multiple exciton generation. Obtaining high efficiency is always a core task for solar cell systems. In addition to dye sensitizers, semiconductor quantum dots have been studied as possible alternative sensitizers.

In recent years, there has been an increase in research interest in QDSSCs on a worldwide scale, attracting researchers from several fields. These researchers include (1) physicists who are developing novel materials for QDSSC manufacturing and investigating the photo physical process of QDSSCs; (2) chemists who are producing appropriate light harvesting materials; and (3) engineers who are creating unique device designs for QDSSCs [28]. High-performance solar cells need materials that can effectively convert light into electricity as well as materials that can effectively capture a broad spectrum of solar energy. The use of QDSSCs can offer several advantages, including greater charge creation, charge separation, and charge extraction within the same material, making them excellent candidates for future solar cells.

#### History

The first QDSSC was created in 2010 by Luther et al. using a bilayer of PbS/ZnO QDs, which exhibited good stability and an efficiency of 2.94%. To increase the efficiency of QDSSCs, researchers have used a range of quantum dot materials[39]. Hao et al. [29] achieved a 16.6% efficient QDSSC this was the highest recorded efficiency for QDSSC until 2020, when UNIST achieved the efficiency of 18.1%, according to the latest National Renewable Energy Laboratory report. According to the Shockley–Queisser model, this still falls short of the 30% theoretically achievable efficiency limit. QDSCs are an improved form of DSSCs in which dye-sensitized materials are substituted by different QD materials.

#### 2.3.1 Components of QDSSC

The various components of QDSSC are shown in Figure 2.8.

##### Transparent conducting oxide

At the front of solar cells, TCO layers act as the optically transparent electrode that allows photons into the solar cell [23] and transports the photogenerated electrons to external device terminals of the solar cell.

##### Electrolyte

Electrolyte consists of species which is an electron donor called reductant and an electron acceptor called oxidant. QDSSC shows a photovoltaic action due to the circulation of charge carriers through an electrolyte. Polysulfide ( $S^{2-}/Sn^{2-}$ ) is used as electrolyte in QDSSC due to its stability with semiconductor QDs and solar cell performance [30].

### Counter Electrode

The collection of electrons from external circuit and reduction of oxidant species in electrolyte are done with the help of component known as counter electrode. This completes the circuit, makes the device ready for photovoltaic action [30]. In QDSSC, Pt results in a poor device performance due to chemical activity with sulfides. With very good electronic mobility for electrolyte species, carbonaceous material such as graphene is considered as CE.

### Photo electrode sensitization with QDs

The photoelectrode is the means of electron transport in solar cells, after dissociation of exciton at metal oxide/ quantum dot interface. The QD absorbs maximum part of solar spectrum to create better exciton density at the interface. QD sensitizers are one of the most important components of QDSSCs, responsible not only for absorbing photons from sunlight but also transferring the excited electrons into CB of a material. QD sensitizers must possess certain qualities to increase QDSC efficiency, including high absorption coefficient to absorb photons from a wide spectrum, an appropriate energy band gap, rapid electron transfer, low cost and good stability. In order to capture a significant amount of light, commonly used materials for QD sensitizers are CISe, CIGSe. Furthermore, combinations of different QDs, such as CdS/CdSe, CdS/CdSe/ZnS, ZCISe, ZCISe/ZnSe have shown impressive performance for light absorption purposes [23].

### Photo anode

TiO<sub>2</sub>, a wide band gap semiconducting metal oxide is employed as photo anode, which serve to create excitons by absorbing photons and transporting electrons to counter electrode. The photo anode is placed on a TCO substrate, which is transparent, has low resistance, and can stand at high temperatures, all of these contribute towards the efficiency of solar cells. To further improve the efficiency of QDSCs, attempts have been made to employ other materials, doping, surface modifications. Nevertheless, TiO<sub>2</sub> remains a strong candidate when compared to other materials and arrangements. Archana et al. and Maiti et al. developed a QDSSC using TiO<sub>2</sub> as photo anode, with CdS and CdSe as a sensitizer, achieving efficiencies of 0.75% and 5.01% respectively. A verified efficiency of 8.55% has been achieved by modifying the band alignment of QD layers using various ligand treatments [23].

