No.: BL/22-23/RCP/47 Dated **16-Apr-24**

Balani Infotech Pvt. Ltd

BALANI INFOTECH PRIVATE LIMITED
B-116, Sector-67, Noida - 201301
Distt. Gautam Budh Nagar
Uttar Pradesh
Regd. Office: 119, Vinoba Puri, Lajpat Nagar Ii
New Delhi-110024
State Name : Uttar Pradesh, Code : 09
CIN: U72300DL2007PTC164136

Receipt Voucher

Received with thanks from : **Tuljaram Chaturchand College of Arts, Science and Commerce**
Dist-Pune 413102
Maharashtra-413102

The sum of : **Rupees One Lakh Twenty Seven Thousand Six Hundred Only**

By : NEFT
Remarks : NEFT (ANEKANT EDUC.)

****₹ 1,27,600.00/-**

***Subject to Realisation*

Authorised Signatory

Balani Infotech Pvt. Ltd.
(Library Information Services)

CIN No: U72300DL2007PTC164136
GSTIN: 09AADCB1970E1ZV

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Reverse Charge	: N	**Subscription Period**	: 23 April 2024 to 22 April 2026
Invoice Number	: BL/n/24-25/17	**Exchange Rate**	: INR
Invoice Date	: 22-Apr-24	**Exchange Rate Base**	: INR
State	: Uttar Pradesh **State Code** 09	**Reference No.**	: Payment Received
		Reference Date	: 16-Apr-24

Details of Receiver | Billed To	**Details of Consignee | Shipped to**
Tuljaram Chaturchand College of Arts, Science and Commerce	Tuljaram Chaturchand College of Arts, Science and Commerce
Dist-Pune 413102	Dist-Pune 413102
Maharashtra-413102	Maharashtra-413102
State : Maharashtra	State : Maharashtra
State Code : 27	State Code : 27
GSTIN :	GSTIN :

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		SAC CODE				VALUE	Rate	Amount	Rs.
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TOTAL INVOICE AMOUNT (IN WORDS)

Rupees One Lakh Twenty Nine Thousand Eight Hundred Only.

Total Amount Before Tax :	**1,10,000.00**
Total Amount:GST	**19,800.00**
Total Amount After Tax	**1,29,800.00**
GST Payable On Reverse Charges :	**No**

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3. 100% advance payment required, after receipt of payment, account required 5-7 working days for the activation
4. Please mention Invoice number in Description / Remarks while making NEFT / RTGS Payment .

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Beneficiary Name	: BALANI INFOTECH PRIVATE LIMITED
Bank Name	: RBL BANK LIMITED
Branch Name	: NOIDA BRANCH (P-7, SECTOR-18, NOIDA)
Account No	: 1383774
RTGS/NEFT Code	: RATN0000114
PAN	: AADCB1970E

For BALANI INF ATE LIMITED

Balani Infotech Pvt. Ltd. Noida 201301

Signatory

BBamal

TULJARAM CHATURCHAND COLLEGE BARAMATI 413 102 PUNE

Balani Infotech Pvt. Ltd.

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Maharashtra-413102	Maharashtra-413102
State : Maharashtra	State : Maharashtra
State Code : 27	State Code : 27
GSTIN :	GSTIN :

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1	DrillBit Extreme Anti Plagiarism Software 01 Admin And 05 Users Accounts 500 Document Submissions Each Year	998431	1	[illegible]		1,10,000.00	18.00 %	19,800.00	1,29,800.00

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RTGS/NEFT Code.	: RATN0000114
PAN	: AADCB1970E

For BALANI INF[illegible]ATE LIMITED

भारत 100 राजस्व REVENUE INDIA

Noida 201301

[illegible] **Signatory**

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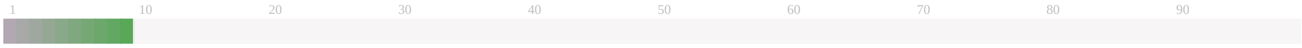

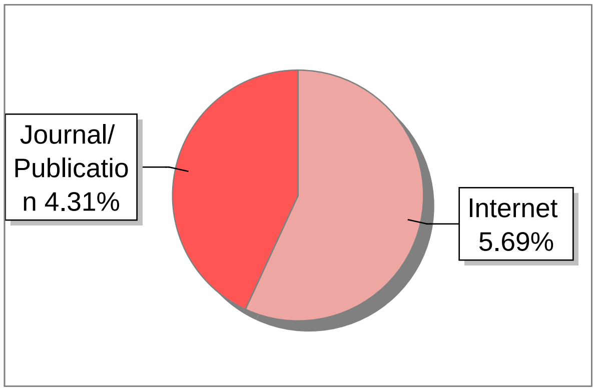

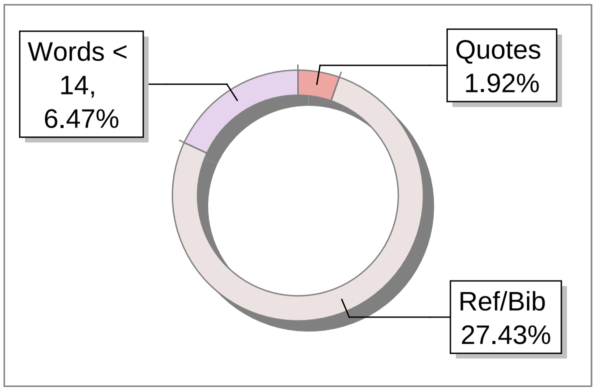

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Advancement in Dye-Sensitized Solar Cells: A Comprehensive Review on materials, Efficiency Enhancement Strategies

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[1,2,4,5]Department of Physics, PDEAS Annasaheb Magar College Hadapsar, Pune, 411028.

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Abstract:

The use of renewable energy sources is becoming increasingly important in the current global energy scenario. Among various renewable energy options, solar energy is considered a crucial solution to energy and environmental challenges. Dye-sensitized solar cells (DSSCs) are a promising technology that has drawn significant attention from the scientific community due to their high efficiency, low cost, and ease of fabrication. This article provides an overview of DSSC technology, including the architecture, materials used, fabrication and characterization techniques, major challenges, and current research efforts. Additionally, discuss the applications and prospects of DSSCs as a clean and sustainable energy source.

Keywords: Renewable energy, photovoltaic cells, dye-sensitized solar cell, photoanode, photosensitizer.

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1. Introduction

1.1. Global Energy Scenario and Renewable Energy

Our world is facing an unprecedented surge in global energy demand, currently standing at 13 terawatts (TW) and projected to skyrocket to approximately 23 TW by 2050[1]. This surge is fueled by our increasing reliance on energy, but the concerning reality is that the rate at which we are burning fossil fuels to meet this demand is simply unsustainable. Currently, these fossil fuels cover about 80% of our global energy needs, but they are depleting rapidly and contribute significantly to the rising levels of atmospheric carbon dioxide, intensifying the challenges of global warming [2].

Given these alarming facts and the pressing challenges they present, it is evident that we urgently need cleaner and renewable energy technologies. One compelling option on the renewable energy horizon is photovoltaic technology, which taps into the vast potential of solar energy. Recognized as one of the most efficient sustainable energy technologies, alongside alternatives like tidal power, solar thermal, hydropower, and biomass [3], harnessing such technologies becomes not just a technological pursuit but a critical scientific imperative.

In many regions around the world, the availability of energy sources and water supply is severely restricted, emphasizing the crucial importance of incorporating renewable energy sources such as solar, wind, hydropower, and others [4]. These renewable sources not only offer a path to sustainable energy but also address the broader challenges of resource scarcity, making them integral to a more resilient and equitable future.

The term "renewable energy" encompasses a diverse range of resources relying on self-renewing sources like sunlight, wind, flowing water, Earth's internal heat, biomass, agricultural and industrial waste, and municipal trash [5]. These sources have the potential to generate electricity for various sectors, power transportation, and provide heating for buildings and industrial processes. The interconnected nature of power energy and water accessibility underscores the urgency of addressing global energy demands while simultaneously reducing greenhouse gas emissions to mitigate climate change [6].

The energy sector has undergone significant transformations since the Industrial Revolution, as illustrated in Fig. 1 [7]. The Fig depicts the changing landscape of world energy use from the 1800s onwards, based on historical primary energy consumption projections and current data. Considering population growth and power generation, the projected global power demand in 2050 is estimated to be 28 terawatts (TW) **[3]**. Solar power emerges as a leading contender to meet renewable power needs globally, with a potential estimate of about 600 TW based on solar energy striking the Earth's surface [5]. Harnessing just 10% of this potential could provide around 60 TW of energy. Notably, solar cell production has grown at approximately 30% per year over the last 15 years, indicating significant progress in the adoption of solar technology **[8]**.

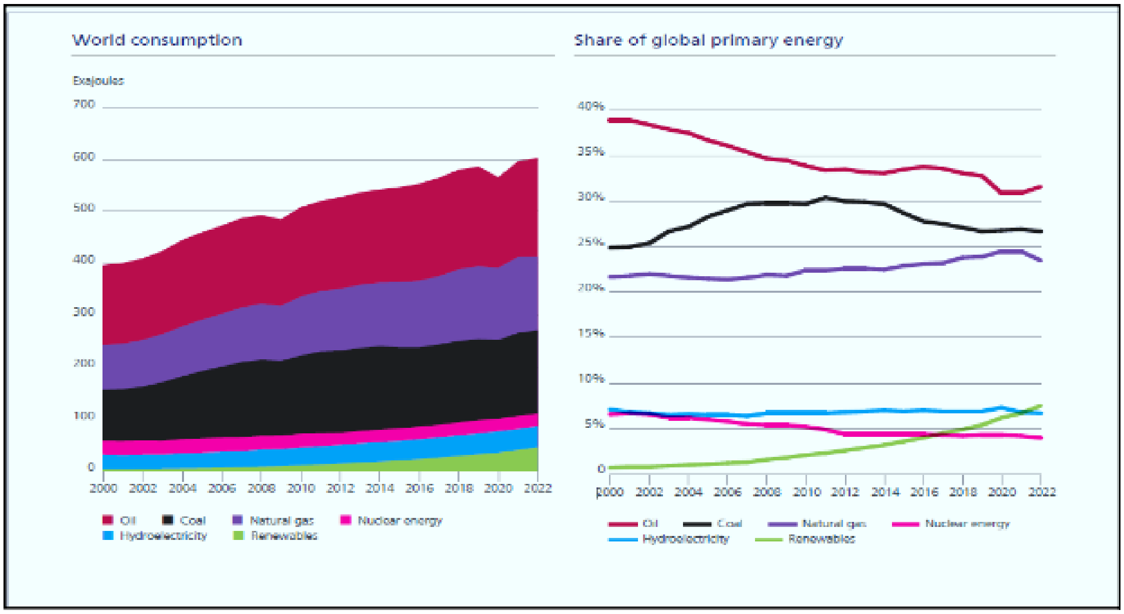


Fig1.Source: 72nd Energy Institute Statistical Review o of World Energy 2023

1.2. Indian Energy Scenario and Renewable Energy

Renewable energy sources are those naturally replenishing energy reservoirs that outpace their consumption rate [9]. With India experiencing a surge in energy demands, it becomes imperative for the nation to explore renewable energy alternatives to ensure energy security and achieve sustainable development objectives. To this end, the government is actively promoting the adoption of various renewable energy resources, including solar, wind, biomass, small-hydro, hydrogen energy, and waste-to-energy [9].

India secured the third global position for renewable energy installations in 2021, as reported by the Renewable 2022 Global Status Report from REN21[9]. Remarkably, about 42% of India's total installed power capacity is now sourced from renewable energy [9].