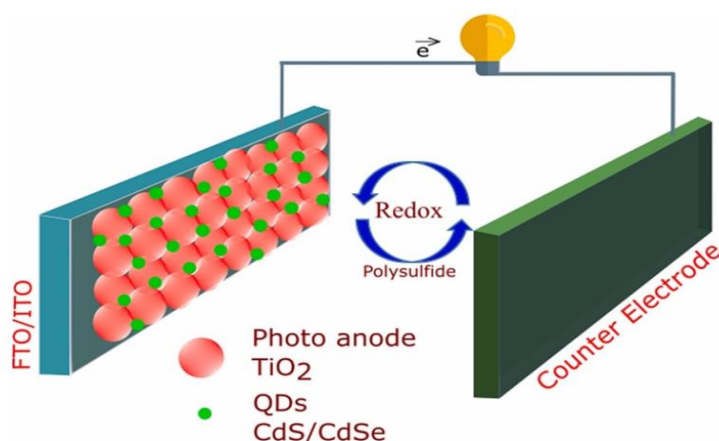


Figure 2.8: Schematic diagram of a QDSSC [23].

### 2.3.2 Working principle of QDSSC

The working of the QDSSC can be illustrated by the energy level representation given in Figure 2.9. It consist of following major steps [23]:

#### Charge separation

QDs are used as light absorbing materials in QSSC which by exposure to sunlight create electron-hole pairs, also called the charge separation process presented in equation 1.

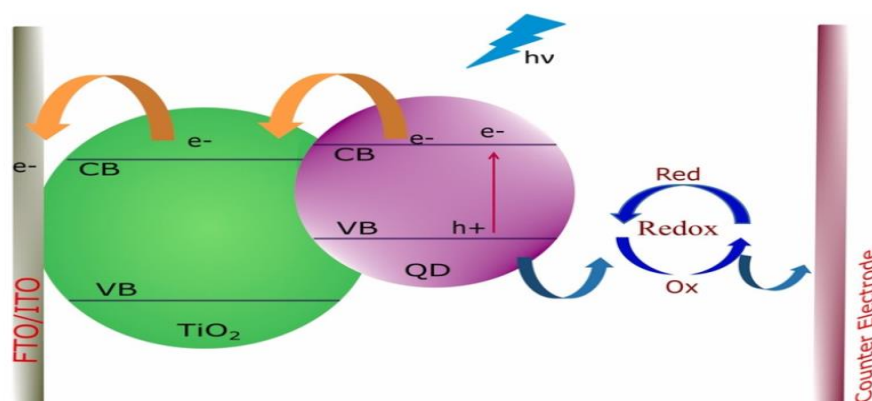


Figure 2.9: Illustration of charge transfer in a QDSSC [23].

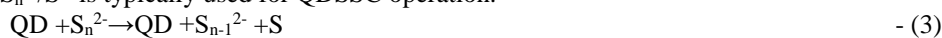
### Electron injection

These generated electrons and holes are then transferred to their respective terminals, i.e. electrons are transferred into the semiconductor metal oxide (acting as electron acceptor) while the holes are moved to the electrolyte or CE. The CE could be either metal or semiconductor electrodes with greater catalytic activity toward the redox couple accepting holes from QDs. Meanwhile, electrons in metal oxide are transferred to transparent conductive oxide substrate and then to the CE (equation 2).



### Hole injection

The electrolyte, which mainly consists of a reversible redox couple, receives holes from QDs. A polysulfide electrolyte with a reversible redox couple  $\text{S}_n^{2-}/\text{S}^{2-}$  is typically used for QDSSC operation.



### Diffusion of polysulfide redox couple

Subsequently the electrons in electrolyte are collected by oxidized  $\text{S}_n^{2-}$  and are converted to  $\text{S}^{2-}$ . This process is called diffusion process or redox reaction.



The key factor prohibiting QDSSCs devices from being used on large scale is their difficulty in maintaining stability. Aside from environmental stability (light, moisture and oxygen in the atmosphere), the most difficult hurdles to overcome in future are intrinsic and component stabilities, which include photochemical instability of QDs, as well as degradation of adhesive materials and sealing. Other issues include substrate type, the electrocatalytic activity of CE material and evaporation of electrolyte.

### Multiple Exciton Generation (MEG)

If the photon energy is larger than the energy gap then the electron will end up in energy levels higher up in conduction band. This energetic electron will quickly fall to bottom levels in conduction band and lose extra energy that is in excess of band gap energy. This extra energy is not really lost but is converted to heat. This is the reason why we cannot pick a semiconductor with a very small band gap to try to absorb all the light because if we could absorb all the photons, much of the energy would be converted to heat and not recovered as electrical energy. Nozik and Klimov discovered that when photons with an integral multiple of band gap energy is absorbed in quantum dots, the excess energy instead of being wasted as heat, ends up producing additional electron hole pairs [31]. For example if quantum dot absorbs a photon with energy three times the band gap energy  $E_g$ , three electron hole pairs are generated and all energy is used to produce current efficiently. In a quantum dot, electron and hole are attracted to each other and are bound to form electron hole pairs called excitons; hence the name MEG. Figure 2.9(a) shows MEG in quantum dots.

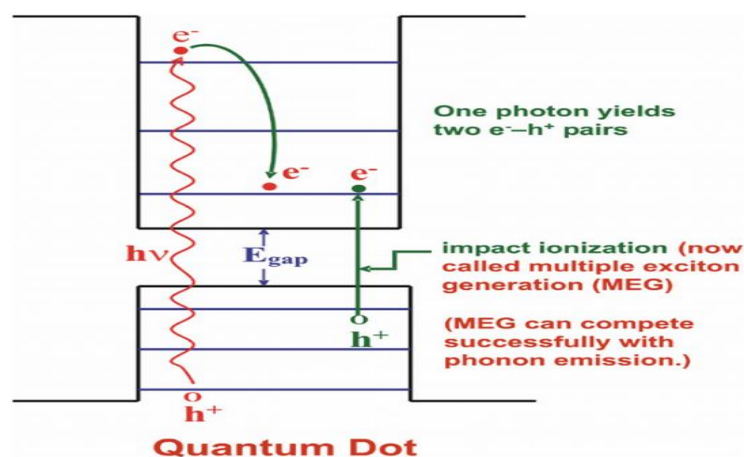


Figure 2.9(a): Multiple electron hole pair(exciton)generation (MEG) in quantum dots [31].

Now, the effect of Photoanode on the efficiency of QDSSC is summarized in table 4.

Table 4. The effect of Photoanode on the efficiency of QDSSC.

QD sensitizers	Photo anode	Electrolyte	Counter electrode	$\eta$ (%)	Reference
ZCISe/ZnSe	TiO <sub>2</sub>	Polysulfide	MC/Ti	13.84	[23]
CdS	TiO <sub>2</sub> nanorods	Polysulfide	Pt	1.75	[19]
Cu <sub>2</sub> AgInSe <sub>4</sub>	TiO <sub>2</sub> nanofibres	Polysulfide	Cu <sub>2</sub> S	4.24	[20]
CdS	N doped TiO <sub>2</sub>	Iodide/triiodide	Pt	8.3	[21]
CdS/CdSe	Zn doped TiO <sub>2</sub>	Polysulfide	NiCo <sub>2</sub> S <sub>4</sub>	3.03	[22]

### 3 CONCLUSION

This review article provides study of structure, properties, synthesis methods and applications of TiO<sub>2</sub> nanoparticles. TiO<sub>2</sub> exist in three crystalline phases: anatase, rutile and brookite. Due to the interesting properties of TiO<sub>2</sub> such as wide band gap, high

refractive index and also its environment friendly nature, it is used in various fields. TiO<sub>2</sub> nanoparticles has been synthesized by using various methods such as sol gel, physical grinding and green synthesis. It has been used in many applications such as solar cells, batteries and anti reflection coating. It is mostly used in third generation solar cells (DSSC, PSC, QDSSC) because they are cheaper than Si based solar cell. Third generation solar cells has tremendous potential to become primary sources to meet energy demands. However, an extensive amount of research is required to improve the stability of these solar cells. Initially, the zinc oxide was used as photoanode in DSSC, its efficiency was low. But when TiO<sub>2</sub> was used as a photoanode in DSSC the efficiency reached up to 8.02%. In QDSSC, initially using a bilayer of PbS/ZnO QDs exhibit an efficiency of 2.94%. But, by using the TiO<sub>2</sub> as photoanode, the efficiency of QDSSC increased up to 13.84%. Initially, PSC have an efficiency of 3.8%. Now the efficiency of PSC using TiO<sub>2</sub> as ETL reached up to 25.5%.