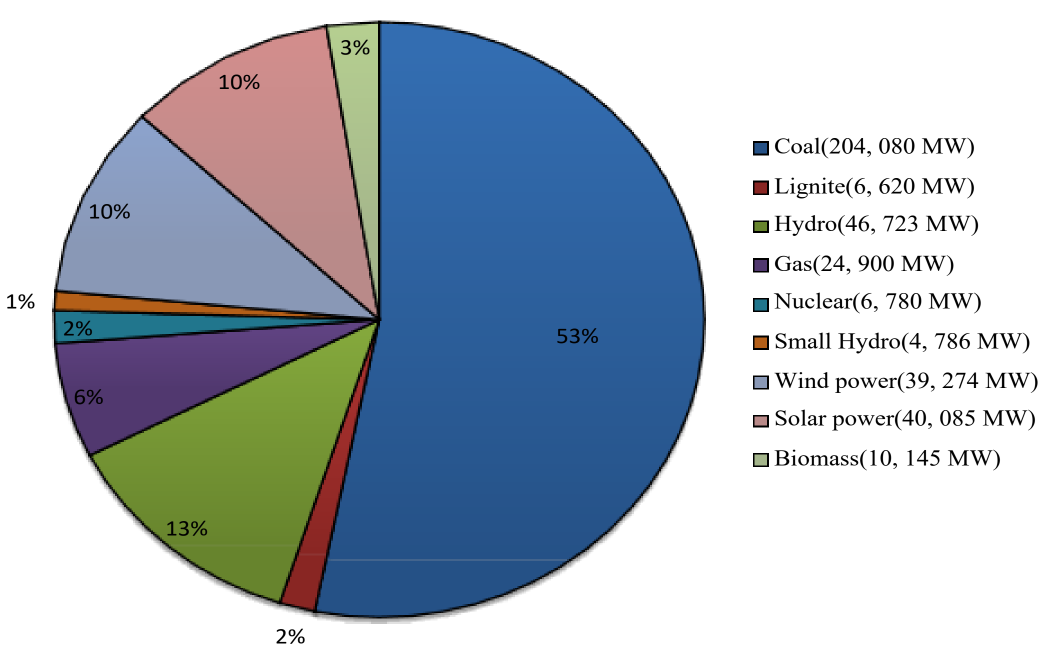
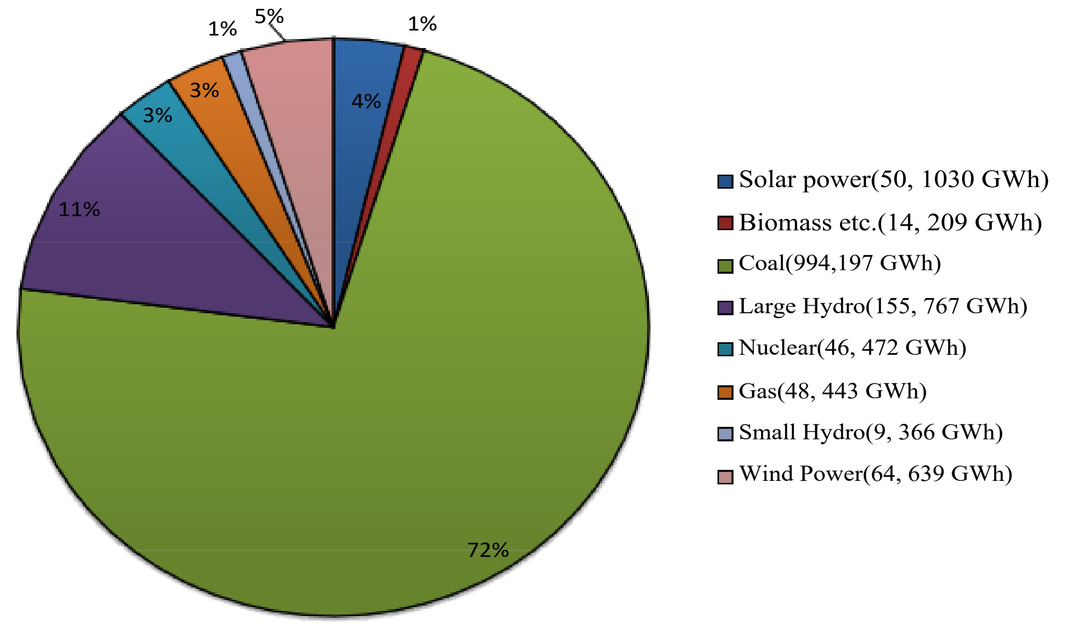


Fig 2. Installed Energy Generation Capacity in India

In the specific realm of solar energy, India achieved the fourth position globally in 2021, boasting an impressive 60.4 GW, surpassing even Germany [10]. According to the Ministry of New and Renewable Energy's December 2022 report, India has operationalized 41.8 GW of wind energy and 61.9 GW of solar energy [11]. Noteworthy projects valued at $200 billion are currently underway in India's renewable energy sector, as highlighted by the International Energy Agency [10].

Despite having nearly 40% of installed renewable capacity, the actual utilization hovers around 25%, factoring in large hydro and nuclear energy [9]. Addressing and surmounting these challenges is crucial to unlocking the full efficiency and impact of renewable energy in India, fostering a more sustainable and resilient energy landscape [9].

Fig 3.Actual Installation of Energy in India



1.3. Solar Energy: A Crucial Solution to Energy and Environmental Challenges

The next 50 years pose significant challenges for humanity, particularly in the realms of energy and the environment. Our current dependence on fossil fuels, despite advancements in battery technology, remains the primary source of energy [12]. The relentless consumption of fossil fuels not only depletes Earth's oil reserves but also contributes to the greenhouse effect and environmental pollution [13]. Projections indicate that the depletion of these non-renewable resources is inevitable in the 21st century, necessitating a global shift towards clean and sustainable energy alternatives [14].

Amidst various sustainable energy resources like tidal, hydro, geothermal, wind, and biomass, solar energy emerges as a prominent and compelling solution [15]. The Earth receives an astounding 3.8 million petajoules of energy annually from the Sun—almost ten thousand times more than humanity consumes daily [16]. Harnessing just 0.1% of the Earth's surface with solar cells boasting 10% efficiency could meet all current energy needs [17]. This underscores the immense potential of solar power for both the present and future generations. Solar energy can be captured and converted into electricity through two primary methods:

a. **Photovoltaic Cells:**
   Solar energy is directed onto photovoltaic cells, generating electricity for immediate use.
b. **Solar Thermal Technology:**
   Focused sunlight is directed onto collectors, generating heat that can be utilized for various purposes. This heat can be channelled through a conventional generator to produce electricity.

India's target of generating 500 GW of renewable energy by 2030 has been widely reported [18]. Interestingly, a study suggests that using only 3% of wasteland for solar units could result in a whopping 768 GW of power [20]. This emphasizes the immense potential and scalability of solar energy in meeting the rising energy demands sustainably.

Solar energy's storability as electrical energy and its versatility in various applications, including chemical processes, has been highlighted in many sources [21]. Experts suggest that due to its abundance, cleanliness, and versatility, solar energy could play a crucial role in building a sustainable and resilient energy future for the entire planet [22-23].

1.4. Evaluation of Photovoltaic devices:

Researchers have long been engaged in harnessing sunlight for chemical reactions or electricity generation. Photovoltaic (PV) devices play a pivotal role in this process, generating direct current or power by absorbing solar radiation through semiconductor materials. The "photovoltaic effect" is the underlying physical process wherein the PV cell converts incident sunlight into electricity. The term "photovoltaic" itself denotes the combination of "photo" meaning light and "voltaic" meaning electricity. PV cells are commonly referred to as "solar cells." Solar photovoltaics stand out as the cleanest, most viable, and sustainable technology among various renewable harvesting technologies [24].

Electricity generation through solar photovoltaics is considered environmentally friendly, emitting no hazardous or toxic gases into the environment. The "photovoltaic effect" was first discovered by the renowned French scientist Edmond Becquerel in 1839. He demonstrated the effect by exposing solid electrodes in an electrolyte solution to sunlight. The first solar cell, built by Charles Fritts in 1883, utilized selenium and gold to form p-n junctions and reported an efficiency of 1% conversion of absorbed solar light [25].

Albert Einstein's theoretical explanation of the "photoelectric effect" in 1905 laid the foundation for understanding how electrons are emitted from a metal surface by absorbing discrete amounts of light, now known as photons. In 1954, the first silicon photovoltaic cell, employing diffused silicon p-n junction technology, was developed, boasting a 6% conversion efficiency. The space industry adopted this technology in the 1960s for powering spacecraft [25].

Over time, intense competition among manufacturers has driven significant advancements in photovoltaic technology, improving efficiency and reducing costs. The energy crisis of the 1970s propelled photovoltaic technology into the spotlight across various non-space and domestic sectors [24].

A photovoltaic cell generates electricity through the following key steps:

- Absorption of solar radiation, creating electron-hole pairs (or excitons in specific solar cells).

- Separation of charge carriers, involving exciton ionization and/or carriers' separation in specific solar cells [25].

1.5. Classification of Photovoltaics

Photovoltaic cells, also known as solar cells, have been categorized into three primary groups by Martin A. Green. This classification revolves around the material composition of the solar cell, the highest attainable solar-to-power conversion efficiency, and the production cost

Solar cells come in three main generations. The first, known as conventional or wafer-based cells, are the oldest and most widely used [26]. Despite being made of crystalline silicon (mono or poly), they have high production costs and modest efficiency, reaching 26.6%. The expense of making single-crystalline Si solar cells hinders the idea of low-cost production.

In contrast, second-generation solar cells, called thin-film solar cells, were developed as an alternative to silicon [27]. These cells are made by depositing thin semiconductor layers on substrates like glass or plastic. Although cheaper than traditional silicon cells, they are less efficient, with challenges in complex deposition, stoichiometry control, and structural defects.

The third generation, often called emerging photovoltaics, includes Dye-Sensitized Solar Cells (DSSCs), Organic Solar Cells (OSCs), Perovskite Solar Cells (PSCs), and Quantum Dot Solar Cells (QDSCs). These aim for low-cost production and increased efficiency by overcoming energy loss issues. They use a "tandem cell" or "multi-junction" approach, stacking layers with varying band gaps.

All third-generation cells operate on the same principle but differ in the light-harvesting layer. Dyes in DSSCs, conductive organic polymers in OSCs, perovskite structured compounds in PSCs, and inorganic/organic quantum dots in QDSCs serve this role. Each type faces unique challenges, like low efficiency in OSCs, film quality issues in PSCs, and difficulty controlling particle size in QDSCs [28].

Despite challenges, DSSCs stand out as a promising alternative due to their performance in various conditions, long life, eco-friendliness, low toxicity and production cost, and simple manufacturing techniques. To boost their efficiency and quicken commercialization, researchers should reconsider the materials used in different components.

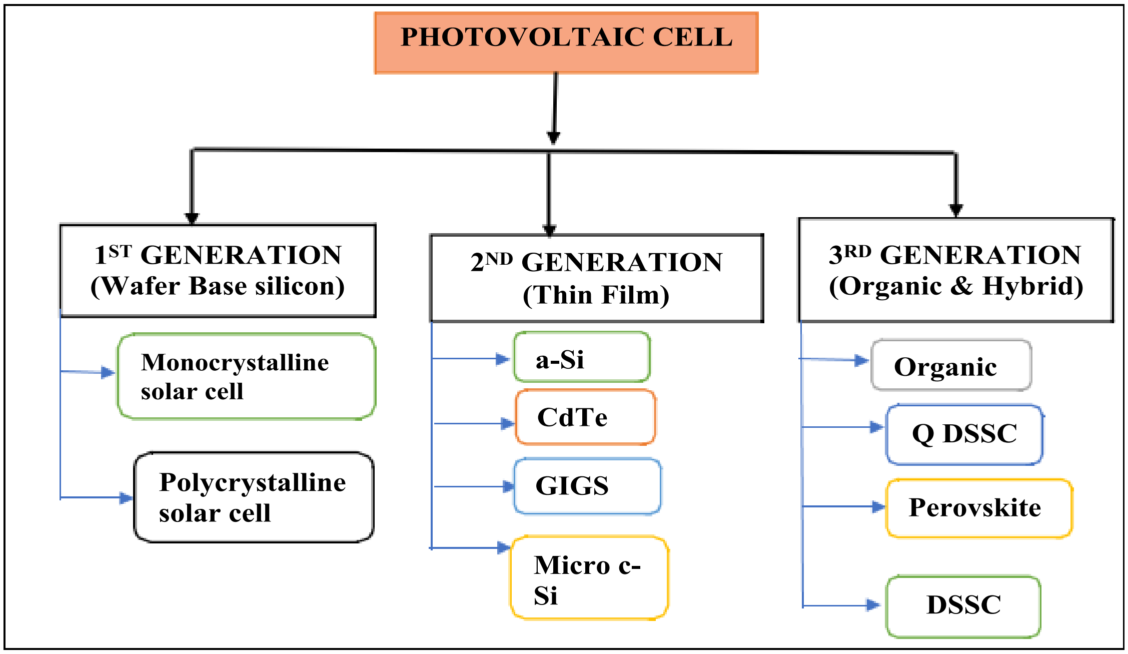


Figure 4. Classification of photovoltaic cell

2. INTRODUCTION TO DYE-SENSITISED SOLAR CELL:

Dye-sensitized solar cells (DSSCs) have emerged as a viable alternative to traditional p-n junction photovoltaic devices, presenting both technical and economic advantages. The concept of generating electricity through illuminated organic dyes in electrochemical cells was initially explored in the late 1960s [29]. However, the efficiency of these dye-sensitized solar cells was initially limited, absorbing only up to 1% of incident light due to the monolayer of dye molecules. Subsequent improvements were achieved by optimizing the porosity of the electrode using fine oxide powder, enhancing dye absorption, and consequently, light harvesting efficiency (LHE) [30]. This led to the discovery of nanoporous titanium dioxide ($TiO2$) electrodes with a roughness factor of approximately 1000, resulting in the invention of DSSCs in 1991 with 7% efficiency [29].