### 3.1 Future Scope

In future, the nanoparticles with different materials are used to develop high efficient solar cells at low cost. A solid platform needed to be established to construct solar cells employing nanomaterials. Also, TiO<sub>2</sub> doped with noble metals can be good candidates to improve the performance of these applications. To further improve the efficiency, new materials are needed that can capture light in the near infrared spectrum. Using a colloidal synthesis approach such novel materials for high efficiency solar cells can be developed. Functionalizing various inorganic semiconductor nanostructures, organic polymers and dyes with appropriate molecules, it is still possible to achieve the aim of capturing an immense number of photons.

### References:

- [1] T. Ali, Investigation of different properties of pure and doped TiO<sub>2</sub> Nanomaterials and their application, University. (2018). <https://shodhganga.inflibnet.ac.in:8443/jspui/handle/10603/250862> (accessed September 1, 2023).
- [2] Catalysts | Free Full-Text | Investigation of Advanced Oxidation Process in the Presence of TiO<sub>2</sub> Semiconductor as Photocatalyst: Property, Principle, Kinetic Analysis, and Photocatalytic Activity, (n.d.). <https://www.mdpi.com/2073-4344/13/2/232> (accessed September 13, 2023).
- [3] H. Zhang, J.F. Banfield, Structural Characteristics and Mechanical and Thermodynamic Properties of Nanocrystalline TiO<sub>2</sub>, *Chem. Rev.* 114 (2014) 9613–9644. <https://doi.org/10.1021/cr500072j>.
- [4] A. Sivaramalingam, S. Thankaraj Salammal, A. Soosaimanickam, T. Sakthivel, S. Paul David, B. Sambandam, Role of TiO<sub>2</sub> in Highly Efficient Solar Cells, in: S. Rajendran, H. Karimi-Maleh, J. Qin, E. Lichtfouse (Eds.), *Met. Met.-Oxides Met. Sulfides Batter. Fuel Cells Sol. Cells Photocatal. Health Sens.*, Springer International Publishing, Cham, 2021: pp. 147–168. [https://doi.org/10.1007/978-3-030-63791-0\\_5](https://doi.org/10.1007/978-3-030-63791-0_5).
- [5] O.U. Akakuru, Z.M. Iqbal, A. Wu, TiO<sub>2</sub> Nanoparticles: Properties and Applications, in: A. Wu, W. Ren (Eds.), *TiO<sub>2</sub> Nanoparticles*, 1st ed., Wiley, 2020: pp. 1–66. <https://doi.org/10.1002/9783527825431.ch1>.
- [6] T. Theivasanthi, M. Alagar, Titanium dioxide, (n.d.).
- [7] J.Y. Kim, J.-W. Lee, H.S. Jung, H. Shin, N.-G. Park, High-Efficiency Perovskite Solar Cells, *Chem. Rev.* 120 (2020) 7867–7918. <https://doi.org/10.1021/acs.chemrev.0c00107>.
- [8] Figure 1: Schematic of different stages of sol-gel process: from..., ResearchGate. (n.d.). [https://www.researchgate.net/figure/Schematic-of-different-stages-of-sol-gel-process-from-precursor-to-aerogel-1-5\\_fig1\\_357324037](https://www.researchgate.net/figure/Schematic-of-different-stages-of-sol-gel-process-from-precursor-to-aerogel-1-5_fig1_357324037) (accessed August 31, 2023).