Gratzel cells, developed by Brian O'Regan and Michael Gratzel, exhibited exceptional efficiency, with over 80% incident photon to current conversion efficiency (IPCE) in simulated solar light [29]. The corresponding reactions involve photoexcitation, electron injection, electron transport, reduction regeneration, and dye regeneration, ultimately leading to electricity generation [35]. Subsequent advancements led to 9.6% efficiency in 1993 and 10% efficiency at the National Renewable Energy Laboratory (NREL) in 1997 [31-32].

The construction of DSSCs involved a transparent conductive oxide (TCO) layer on two glass sheets—one coated with a sensitized photoanode and the other with a counter electrode [33]. DSSCs mimic natural photosynthesis, with dye molecules absorbing sunlight and injecting electrons into the semiconductor [34]. The review by Anandan until 2007 focused on aspects such as light-harvesting inorganic dye molecules, p-CuO nanorod counter electrodes, and the self-organization of electroactive polymers [30]. Another review by Bose et al. (2015)

highlighted developments in photoelectrode, photosensitizer, and electrolyte components, underscoring DSSC's superior performance compared to Si-based modules [35]. Shalini et al. (2018) delved into sensitizers, while Jihuai Wu et al. (2012) concentrated on counter electrodes.

The review offers a detailed examination of diverse components and their applications within DSSCs. Furthermore, it provides insights into the construction and operational principles of these cells. The overarching goal of the article is to cultivate a thorough understanding of DSSC components and applications, elucidating the development and operational principles underlying these innovative solar cells.

2.1. History and Development of Dye-Sensitized Solar Cells

The development of DSSCs has evolved over the years, marked by significant milestones and breakthroughs:

- **Initial Investigations (1839)**: Alexandre-Edmond Becquerel initiated the investigations of solar-to-electric devices [36].
- **First Efficient Solar Cell (1883)**: Charles Fritts developed a 1% efficient solar cell [36].
- **First Solar Cell Patent (1888)**: Edward Weston received the first solar cell patent.
- **Photoelectric Effect (1921)**: Albert Einstein was awarded the Nobel Prize in Physics for his work on the photoelectric effect.
- **First Practical Silicon Solar Cell (1954)**: Bell Labs announced the first practical silicon solar cell with about 6% efficiency.
- **Alternatives to Silicon Solar Cells (~1950s)**: Gallium arsenide (GaAs), copper gallium indium diselenide (CIGS), cadmium telluride (CdTe), and amorphous silicon alternatives emerged.
- **Dye-Sensitized Solar Cells (DSCs, 1991)**: The modern version of a dye solar cell, also known as the Grätzel cell, was co-invented by Brian O'Regan and Michael Grätzel at UC Berkeley and later developed at the École Polytechnique Fédérale de Lausanne (EPFL).
- **Organic Photovoltaics (OPVs, 2001)**: More recently, the processability approach has been the focus of multiple modern advances in dye-sensitized solar cells (DSCs).
- **Perovskite Solar Cells (PSCs, ~2009)**: All of these technologies can be processed via solution-based techniques which dramatically lowers pricing.
- **Current Developments (2022)**: Scientists at EPFL have increased the power conversion efficiency of dye-sensitized solar cells beyond 15% in direct sunlight and 30% in ambient light conditions.

The field of DSSCs continues to progress, with efforts directed toward enhancing their performance, reducing production costs, and expanding their applications in renewable energy technologies. As an intriguing and sustainable photovoltaic option, DSSCs hold promise for the future of solar energy.

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3. ARCHITECTURE OF DSSC

The architecture of a Dye-Sensitized Solar Cell (DSSC) comprises several key components, each playing a crucial role in the conversion of sunlight into electrical energy. The schematic representation of a standard Dye-Sensitized Solar Cell (DSSC) is depicted in the figure 5. Here is an overview of the architecture of a typical DSSC:

3.1. Photoanode:

The photoanode is a critical component responsible for capturing sunlight and initiating the conversion process in Dye-Sensitized Solar Cells (DSSCs) [29]. Typically composed of semiconducting metal oxides (SMOs) with wide bandgaps, such as titanium dioxide (TiO2) or zinc oxide (ZnO), these metal oxides are coated onto transparent conducting glass substrates. The photoanode also contains a layer of photosensitizer (dye) anchored to the metal-oxide layer, making it the backbone of the DSSC [29].

Key characteristics of an ideal photoanode can be succinctly summarized:

- **High Surface Area:** To enhance the capacity for picking up and adsorbing dye molecules, the photoanode should possess a high surface area [37].
- **Facilitation of Fast Electron Transfer:** It should facilitate rapid electron transfer from the dye to the external circuit and ensure fast electron injection from the dye into the semiconductor [37].
- **Optimized Pore Size:** The pore size of the photoanode should be carefully engineered to enable the optimum diffusion of both dye molecules and electrolyte, promoting efficient charge transport.
- **High Resistance to Photo-corrosion:** The photoanode should exhibit resistance to photo-corrosion, ensuring stability and longevity under prolonged exposure to light.
- **Light Absorption/Scattering Capability:** The photoanode should efficiently absorb or scatter sunlight, contributing to the effective functioning of the dye and the overall energy conversion process.
- **Effective Electron Acceptor:** Acting as a good electron acceptor, the photoanode should efficiently accept electrons from the dye molecules [38] .
- **Optimal Interface Contact:** Establishing an optimum interface contact with both the dye molecules and the conductive layer on the substrate is crucial for facilitating efficient electron transfer throughout the cell [37].

3.2. Photosensitizer (Dye):

The dye in a Dye-Sensitized Solar Cell (DSSC) plays a crucial role in absorbing incident light. For optimal performance, the dye should possess specific photophysical and electrochemical properties:

- **Luminescence:** The dye should exhibit luminescent properties.
- **Absorption Spectra:** The absorption spectra of the dye should cover both ultraviolet-visible (UV-vis) and near-infrared (NIR) regions.
- **HOMO and LUMO Placement:** The Highest Occupied Molecular Orbital (HOMO) should be situated far from the surface of the TiO2 conduction band, while the Lowest Unoccupied Molecular Orbital (LUMO) should be positioned close to

the TiO2 surface. The LUMO should also be higher than the TiO2 conduction band potential [39].

- **HOMO Energy Level:** The HOMO energy level should be lower than that of redox electrolytes.
- **Hydrophobic Periphery:** The periphery of the dye should be hydrophobic to enhance long-term stability. This property minimizes direct contact between the electrolyte and the anode, preventing water-induced distortion of the dye from the TiO2 surface, which could compromise cell stability [40].
- **Preventing Aggregation:** To avoid dye aggregation on the TiO2 surface, co-absorbents like chenodeoxycholic acid (CDCA) and anchoring groups such as alkoxy-silyl, phosphoric acid, and carboxylic acid groups are introduced between the dye and TiO2. This insertion prevents dye aggregation, limits recombination reactions between the redox electrolyte and electrons in the TiO2 nanolayer, and promotes the formation of stable linkages. [41].

3.3. Electrolyte:

Electrolytes in Dye-Sensitized Solar Cells (DSSCs), such as I^-/I_3^-, Br^-/Br_2^-, SCN^-/SCN_2, and Co (II)/Co (III), consist of redox couples, solvents, additives, ionic liquids, and cations. Key properties expected in an electrolyte include:

- **Efficient Redox Regeneration:** The redox couple should effectively regenerate the oxidized dye.
- **Stability:** The electrolyte should exhibit long-term chemical, thermal, and electrochemical stability.
- **Non-Corrosiveness:** It should not corrode DSSC components.
- **Facilitate Charge Carrier Diffusion:** The electrolyte should enable fast diffusion of charge carriers, enhance conductivity, and establish effective contact between working and counter electrodes.
- **Non-overlapping Absorption Spectra:** The absorption spectra of the electrolyte should not overlap with that of the dye.

While I^-/I^-_3 has shown high efficiency, it has limitations, including corrosion, volatility, photodegradation, and poor long-term stability. Solvents like acetonitrile (ACN), N-methylpyrrolidine (NMP), and solvent mixtures (e.g., ACN/valeronitrile) are used, with 4-tert-butylpyridine (TBP) as an additive to shift the conduction band of TiO2 upwards. However, TBP has drawbacks like reduced photocurrent and injection driving force. Ionic liquids (ILs) face challenges like leakage, leading to the development of solid-state electrolytes as alternatives. To address issues like redox electrolyte failure or sealing under prolonged illumination, extensive long-term light soaking tests on sealed cells have been advanced over the years [42].

3.4. Counter Electrode:

The counter electrode plays an important role in catalyzing the reduction of the electrolyte and collecting holes from HTMs[43]. Platinum is often preferred due to its high efficiency [43]. However, more cost-effective and abundant alternatives such as carbon, CoS, FeSe, and CoNi0.25 are being explored [43-44].

Working in conjunction with the redox electrolyte, the counter electrode gathers electrons from the external circuit [45]. The creation of the counter electrode often involves applying thin layers of noble metals onto transparent glass substrates [44]. In a bid to find more cost-effective solutions, conductive carbonaceous materials are being investigated as potential substitutes for the counter electrode [45].

3.5. Transparent Conductive Substrates:

conductive materials, which serve both as a substrate for depositing semiconductors and catalysts and as collectors for electric current [46]. The chosen substrate for DSSCs should possess two key characteristics. Firstly, it needs to have a transparency level exceeding 80% to allow optimal sunlight to reach the cell's effective area [47]. Secondly, to ensure efficient charge transfer and minimize energy loss in DSSCs, the substrate should exhibit high electrical conductivity.

Fluorine-doped tin oxide (FTO, SnO_2: F) and indium-doped tin oxide (ITO, In_2O_3: Sn) are commonly employed as conductive substrates in DSSCs [29]. These substrates consist of soda lime glass layered with indium-doped tin oxide and fluorine-doped tin oxide. Specifically, ITO films demonstrate a transmittance greater than 80% and a sheet resistance of 18 Ω/cm2, whereas FTO films exhibit a slightly lower transmittance of approximately 75% in the visible region, coupled with a sheet resistance of 8.5 Ω/cm2[25].

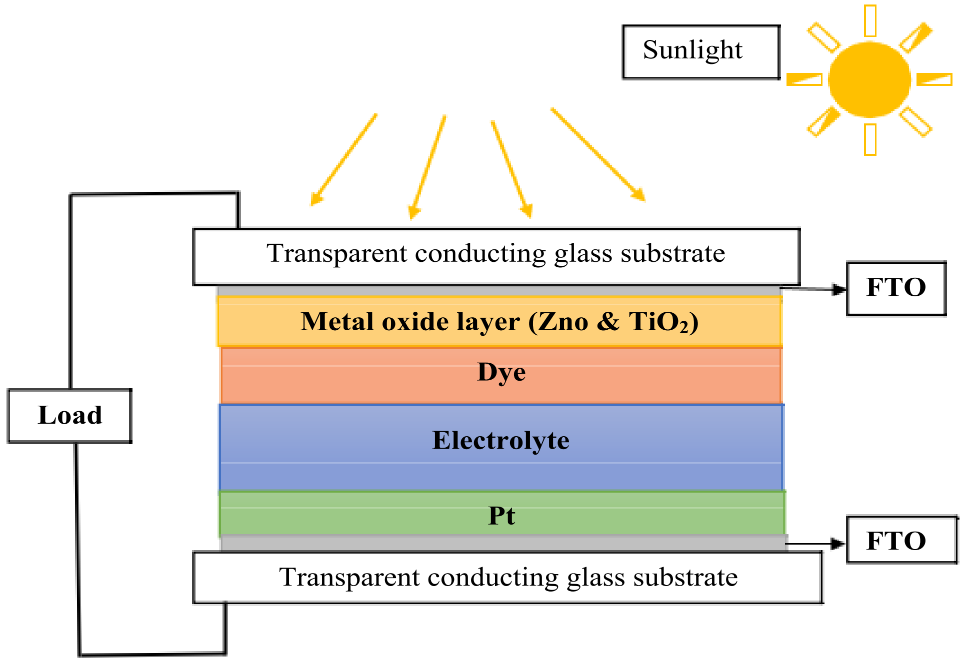


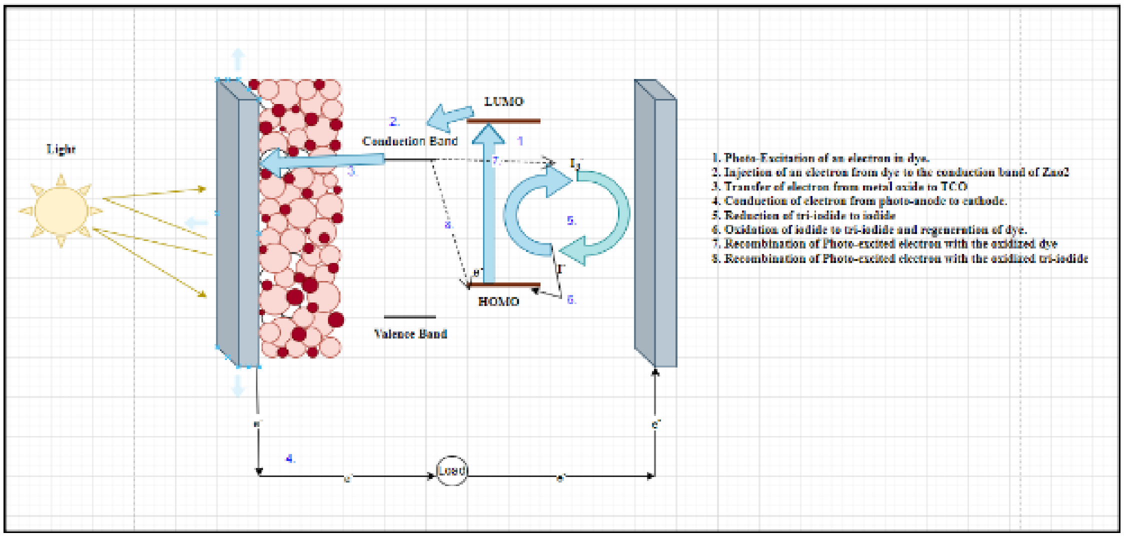
Fig 5. Schematic View of a dye-sensitized solar cell

4. WORKING OF DSSC

The operation of a Dye-Sensitized Solar Cell (DSSC) involves a sequence of steps that convert sunlight into electrical energy. The following steps are involved in the conversion of photons into current [48]. (as shown in Fig. 6):

- **Photon Absorption:**
  Incident light (photon) is absorbed by a photosensitizer (dye), causing electrons to be promoted from the ground state (S^{+}/S) to the excited state (S^{+}/S^{*}):
  $$S^{+} + h\nu \longrightarrow S^{*}+e^{-}$$
- **Electron Injection:**
  Excited electrons are injected into the conduction band of a nanoporous TiO_2 electrode, leading to the oxidation of the dye:
  $$S^{*}\longrightarrow S^{+}+e^{-}(TiO_2 \text{ absorption})$$
- **Electron Transport:**
  Injected electrons move through the TiO_2 nanoparticles, diffusing towards the back contact (transparent conducting oxide, TCO). Through the external circuit, electrons reach the counter electrode.
- **Redox Reaction and Electrolyte:**
  Electrons reaching the counter electrode reduce I_3^{-} to I^{-}, regenerating the ground state of the dye:
  $$S^{*}+e^{-}\longrightarrow S^{+}+I_3^{-}$$
  $$I_3^{-}+2e^{-}\longrightarrow 3I^{-}$$
- **Counter Electrode:**
  The oxidized mediator (I_3^{-} diffuses back toward the counter electrode and is reduced to I^{-})

This cyclic process allows DSSCs to continuously convert sunlight into electricity, with equations illustrating the photon absorption, electron injection, transport, redox reaction, and regeneration steps.



1. Photo-Excitation of an electron in dye.
2. Injection of an electron from dye to the conduction band of Zno2
3. Transfer of electron from metal oxide to TCO
4. Conduction of electron from photo-anode to cathode.
5. Reduction of tri-iodide to iodide
6. Oxidation of iodide to tri-iodide and regeneration of dye.
7. Recombination of Photo-excited electron with the oxidized dye
8. Recombination of Photo-excited electron with the oxidized tri-iodide

Fig 6. Working principle of DSSCs

5. MATERIALS USED IN DYE-SENSITIZED SOLAR CELLS

Dye-Sensitized Solar Cells (DSSCs) involve the use of various materials to construct the different components of the cell. The key materials used in DSSCs include:

5.1. Photosensitizer (Dye):

Photosensitizers, crucial components responsible for light absorption and electron generation, are pivotal in DSSCs [49]. They encompass both organometallic and organic dyes, with examples such as ruthenium-based N719 and N3, as well as organic compounds like coumarins and porphyrins. These dyes play a vital role in capturing sunlight, initiating the electron injection process, and contributing to the overall efficiency of the solar cell. Researchers continually strive to develop novel photosensitizer materials to improve DSSC performance and sustainability [50].

Indian researchers have made significant strides in the exploration of sensitizers utilized in dye-sensitized solar cells (DSSCs), with a specific focus on three main categories: organometallic dyes, metal-free dyes, and natural dyes [51] (fig.7)

- **Organometallic Dyes:** In the realm of DSSCs, organometallic dyes stand out as promising candidates, incorporating transition elements such as Ru, Os, and Ir along with organic materials. Ru (II) is particularly favoured due to its advantageous octahedral geometry, appealing photoluminescence, electrochemical features, sustainability, and resilience in various solutions. Noteworthy contributions from researchers like Praveen Naik et al. involve the development of dyes by combining aniline-based dyes with an N3 dye, achieving a commendable solar panel with a PCE of 7.02%. Another study by Subramaniam, K., et al. introduced a heteroleptic dual-anchored Ru (II) complex (RNPDA) with a PCE of 3.42% [50].

- **Metal-Free Dyes:** Metal-free natural dyes have emerged as an alternative for DSSCs, showcasing PCEs comparable to Ru-based sensitizers (Singh et al., 2021). These dyes offer high extinction factors, programmable absorption frequencies, and cost advantages. Most metal-free natural pigments follow a D—A pattern, incorporating electron-rich substances like phenylamine, aminocoumarin, and indoline as donors, and thiophenes, polyenes, and benzothiadiazole as conjugated compounds [52]. Novel metal-free D-A-π-A pattern dyes, such as (E)-2-cyano-3-(10-(4-(diphenyl amino) phenyl)-1-(4-(diphenylamino)phenyl)-1-(4-(diphenylamino)phenyl)-1-(4-(diphenylamine)phenyl)(2-ethylhexyl)-1H-phenanthrocarbazol-3-yl) acrylic acid (NPS-4), have been developed, exhibiting an aggregate PCE of 4.12% [50],[52].
- **Natural Dyes:** Natural dyes extracted from various sources, including fruits, flowers, leaves, and microbes, have garnered attention for their potential use in DSSCs [53]. These organic dyes offer advantages such as high visual absorption coefficients, abundant availability, straightforward synthesis methods, and environmental friendliness. For instance, chlorophyll, - a significant natural pigment found in photosynthetic organisms, has been studied. Despite generally lower performance compared to Ru-based dyes, researchers have explored combining natural dyes to enhance their potential [50][53].

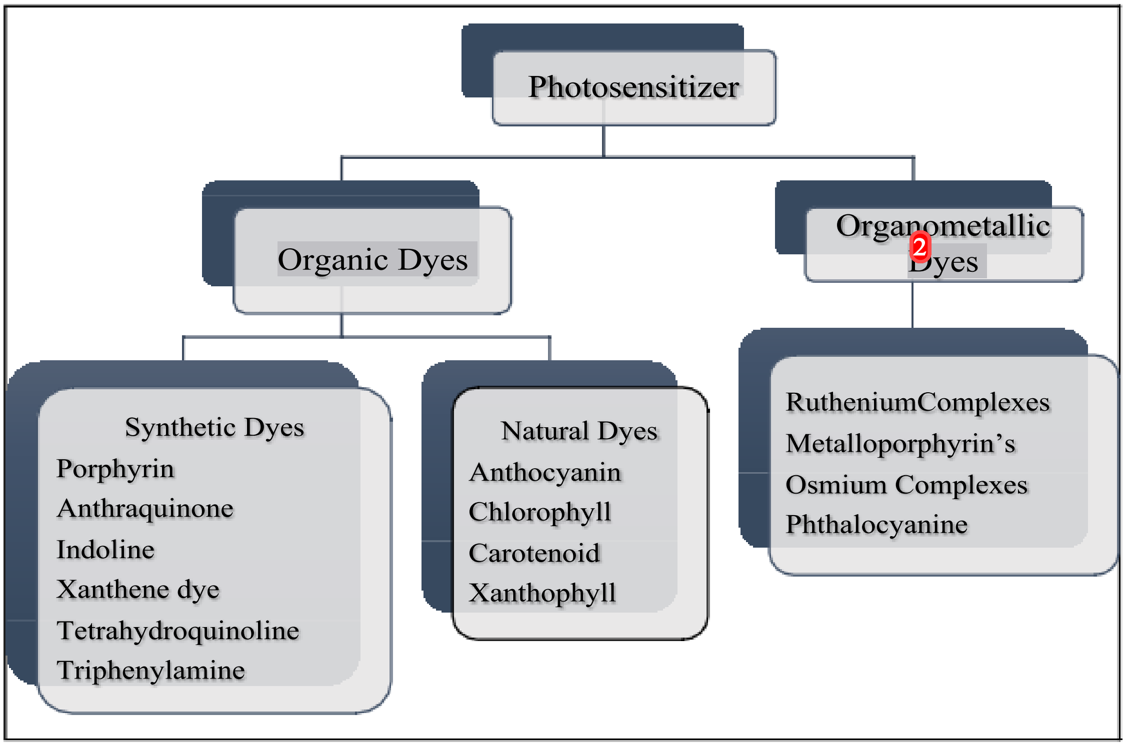


Fig 7. Overview of Different Photosensitizers or Dyes.

5.2. Metal oxide-based photoanodes:

The metal oxide semiconductor is a crucial component of the photoanode in Dye-Sensitized Solar Cells (DSSCs) [54]. These wide bandgap metal oxides serve as electron carriers and provide a surface for dye adsorption. Various metal oxides, such as TiO2, ZnO, SnO2, Nb2O5, WO3, In2O3, SrTiO3, Zn2SnO4, BaSnO3, and CoTiO3, have been investigated for their suitability in DSSCs [55]. The selection of a particular metal oxide depends on the energy levels of the valence band and conduction band, aiming to achieve effective charge separation and reduced recombination [50][56].