- [9] G.R. Kandregula, D. Chinthakuntla, K. Rao, S. Chidurala, V. Rajendar, SYNTHESIS OF TiO<sub>2</sub> NANOPARTICLES FROM ORANGE FRUIT WASTE, *Int. J. Multidiscip. Adv. Res. TRENDS.* 2 (2015) 82–90.
- [10] G. Nandan Arka, S. Bhushan Prasad, S. Singh, Comprehensive study on dye sensitized solar cell in subsystem level to excel performance potential: A review, *Sol. Energy.* 226 (2021) 192–213. <https://doi.org/10.1016/j.solener.2021.08.037>.
- [11] R. S, Synthesis and characterization of tio<sub>2</sub> and modified tio<sub>2</sub> nanoparticles by green approach as photoanodes for dye sensitized solar cells, University. (2020). <https://shodhganga.inflibnet.ac.in:8443/jspui/handle/10603/365255> (accessed August 29, 2023).
- [12] K.-W. Min, M.-T. Yu, C.-T. Ho, P.-R. Chen, J.-K. Tsai, T.-C. Wu, T.-L. Wu, Application of doping graphene quantum dots and gold nanoparticles on dye-sensitized solar cells, *Mod. Phys. Lett. B.* 36 (2022) 2141017. <https://doi.org/10.1142/S0217984921410177>.
- [13] S. Ni, F. Guo, D. Wang, S. Jiao, J. Wang, Y. Zhang, B. Wang, P. Feng, L. Zhao, Modification of TiO<sub>2</sub> Nanowire Arrays with Sn Doping as Photoanode for Highly Efficient Dye-Sensitized Solar Cells, *Crystals.* 9 (2019) 113. <https://doi.org/10.3390/cryst9020113>.
- [14] Y.-H. Nien, G.-M. Hu, M. Rangasamy, H.-H. Chen, H.-H. Hsu, J.-C. Chou, C.-H. Lai, P.-Y. Kuo, C.-C. Ko, J.-X. Chang, Investigation of Dye-Sensitized Solar Cell With Photoanode Modified by TiO<sub>2</sub>-ZnO Nanofibers, *IEEE Trans. Semicond. Manuf.* 33 (2020) 295–301. <https://doi.org/10.1109/TSM.2020.2984273>.
- [15] S.S. Nishat, M.J. Hossain, F.E. Mullick, A. Kabir, S. Chowdhury, S. Islam, M. Hossain, Performance Analysis of Perovskite Solar Cells Using DFT-Extracted Parameters of Metal-Doped TiO<sub>2</sub> Electron Transport Layer, *J. Phys. Chem. C.* (2021). <https://doi.org/10.1021/acs.jpcc.1c02302>.
- [16] M. Kim, I. Choi, S.J. Choi, J.W. Song, S.-I. Mo, J.-H. An, Y. Jo, S. Ahn, S.K. Ahn, G.-H. Kim, D.S. Kim, Enhanced electrical properties of Li-salts doped mesoporous TiO<sub>2</sub> in perovskite solar cells, *Joule.* 5 (2021) 659–672. <https://doi.org/10.1016/j.joule.2021.02.007>.
- [17] Y. Lee, S. Paek, K.T. Cho, E. Oveisi, P. Gao, S. Lee, J.-S. Park, Y. Zhang, R. Humphry-Baker, A.M. Asiri, M.K. Nazeeruddin, Enhanced charge collection with passivation of the tin oxide layer in planar perovskite solar cells, *J. Mater. Chem. A.* 5 (2017) 12729–12734. <https://doi.org/10.1039/C7TA04128D>.
- [18] D.H. Kim, G.S. Han, W.M. Seong, J.-W. Lee, B.J. Kim, N.-G. Park, K.S. Hong, S. Lee, H.S. Jung, Niobium Doping Effects on TiO<sub>2</sub> Mesoscopic Electron Transport Layer-Based Perovskite Solar Cells, *ChemSusChem.* 8 (2015) 2392–2398. <https://doi.org/10.1002/cssc.201403478>.