TiO2 photoanodes are extensively explored due to TiO2 being relatively cost-effective, abundant, biocompatible, and non-toxic, making it a stable n-type semiconductor material [57]. Three crystalline polymorphs of TiO2 are designed for DSSCs: anatase (bandgap 3.2 eV), rutile (bandgap 3.0 eV), and brookite (bandgap 3.4 eV). Among these, anatase TiO2 is widely considered superior in TiO2-based DSSCs.58[56].

Another metal oxide explored as a photoanode is WO3, a transition metal oxide with a bandgap ranging from 2.6 to 3.1 eV in the blue-UV region [58]. Porous WO3 nanoparticle films in DSSCs achieved an initial efficiency of 0.75%, which was later improved to 1.46% through treatment with TiCl4.

In2O3, a wide bandgap material with an energy level of 3.6 eV, is less commonly used but has been studied. Nanostructures of In2O3, such as spheres, nanotubes, nanocubes, pyramids, and inverse opals, have been investigated, influencing the overall photovoltaic performance [55].

SnO2 is another alternative semiconductor with high electron mobility and a sizable bandgap of about 3.6 eV. Nanostructured SnO2 materials, including nanowires, nanocrystallites, and coral-like porous hollow architectures, have been explored as efficient photoanodes [55].

The reported efficiencies for different metal oxides based on their energy band gaps are summarized and the advantages and disadvantages of various metal oxides are presented in Table 1. These comparative tables offer insights into the performance characteristics of different metal oxides in DSSCs.

Table 1. Efficiencies of different metal oxides in Dye-Sensitized Solar Cells, and a comparative analysis of the advantages and disadvantages associated with their use as photoanodes.

Metal Oxides	**Band Gap (eV)**	**Best Efficiency (%)**	**Advantages**	**Disadvantages**	**Ref**
TiO2 – Anatase	3.2	8.75	Cost-effective, abundant, biocompatible & non-toxic, Stable n-type semiconductor, Better photostability, Fast electron injection rate.	Limited electron mobility.	[57]
Rutile	3.0	6.23			
Brookite	3.4	4.1			
ZnO	3.37	7.5	Heterogeneity in ZnO nanostructures., High electron mobility.	Complexation with dyes, Dyes dependent performance.	[55]
SnO2	3.6	8.23	High electron Mobility, Sizeable bandgap.	Lower electron injection, Faster electron,recombination, Less adsorption of dye.	[55]
Nb2O5	3.4	4.1	Wider bandgap. Reduced electron scattering, Greater surface area.	Reduction in the dye loading sites.	[54]

WO3	2.6-3.1	1.46	Extremely stable material. Good carrier mobility.	Acidic surface, More positive conduction band edge.	[58]
In2O3	3.6	<2	Higher electron lifetime. Large surface area with hollow porous structure.	Wide bandgap, More positive potentials of bands.	[55]
SrTiO3(Strontium Titanate)	4.15	0.58	High dielectric constant, good thermal stability	Low electrical conductivity	[55]
Zn2SnO4(Zinc Stannate)	3.6	3.8	High transparency in the visible light range, good stability	Lower electrical conductivity compared to other TCOs	[55]
BaSnO3(Barium Stannate)	2.9-4.0	5.2	High electron mobility, transparency in the visible light range	Requires high-temperature processing	[55]
CoTiO3 (Cobalt Titanate)	2.25	7.67	High thermal, stability, good chemical resistance	Not a good conductor of electricity	[55]

5.3 Electrolyte:

The utilization of liquid electrolytes in dye-sensitized solar cells (DSSCs) presents practical challenges, including leakages, volatilization, corrosion of the platinum secondary electrode, desorption, and photodegradation of the dye. Additionally, issues such as the precipitation of salts at low temperatures and ineffective sealing limit the long-term applications of DSSCs in solar modules. To overcome these disadvantages, considerable efforts have been directed toward replacing liquid electrolytes with alternatives such as ionic liquids (ILs), polymer gels, and solid-state electrolytes [58].

5.3.1. Role of Redox Couples: Redox couples are crucial in DSSCs as they facilitate electron transfer from the counter electrode to the oxidized dye (Chen et al., 2017). Commonly used redox couples include I^-/I_3^-, Br^-/Br_2, SCN^-/SCN_2, and Co (II)/Co (III) [59].

5.3.2. Solvents and Additives: These redox couples are dissolved in solvents such as acetonitrile (ACN) or N-methylpyrrolidine (NMP). Additives like 4-tert-butylpyridine (TBP) are often included to enhance cell performance [59].

5.3.3. Effectiveness of Redox Electrolytes: The efficiency of redox electrolytes is influenced by factors like solubility, ionic mobility, the driving force for dye regeneration, and fast electron transfer kinetics with minimal overpotential at the counter electrode [59].

5.3.4. Types of Electrolytes: Electrolytes can be categorized into liquid, quasi-solid, and solid-state. Each type has its advantages and disadvantages, impacting the efficiency and stability of DSSCs.

- **Ionic Liquids:** Ionic liquids have emerged as promising alternatives for electrolyte solvents in DSSCs. These organic salts, with melting points near room temperature, consist of organic cations paired with various anions. Their unique properties, including good ionic conductivity, high chemical and thermal stability, non-flammability, and negligible vapor pressure, make them attractive for DSSCs [60]. Numerous imidazolium-based ILs with different anions have been synthesized and investigated for their application in DSSCs. Despite their promising properties, the high viscosities of ILs result in low ion mobility, leading to lower DSSC device efficiencies compared to organic solvent-based electrolytes [60].

- **Polymer Gel Electrolyte:** Polymer gel electrolytes, a combination of polymers and redox couples, are commonly employed in DSSCs. Various types of gel electrolytes have been reported, utilizing polymers such as polyacrylonitrile, poly(vinyl chloride) (PVC), poly(methylmethacrylate), polyvinyl pyrrolidone, and polyethylene glycol. The conductivity of these electrolytes depends on the morphology and molecular weight of the polymers. Introducing disorder in the structure, achieved through blends of different polymers or the addition of plasticizers, can enhance ionic conductivity [61]. Despite achieving efficiencies of 8–9%, polymer gel electrolytes suffer from thermodynamic instability under high temperatures, necessitating careful sealing treatments [61].

- **Solid-State Electrolytes:** Solid-state electrolytes, involving inorganic p-type semiconductors or various hole-transporting materials (HTMs), have been explored as hole acceptors to replace liquid electrolytes. Inorganic materials like copper compounds (CuI, CuSCN), CsSnI3, $Cs_2SnI_3Br_3$, and organic polymers (P_3HT, PEDOT, spiroMeOTAD) have been successfully utilized in solid-state DSSCs. Challenges include issues with crystallization rates and control, with inhibitors like triethylaminehydrothiocyanate showing some improvement. SpiroMeOTAD, despite its effectiveness, faces hurdles due to high production costs and low hole mobility. Achieving high conductivity for effective hole transfer and good HTM diffusion into the photoanode electrode remains crucial for the success of solid-state electrolytes in DSSCs [62].

Table 2. concise overview of the advantages and disadvantages of each electrolyte type in DSSCs.

Electrolyte Type	Examples	Advantages	Disadvantages	Ref.
Liquid	Iodide–triiodide (I3−/I−) system	Satisfactory kinetic properties	Absorption of visible light, potential leakage, volatility	[60]
Polymer Gel	Polyacrylonitrile, PVC, etc.	Enhanced ionic conductivity, flexibility	Thermodynamic instability under high temperatures	[61]
Solid-State	Copper compounds, organic polymers	Improved stability, reduced leakage, potential for scale-up	Challenges in achieving high conductivity and cost concerns	[62]
Quasi-solid	Ionic liquids or polymer gels with redox couples	Addresses sealing and durability issues	Thermodynamic instability under high temperature	[62]

5.4. Counter Electrode Catalyst:

Dye-sensitized solar cells (DSSCs) stand out among various photovoltaic devices due to their cost-effectiveness, ease of fabrication, and environmentally friendly characteristics. The fundamental components of DSSCs, including the photoanode, sensitizer, electrolyte, and counter electrode (CE), collectively influence their performance. The choice of CE materials is particularly crucial in determining the overall efficiency of DSSCs [63].

To enhance the cost-effectiveness of photovoltaic applications, there is a growing emphasis on developing alternative CE catalysts. While platinum-based CEs are effective, they are expensive. Several economical and highly stable materials, such as conducting polymers, sulfides, oxides, and carbonaceous substances like N-doped core–shell structures, have emerged as promising alternatives. Remarkably, N-doped core–shell-based DSSCs have demonstrated a power conversion efficiency of 7.89%, surpassing that of platinum-based cells (7.48%) [63].

In the pursuit of efficient CE catalysts, researchers have explored various materials. For instance, Cr-doped SiC exhibited superior activity in triiodide splitting but demonstrated limitations in further iodine splitting into mono-iodides compared to Pt-doped SiC slabs. Additionally, graphene nanoplatelet-based CEs showed a charge transfer resistance of 3.36 Ω, slightly higher than platinum (1.18 Ω), resulting in slightly elevated oxidation [63].

- The role of the Counter Electrode (CE) in Dye-Sensitized Solar Cells (DSSCs) is to collect electrons from the external circuit and catalyze the reduction of the redox electrolyte, or transport holes in solid-state electrolyte. It requires high conductivity, excellent electrocatalytic activity, and overall stability [63].
- Noble metals like Platinum (Pt), Gold (Au), and Silver (Ag) have traditionally been used as CE materials due to their high electrocatalytic activity. However, their high cost and susceptibility to corrosion have led to the exploration of alternative materials [64].

- Carbon materials, including porous carbon, carbon nanotubes (CNTs), and graphene, are favored for their low cost, good electrocatalytic activity, high electrical conductivity, thermal stability, and corrosion resistance. Enhancements in electrocatalytic activity have been achieved by combining different carbon materials [65-66].
- Inorganic compounds like sulfides, carbides, nitrides, phosphides, tellurides, and metal oxides have potential applications in low-cost and large-scale DSSCs. However, they require further improvements in performance and stability [67].
- Conductive polymers, such as polyaniline (PANI), poly(3,4-ethylenedioxythiophene) (PEDOT), and polypyrrole (PPy), are used as CE materials, especially for transparent and flexible DSSCs. PEDOT is commonly used, and its solubility and electrical conductivity are enhanced through doping [68-69].
- Composite CEs, composed of two or more materials, combine the merits of each component. They have been extensively investigated, with examples including composites of carbon materials with other organic/inorganic materials.

Table 3. Summary table for the types of CE materials:

CE Material Type	Examples	Advantages	Disadvantages	Ref
Noble Metals	Pt, Au, Ag	High electrocatalytic activity	High cost, susceptibility to corrosion	[64]
Carbon Materials	Porous carbon, CNTs, Graphene	Low cost, good electrocatalytic activity, high electrical conductivity, thermal stability, corrosion resistance	Requires combination for enhanced activity	[65-66]
Inorganic Compounds	Sulfides, Carbides, Nitrides, Phosphides, Tellurides, Metal Oxides	Potential for low-cost and large-scale DSSCs	Requires further improvements in performance and stability	[67]
Conductive Polymers	PANI, PEDOT, PPy	Used for transparent and flexible DSSCs, solubility and electrical conductivity can be enhanced through doping	Specific to certain types of DSSCs	[68-69]
Composite CEs	Composites of carbon materials with other organic/inorganic materials	Combines the merits of each component	Performance depends on the combination of materials	[67]

5.5 Back Contact (Transparent Conducting Oxide - TCO):

In Dye-Sensitized Solar Cells (DSSCs), the back contact, also known as the Transparent Conducting Oxide (TCO), plays a crucial role. It allows light to pass through to the semiconductor layer while also serving as an electrical contact. The most commonly used materials for this purpose are Fluorine-doped Tin Oxide (FTO) and Indium Tin Oxide (ITO).

5.5.1.Fluorine-doped Tin Oxide (FTO): FTO is a transparent conducting oxide that is well-suited for use in DSSCs due to its transparent and conductive nature[70]. It is composed of abundant elements, making it a cost-effective alternative to ITO. FTO has high thermal stability and is resistant to corrosion, making it suitable for high-temperature processes [70]. However, FTO has a higher surface roughness compared to ITO, which can be reduced by introducing an additional SnO2 coating[71].

5.5.2. Indium Tin Oxide (ITO): ITO is another transparent conducting oxide commonly used in DSSCs. It is popular due to its lower surface roughness and excellent optical and electrical properties. However, the cost of ITO is relatively high due to the scarcity of indium. Moreover, indium migration from ITO can cause stability issues in DSSCs[70].

5.5.3. Antimony-doped Tin Oxide (ATO): ATO is an excellent candidate for transparent conducting oxides (TCOs) due to its high transparency with a large band gap (>3.6 eV), an inexpensive source, and good electrical conductivity. The doping of Sb in the SnO2 lattice without structural change leads to an improvement in the properties and performance of DSSCs. However, it is limited by its opto-electrical properties. The surface of the ATO conductive electrode increases the hydrophilicity due to high surface roughness compared to that of the undoped tin oxide (TO) electrode [72-73].

5.5.4. Aluminium-doped ZnO Film (AZO): AZO is another transparent conducting oxide used in DSSCs. Both zinc oxide (ZnO) nanorods and aluminium-doped zinc oxide (AZO) nanosheets were deposited by hydrothermal growth on fluorine-doped tin oxide (FTO) glass. After a photoanode was added to ZnO nanorods or AZO nanosheets, the photovoltaic conversion efficiency (PCE) increased due to improved electron transport and enhanced dye absorption. The addition of the ZnO nanorods increased the short-circuit current density (Jsc) from 9.07 mA/cm2 to 10.91 mA/cm2, the open circuit voltage (Voc) from 0.68 V to 0.70 V, and the PCE from 3.70% to 4.73%, respectively [74-76].

Table 4. FTO and ITO:

Material	Advantages	Disadvantages	Ref.
FTO	High thermal stability, corrosion resistance, cost-effective	Higher surface roughness	[70-71]
ITO	Lower surface roughness, excellent optical and electrical properties	High cost, potential stability issues due to indium migration	[70-71]
Antimony doped tin oxide (ATO)	Excellent candidate for transparent conducting oxides (TCOs), shows	Limited by its opto-electrical properties	[72-73]

	excellent electrical properties		
Aluminium doped ZnO Film (AZO)	Transparent and electrically conductive, high transmission in the visible region	Low electrical conductivity and charge concentration	[74-76]

5.6. Substrates:

In Dye-Sensitized Solar Cells (DSSCs), the substrate plays a vital role by providing the necessary structural support. The substrate, whether it’s glass or plastic, provides crucial structural support and influences the efficiency, stability, and potential applications of the solar cell [65][77].

The choice between glass and plastic substrates indeed depends on the specific requirements of the solar cell. Glass substrates offer excellent durability and resistance to high temperatures, but they are heavier and more fragile compared to plastic substrates [78-79].

On the other hand, plastic substrates are lightweight and flexible, making them suitable for portable and flexible solar applications [80].

The substrate must be carefully prepared and treated to ensure good adhesion of the subsequent layers and overall performance of the DSSC. This often involves processes such as cleaning, etching, and the application of various coatings to enhance light absorption and reduce reflection [65].

Researchers continually explore new materials to improve the performance and sustainability of DSSCs [81]. The specific choice of materials can vary based on the design, efficiency requirements, and cost considerations of the DSSC [82].

6. Fabrication and Characterization of Dye-Sensitized Solar Cells (DSSCs)

Dye-sensitized solar cells (DSSCs) are a type of thin-film solar cell that convert sunlight into electricity. They consist of a semiconductor photoanode, a sensitizing dye, an electrolyte, and a counter electrode. The fabrication and characterization of DSSCs involve several key steps:

6.1. Fabrication Process:

- **Substrate Preparation**: The substrate, usually a transparent conducting material like fluorine-doped tin oxide (FTO) or indium tin oxide (ITO), is thoroughly cleaned to remove any contaminants [65][77].
- **Photoanode Preparation**: A layer of a semiconductor, typically titanium dioxide (TiO2), is deposited onto the substrate. The TiO2 layer is often nanoparticulate to provide a large surface area for dye adsorption [83].
- **Dye Adsorption**: A photosensitizing dye, often a metal complex like ruthenium-based dyes (e.g., N719 or N3), is adsorbed onto the TiO2 layer. The dye absorbs photons and generates electron-hole pairs [84-85].
- **Electrolyte Filling**: A liquid electrolyte containing a redox couple (e.g., I^-/I_3^-) is introduced into the cell to facilitate electron transport. Alternatively, solid-state or quasi-solid-state electrolytes can be used [81][86].

- **Counter Electrode Preparation**: A counter electrode, often composed of platinum-coated FTO or a conductive carbon material, is prepared. This electrode facilitates the reduction of the redox couple [87-89].
- **Sealing**: The DSSC is sealed to prevent the leakage of the electrolyte and protect the components. Sealing methods include thermoplastic seals or epoxy resins [81][90].

6.2. Characterization Techniques:

6.2.1. Current-Voltage (I-V) Characteristics: To understand how well a dye-sensitized solar cell (DSSC) performs, we look at several key parameters that act as indicators of its effectiveness. These parameters include the incident photon to current conversion efficiency (IPCE, %), short circuit current (JSC, $mAcm^{-2}$), open circuit voltage (VOC, V), maximum power output (Pmax), overall efficiency (η, %), and fill factor (FF). These metrics play a crucial role in evaluating the cell's performance under consistent exposure to light [77]

- **Power Conversion Efficiency (PCE):** PCE is a measure of how efficiently a solar cell converts incident light energy into usable electrical power. It is determined by three properties of the solar cell and one property of the incident spectrum.
- **Open-Circuit Voltage (Voc):** Voc is the maximum voltage achievable from a solar cell when no current is flowing. It corresponds to the forward bias on the solar cell due to the junction bias with light-generated current.
- **Short-Circuit Current (Jsc):** Jsc is the current through the solar cell when the voltage across it is zero, typically occurring when the cell is short-circuited. The short-circuit current is identical to the light-generated current.
- **Fill Factor (FF):** When the negative and positive electrodes of the cell are short-circuited at zero mV voltage, a current is generated. VOC represents the voltage across these electrodes under open circuit conditions at zero milliampere (mA) current. It essentially signifies the potential difference between the conduction band energy of the semiconducting material and the redox potential of the electrolyte. Pmax reflects the maximum efficiency of the DSSC in converting sunlight into electricity. The ratio of the maximum power output (Jmp × Vmp) to the product (VOC × JSC) gives the FF.

$$\mathrm{FF} = \frac{(\mathrm{Jmp} \times \mathrm{Vmp})}{(\mathrm{VOC} \times \mathrm{JSC})}$$

The overall efficiency (η) indicates the percentage of solar energy converted into electrical energy on a photovoltaic (PV) device. η increases with a decrease in JSC and an increase in VOC, FF, and the molar coefficient of the dye.

External quantum efficiency, or IPCE, is the ratio of electrons flowing through the external circuit to photons incident on the cell's surface at any wavelength λ. The IPCE values are linked to light harvesting efficiency (LHE), electron injection quantum efficiency (φE1), and the efficiency of collecting electrons in the external circuit (ηEC).

Equations for these parameters are provided as follows:

Overall Efficiency: $$\eta\% = \frac{JSC \times VOC \times FF}{Pin}$$

External Quantum Efficiency (IPC (%) $$= 1240 \times \frac{JSC}{\lambda Pin}$$

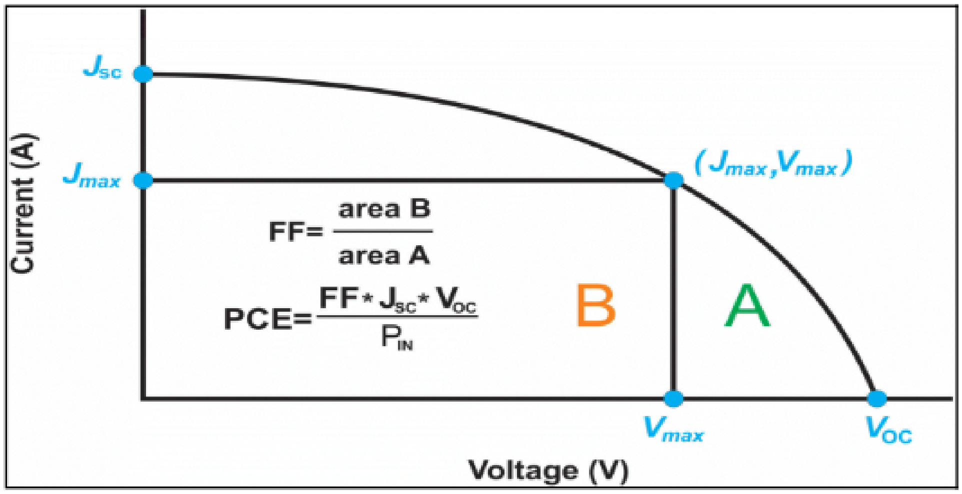


Fig 8. I–V curve to evaluate the cells performance (taken from [Sharma et al., 2018])

6.2.2. Electrochemical Impedance Spectroscopy (EIS): Electrochemical Impedance Spectroscopy (EIS) is a technique utilized to investigate the charge transfer and transport mechanisms within a Dye-Sensitized Solar Cell (DSSC). It offers insights into electron recombination, dye regeneration, and the properties of the electrolyte. This method has become an essential tool for characterizing DSSCs. By analyzing the impedance spectrum with its equivalent circuit model, EIS can provide a comprehensive understanding of the electron transport processes and performance of DSSCs [91-93].

6.2.3. UV-Visible Absorption Spectroscopy: UV-Visible Absorption Spectroscopy emerges as a pivotal technique for examining the absorption characteristics of the dye on the TiO2 layer within Dye-Sensitized Solar Cells (DSSCs). This method plays a crucial role in understanding the efficiency of dye absorption of light. The absorption occurring in the visible range directly influences the perceived color of the involved chemical. This technique holds significance in the study of DSSCs, providing valuable information on the interaction between the dye and the TiO2 layer [94].

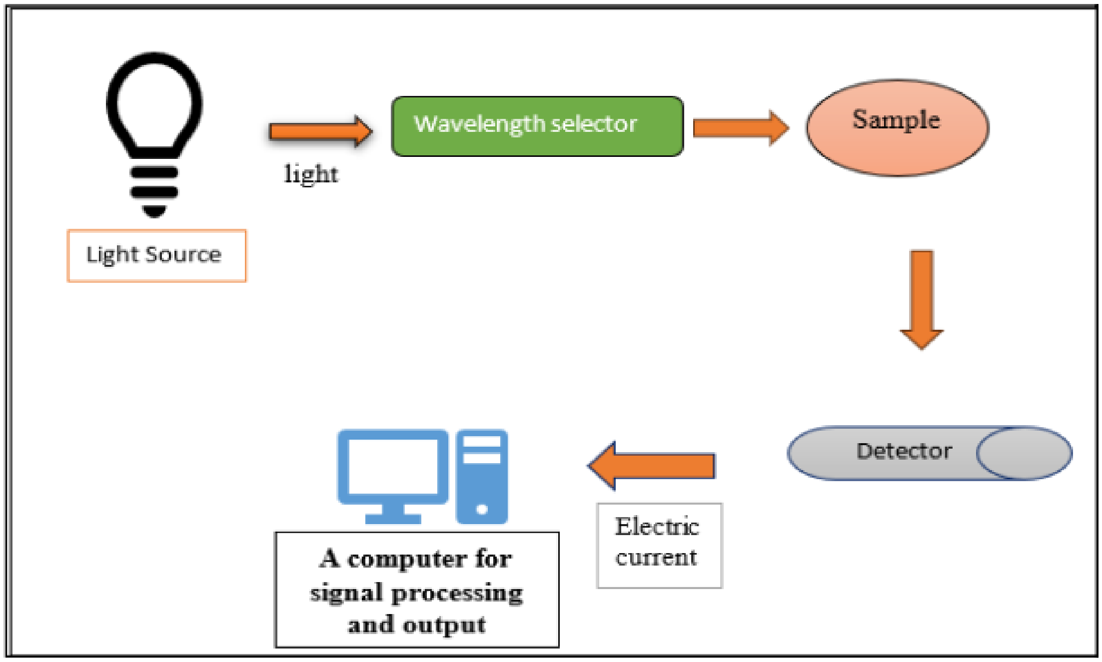


Fig 9. A simplified schematic of the main components in a UV-Vis spectrophotometer.