- [19] S.A. Pawar, D.S. Patil, A.C. Lokhande, M.G. Gang, J.C. Shin, P.S. Patil, J.H. Kim, Chemical synthesis of CdS onto TiO<sub>2</sub> nanorods for quantum dot sensitized solar cells, *Opt. Mater.* 58 (2016) 46–50. <https://doi.org/10.1016/j.optmat.2016.05.019>.
- [20] R. Kottayi, P. Panneerselvam, V. Murugadoss, R. Sittaramane, S. Angaiah, Cu<sub>2</sub>AgInSe<sub>4</sub> QDs sensitized electrospun porous TiO<sub>2</sub> nanofibers as an efficient photoanode for quantum dot sensitized solar cells, *Sol. Energy.* 199 (2020) 317–325. <https://doi.org/10.1016/j.solener.2020.02.010>.
- [21] K. Sugiyarto, C. Kusumawardani, A. Prodjosantoso, N-Doped TiO<sub>2</sub>/CdS Nanocomposite Films: SILAR Synthesis, Characterization and Application in Quantum Dots Solar Cell, *Orient. J. Chem.* 34 (2018) 1297–1302. <https://doi.org/10.13005/ojc/340313>.
- [22] J. Deng, M. Wang, J. Fang, X. Song, Z. Yang, Z. Yuan, Synthesis of Zn-doped TiO<sub>2</sub> nano-particles using metal Ti and Zn as raw materials and application in quantum dot sensitized solar cells, *J. Alloys Compd.* 791 (2019) 371–379. <https://doi.org/10.1016/j.jallcom.2019.03.306>.
- [23] N. Shah, A.A. Shah, P.K. Leung, S. Khan, K. Sun, X. Zhu, Q. Liao, A Review of Third Generation Solar Cells, *Processes.* 11 (2023) 1852. <https://doi.org/10.3390/pr11061852>.
- [24] Chlorophyll a, Wikipedia. (2023). [https://en.wikipedia.org/w/index.php?title=Chlorophyll\\_a&oldid=1172907242](https://en.wikipedia.org/w/index.php?title=Chlorophyll_a&oldid=1172907242) (accessed September 1, 2023).
- [25] Structures of Ru dyes studied in this paper (N719 dye (a), Z907 dye..., ResearchGate. (n.d.). [https://www.researchgate.net/figure/Structures-of-Ru-dyes-studied-in-this-paper-N719-dye-a-Z907-dye-b-and\\_fig1\\_258394595](https://www.researchgate.net/figure/Structures-of-Ru-dyes-studied-in-this-paper-N719-dye-a-Z907-dye-b-and_fig1_258394595) (accessed September 1, 2023).
- [26] 07\_chapter 1.pdf, (n.d.). [https://shodhganga.inflibnet.ac.in/bitstream/10603/372492/7/07\\_chapter%201.pdf](https://shodhganga.inflibnet.ac.in/bitstream/10603/372492/7/07_chapter%201.pdf) (accessed August 12, 2023).
- [27] N. Suresh Kumar, K. Chandra Babu Naidu, A review on perovskite solar cells (PSCs), materials and applications, *J. Mater. Chem. A.* 6 (2018) 9629–9641. <https://doi.org/10.1039/C8TA01064A>.
- [28] Y.-H. Chiang, K.-Y. Lin, Y.-H. Chen, K. Waki, M.A. Abate, J.-C. Jiang, J.-Y. Chang, Aqueous solution-processed off-stoichiometric Cu–In–S QDs and their application in quantum dot-sensitized solar cells, *J. Mater. Chem. A.* 6 (2018) 9629–9641. <https://doi.org/10.1039/C8TA01064A>.
- [29] M. Hao, Y. Bai, S. Zeiske, L. Ren, J. Liu, Y. Yuan, N. Zarrabi, N. Cheng, M. Ghasemi, P. Chen, M. Lyu, D. He, J.-H. Yun, Y. Du, Y. Wang, S. Ding, A. Armin, P. Meredith, G. Liu, H.-M. Cheng, L. Wang, Ligand-assisted cation-exchange engineering for high-efficiency colloidal Cs<sub>1-x</sub>FaxPbI<sub>3</sub> quantum dot solar cells with reduced phase segregation, *Nat. Energy.* 5 (2020) 79–88. <https://doi.org/10.1038/s41560-019-0535-7>.
- [30] H. Song, H. Rao, X. Zhong, Recent advances in electrolytes for quantum dot-sensitized solar cells, *J. Mater. Chem. A.* 6 (2018) 4895–4911. <https://doi.org/10.1039/C7TA11388A>.
- [31] A.J. Nozik, Multiple exciton generation in semiconductor quantum dots, *Chem. Phys. Lett.* 457 (2008) 3–11. <https://doi.org/10.1016/j.cpllett.2008.03.094>.