6.2.4. Scanning Electron Microscopy (SEM): SEM is used for morphological analysis of the TiO2 layer, dye coverage, and overall cell structure. It provides insights into the surface properties of the photoanode [95-96]. Scanning Electron Microscopy (SEM) is a powerful tool used in the analysis of the TiO2 layer, dye coverage, and overall cell structure. Here's a simplified explanation of how it's used:

- **Morphological Analysis of the TiO2 Layer**: SEM helps in understanding the structure and form of the TiO2 layer. For instance, in the field of dye-sensitized solar cells (DSSCs), SEM has been used to analyze the effect of multidimensional TiO2 nanostructures on the performance of the cells. The hydrothermal method was used to synthesize TiO2 nanoparticles (TNPs), TiO2 nanorods (TNRs), and TiO2 nanotubes (TNTs) for photoanodes. The crystallinity, surface, and internal morphological changes were analyzed with SEM.
- **Dye Coverage**: SEM can provide insights into how well the dye covers the TiO2 layer. This is crucial in applications like DSSCs where the dye plays a key role in light absorption and the transfer of excited electrons.
- **Overall Cell Structure**: SEM is used to study the overall structure of cells. For example, in DSSCs, SEM images showed the formation of TiO2 film nanocoral with morphologies due to the effect of increasing the reaction times.

6.2.5. X-ray Diffraction (XRD): XRD is used to analyze the crystal structure of the TiO2 layer. It helps in understanding the crystallinity and phase composition of the semiconductor. X-ray Diffraction (XRD) is indeed a powerful technique used to analyze the crystal structure of the TiO2 layer. Here's a simplified explanation:

- **Crystal Structure Analysis**: XRD can provide insights into the crystal structure of the TiO2 layer. For instance, it can help identify whether the TiO2 is in the anatase or rutile phase [97]. These phases have different properties and are used in different applications.
- **Crystallinity**: XRD can determine the degree of crystallinity in the TiO2 layer. This is important because the crystallinity can affect the properties of the material.
- **Phase Composition**: XRD can also be used to understand the phase composition of the TiO2 layer. This can provide information about the presence of different phases (like anatase or rutile) in the material.

6.2.6. Photocurrent Spectroscopy: This technique involves illuminating the DSSC with monochromatic light and measuring the resulting photocurrent. It provides information about the action spectrum and efficiency of the dye [98-100]. Photocurrent Spectroscopy is indeed a valuable technique used in the study of Dye-Sensitized Solar Cells (DSSCs). Here's a simplified explanation:

- **Illumination and Measurement**: In this technique, the DSSC is illuminated with monochromatic light, and the resulting photocurrent is measured. This process is similar to Electrochemical Impedance Spectroscopy (EIS), but in this case, light is used instead of an electrical signal.
- **Action Spectrum Information**: The action spectrum refers to the relative effectiveness of different wavelengths of light at producing a response. In the case of DSSCs, this response is the generation of photocurrent. Photocurrent Spectroscopy can provide information about the action spectrum of the dye used in the DSSC.
- **Efficiency of the Dye**: The efficiency of the dye refers to how effectively it can absorb light and generate photocurrent. Photocurrent Spectroscopy can provide insights into the efficiency of the dye.

6.2.7. Stability Testing: DSSCs are subjected to stability tests under different conditions (e.g., prolonged light exposure, temperature variations) to assess their long-term performance and durability [101-104]. Stability Testing is indeed a critical aspect of Dye-Sensitized Solar Cells (DSSCs) research. Here's a simplified explanation:

- **Prolonged Light Exposure**: DSSCs are often subjected to long-term light exposure to assess their stability. This is because in real-world applications, these cells will be exposed to sunlight for extended periods. The performance of DSSCs can degrade over time due to factors like dye degradation, electrolyte evaporation, etc.
- **Temperature Variations**: DSSCs are also tested under different temperature conditions. High temperatures can affect the performance of DSSCs. For instance, exposure to sunlight increases the temperature of the internal component of DSSC and consequently degradation in device performance.
- **Long-term Performance and Durability**: The long-term stability of DSSCs is a crucial factor for their practical application. Studies have shown that with the right choice of materials and protective measures like plastic covers, long-term stability can be achieved.

6.2.8. Optimization and Improvement: Based on the characterization results, researchers aim to optimize DSSCs by improving various parameters such as the choice of dye, semiconductor materials, electrolyte composition, and overall cell design. Continuous research efforts focus on enhancing efficiency, stability, and cost-effectiveness for practical applications [81][85] [105-106]. Optimization and improvement of Dye-Sensitized Solar Cells (DSSCs) are indeed crucial areas of research. Here’s a simplified explanation:

- **Choice of Dye**: The choice of dye is a significant factor in the performance of DSSCs. Researchers are exploring both organic (natural and synthetic) and inorganic (ruthenium) dyes. Natural dyes are considered a viable alternative due to their low cost, easy utility, abundant supply of resources, and no environmental threat.
- **Semiconductor Materials**: The type of semiconductor material used can greatly affect the efficiency of DSSCs. For instance, TiO2 is commonly used, but researchers are exploring other materials as well.
- **Electrolyte Composition**: The composition of the electrolyte can also impact the performance of DSSCs. Researchers are investigating different electrolyte compositions to enhance the efficiency of DSSCs.
- **Overall Cell Design**: The design of the cell, including factors like the thickness of the film, the nature of FTO/ITO glasses, and the anode and cathode electrodes, plays a crucial role in the performance of DSSCs.
- **Efficiency, Stability, and Cost-effectiveness**: Continuous research efforts are focused on enhancing the efficiency, stability, and cost-effectiveness of DSSCs for practical applications. For instance, six different optimization algorithms are used for DSSC parameter extraction, including the genetic algorithm, grey wolf algorithm, dragonfly algorithm, moth flame algorithm, ant-lion algorithm, and whale algorithm.

7. Major challenges and limitations faced by dye-sensitized solar cells

Dye-sensitized solar cells (DSSCs) have shown promise in various applications, but they face several challenges and limitations that impact their widespread adoption. Here's a discussion on some of the major challenges:

7.1. Degradation Mechanisms:

- **Dye Degradation:** Organic dyes used as sensitizers can degrade over time due to exposure to light, temperature, and other environmental factors, leading to reduced light absorption and cell efficiency[107-108].
- **Electrolyte Decomposition:** The liquid electrolyte in traditional DSSCs may undergo decomposition over extended periods, impacting cell performance and stability [109-110] .

7.2. Long-Term Stability:

- **Sensitivity to Moisture:** DSSCs are sensitive to moisture, which can lead to corrosion of electrodes and degradation of the electrolyte [77][111].
- **Encapsulation Challenges:** Ensuring effective encapsulation to protect the cell components from environmental factors is a challenge, especially for flexible and lightweight DSSCs [111].

7.3. Scalability for Large-Scale Production:

- **Complex Fabrication Processes:** The traditional fabrication processes involve multiple steps, such as sensitization, electrode deposition, and electrolyte filling, which can be complex and time-consuming [85].
- **Material Costs:** While some materials used in DSSCs are cost-effective, the reliance on expensive counter electrodes (platinum or gold) can impact overall production costs.
- **Limited Scalability:** Scalability for large-scale production remains a challenge, especially when compared to well-established technologies like silicon solar cells.

7.4. Efficiency and Performance Variability:

- **Sensitivity to Fabrication Conditions:** DSSC performance can vary based on the fabrication conditions, making reproducibility and quality control challenging [113-114].
- Spectral Sensitivity: DSSCs may have a limited spectral sensitivity, especially in the infrared region, which can affect overall energy conversion efficiency [85][115].

7.5. Electrolyte Volatility:

- **Liquid Electrolyte Issues:** Liquid electrolytes used in traditional DSSCs can be volatile and susceptible to leakage or evaporation, leading to long-term stability concerns [109][116].

7.6. Toxicity and Environmental Impact:

- **Heavy Metal Usage:** Some DSSCs may use heavy metals in components like counter electrodes, posing environmental concerns and limiting their sustainability [86][117].

7.7. Competition with Emerging Solar Cell Technologies:

- **Rapid Advancements in Perovskite Cells:** Perovskite solar cells have emerged as a strong competitor with rapid advancements in efficiency and stability, posing a challenge to the adoption of DSSCs [109][118].

7.8. Temperature Sensitivity:

- **Performance in Extreme Temperatures:** DSSCs may exhibit performance degradation in extreme temperature conditions, affecting their suitability for certain environments [119].

While DSSCs have unique advantages, including flexibility and ease of fabrication, addressing the challenges related to degradation mechanisms, long-term stability, and scalability for large-scale production is crucial for their continued development and commercial viability. Ongoing research focuses on mitigating these challenges through the exploration of new materials, fabrication techniques, and encapsulation strategies. As advancements in materials science and engineering continue, DSSCs may become more competitive and find niche applications in the broader landscape of solar energy technologies.

8. Current Research Efforts and Technological Advancements in Dye-Sensitized Solar Cells (DSSCs):

8.1. Novel Materials for Sensitizers and Electrolytes:

- **Perovskite Sensitizers:** Research focuses on incorporating perovskite materials as sensitizers to enhance light absorption and improve stability [120].
- **Metal-Free Organic Dyes:** Exploration of metal-free organic dyes with improved stability and absorption characteristics [121-123].

8.2. Stability-Enhancing Strategies:

- **Molecular Design:** Tailoring the molecular structure of sensitizers and electrolytes to improve chemical stability and reduce degradation [124-125].
- **Inorganic Electrolytes:** Investigation of inorganic electrolytes to address the volatility and stability issues associated with liquid electrolytes [126-129].

8.3. Advanced Device Engineering:

- **Tandem and Multiple Cells:** Implementing tandem and multiple-cell configurations to maximize light absorption and minimize recombination losses [130].
- **Transparent Conductive Oxides (TCOs):** Utilizing TCOs with enhanced conductivity and stability as alternatives to traditional counter electrodes [65][131-133].

8.4. Surface Passivation Techniques:

- **Advanced Passivation Layers:** Employing advanced passivation layers, such as ALD-deposited materials, to reduce recombination and improve long-term stability [81]
- **Functional Coatings:** Developing functional coatings to protect the semiconductor surface from environmental factors [134] .

8.5. Innovative Manufacturing Techniques:

- **Printing Technologies:** Exploring printing techniques, such as inkjet and screen printing, for cost-effective and scalable production [135-137].
- **Roll-to-Roll Processing:** Implementing continuous roll-to-roll processing for large-scale manufacturing, enhancing scalability and reducing production costs [138-139].

8.6. Dye and Material Engineering:

- **Quantum Dot Sensitizers:** Investigating the use of quantum dots as sensitizers to enhance electron injection and reduce recombination [120].
- **Conductive Polymers:** Incorporating conductive polymers as charge transport materials to improve overall cell performance [120].

8.7. Advanced Encapsulation Techniques:

- **Nanostructured Encapsulation:** Developing nanostructured encapsulation materials to enhance barrier properties and protect against moisture and environmental degradation [81].
- **Flexible Encapsulation:** Designing flexible encapsulation methods for use in lightweight and flexible DSSCs [81].

8.8. Machine Learning and Optimization Algorithms:

- **Computational Modeling:** Employing machine learning and computational modeling to optimize device parameters, sensitizers, and electrolytes for enhanced performance.
- **Data-Driven Design:** Utilizing data-driven design approaches to predict and optimize material properties for improved stability and efficiency [120].

8.9. **Environmental Sustainability:**

- **Green Synthesis:** Exploring environmentally friendly and sustainable synthesis methods for materials to minimize the environmental impact of DSSC production [120].

9. Applications and Future Prospects of Dye-Sensitized Solar Cells

Dye-Sensitized Solar Cells (DSSCs) are a promising technology in the field of renewable energy. Here are some applications and future prospects of DSSC technology:

9.1. Applications:

- **Powering Electronic Applications**: DSSCs are an efficient photovoltaic technology for powering electronic applications such as wireless sensors with indoor light [81].
- **Flexible Solar Modules**: Their capability to be manufactured as thin and lightweight flexible solar modules highlights their potential for economic indoor photovoltaics [81].
- **Portable Electronics and IoT Devices**: There is a need to design new stability testing protocols to assess the probable deployment of DSSCs in portable electronics and internet-of-things devices [81].

9.2. Future Prospects:

- **Use of Organic and Inorganic Dyes**: Currently, DSSCs utilize organic (natural and synthetic) dye and inorganic (ruthenium) as a sensitizer [85] . The nature of these dyes, combined with different variables, has brought about a change in their use [85].
- **Alternative to Expensive Dyes**: Natural dyes are being seen as a viable alternative to expensive and rare ruthenium dye due to their low cost, easy utility, abundant supply of resources, and no environmental threat [85].
- **Advancements in DSSC Components**: There has been significant progress in the development of new device structures, alternative redox shuttles, solid-state hole conductors, TiO2 photoelectrodes, catalyst materials, and sealing techniques [81].
- **Sustainability and Safety**: The focus is also on the sustainability of materials and processes in DSSC fabrication [81].
- **Use of Renewable Materials**: There is interest in bio- or waste-derived renewable materials for DSSCs [81].
- **Flexible and Wearable DSSCs**: DSSCs are being developed for flexible and wearable applications [81].
- **Integrated Devices**: Efforts are being made to integrate DSSCs with an energy storage unit, like batteries or supercapacitors [81].

These advancements are expected to enhance the efficiency, sustainability, and applicability of DSSCs in the future. However, more research and development are needed to overcome the challenges and realize the full potential of this technology.

10. CONCLUSION

In closing, dye-sensitized solar cells (DSSCs) present an exciting prospect for reshaping the energy paradigm, given their unique advantages, such as affordability, ease of fabrication, and adaptability across a wide spectrum of light wavelengths [29]. The lightweight and flexible characteristics of DSSCs further amplify their potential applications, extending to portable electronics, building-integrated photovoltaics, and wearable technology.

Despite these promising attributes, challenges persist in the realm of DSSCs, notably their lower efficiency when compared to conventional silicon-based solar cells, acting as a hurdle to widespread adoption [140]. To unlock their full potential, it is imperative to sustain research and development endeavors. Resolving efficiency, stability, and scalability issues stands paramount to transforming DSSCs into a commercially viable and competitive option for sustainable energy generation.

In summary, while DSSCs offer a compelling avenue for clean energy production, their journey into mainstream energy usage necessitates ongoing dedication to surmount existing limitations. Through unwavering research and development efforts [29][140], DSSCs could emerge as a pivotal and influential player in realizing a more sustainable and renewable energy future.

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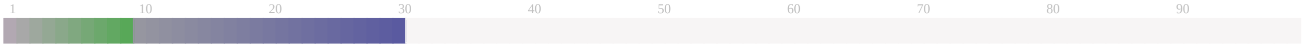

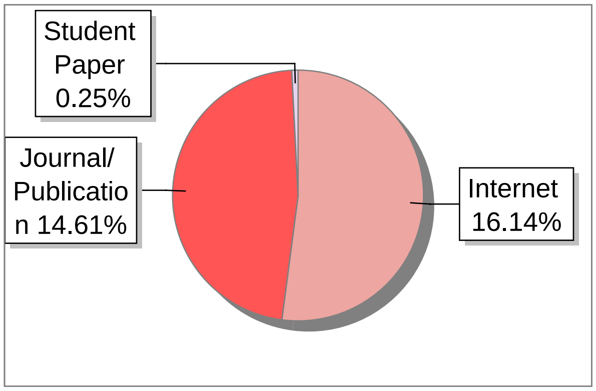

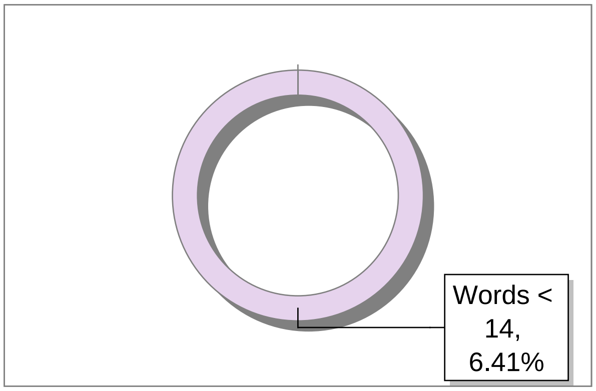

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A comprehensive review on Advancements in Metal Oxide photocatalysis: Exploring Ternary and Binary Systems

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Abstract:

Metal oxide have emerged as distinguished candidates for photocatalysis, presenting sustainable answers for harnessing solar power and environmental remediation. This evaluation delves into recent tendencies in each binary and ternary metallic oxide as photocatalysis. Binary oxides, together with titanium dioxide (TiO2) and Zinc oxide (ZnO), have been significantly studied, but their barriers have spurred investigated into ternary systems. Ternary metal oxide (TMOs), incorporating three one of a kind metallic factor, exhibit better photocatalytic properties due to synergistic consequences arising from diverse digital and optical traits. This summary gives a view of compositions of binary and ternary metallic oxides, emphasizing their roles in tactics like water splitting, pollutant degradation and hydrogen manufacturing. The challenges and future possibilities in metal oxide photocatalysis also are mentioned, highlighting the possible combination of binary and ternary metal oxides with their roles. At the same time as binary metallic oxides have laid the foundation for photocatalysis, the inherent boundaries have inspired the investigation of ternary counterparts, unveiling synergistic results that decorate performance. TMOs photocatalysts exhibit various compositions and programs, showcasing their potential in addressing global challenges. Understanding mechanisms consisting of price carriers, surface states, and doping techniques gives important insights for optimizing each binary and ternary systems. This overview underscores the significance of modern substances layout and synthesis techniques to liberate the total potential of metal oxide photocatalysts. As studies in this discipline keeps, metal oxides stand poised to contribute substantially to a sustainable and cleanser future.

Keywords: Metal oxide, Binary and ternary metal oxide, Photocatalyst.

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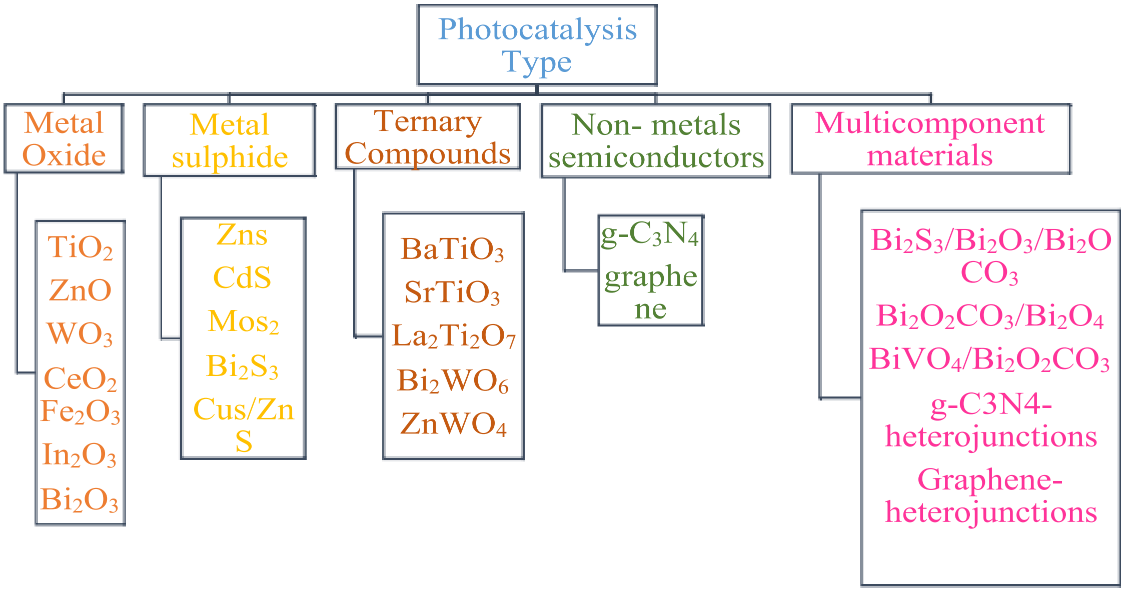
Introduction:

Water covers across the earth is about (70%) of planet's surface. Water which is smooth and secure is essential to all residing beings [1]. It plays a vital role in biological process including hydration, digestion and cellular functions. Human activities, industrial process, and agriculture have significant impacts on water quality and availability. Issues such as water pollution, over extraction of ground water, and climate change can affect the balance of water resources. Sustainable management of water is crucial for maintaining ecosystem and ensuring the well- being of human societies. Due to fast increasing industrialization and world population is mainly responsible for water pollution, because hazardous waste is directly mixed into the water and it is not only effect on human but also aquatic life which present in water [2]. During each year about 1.8 million children are dying due to drinking polluted water, [3-4] also lot of diseases causes due to polluted water and thus purification of water is paramount importance. However, availability of surface water mostly invariable and also qualities of water is always being declined due to continuous release of chemicals direct to environment, mainly due to aggravation of agricultural, industrial, domestic, pharmaceutical, etc. production [5-6]. There are a lot of techniques used for water purification. Now a days purification of water is carried out usually form physical and chemical techniques like UV treatment, chlorination, ozonation, etc. Purification techniques are depending on the region, available sources and also pollutants present in water [7-11].

Photocatalysis plays crucial role in the development of sustainable technologies, particularly in the context environmental protection clean energy production. Photocatalysis is a process that uses light to activate a substance (catalyst) to speed up a chemical reaction. The catalyst involved in photocatalysis is typically a semiconductor material that absorbs photons of light and uses that energy to drive a chemical reaction. This process is widely studied and applied in various fields, including environmental remediation, water purification, and energy conversion. In this process it utilizes solar energy or UV- visible light for degradation of organic pollutants into inorganic particle [12-18]. Since there are a variety of metallic semiconductor which used as a photocatalytic material such as (TiO_2, CaO, ZnO, Wo_3, $ZnWO_4$, ZrO_2, $BiTiO_3$, $SrTiO_3$, Fe_2O_3, Ag_2CO_3, BiOBr, BiOCl, $CaFe_2O_4$, BiOCl, $ZnFe_2O_4$) and metal sulphide such as (ZnS, CdS, $CuInS_2$, $AgIn_5S_8$ etc.) Metal oxide have gained significant attention in the field of photocatalysis due to their unique properties and potential applications in various environmental and energy- related process. It’s important to note that the effectiveness of a photocatalyst depends on various factors, along with specific application, light source, and target molecules. Researchers continue to explore and develop new material oxide photocatalysts for improved performance and expanded applications. Depending upon the properties of metal oxide there are a various type of photocatalysis found in nanoscience which are used for water purification. Some of them are listed below [19-33].

Fig.No.1: Types of Photocatalysis used to remove pollutants from water.



There are a various deposition techniques are used to deposit above metal oxide in nanoscale range like a thin layer on glass/conducting plate or as an electrode [34]

Table No.1: Thin film deposition Techniques with materials and application.

Sr.No.	Deposition Method	Thin film material	Application
1.	Ultrasonic Spray Pyrolysis	ZnO, SnO_2-Fe_2O_3, TiO_2, Gd-CeO_2	Solar cell, sensors, Metal oxide coating, solid oxide fuel Cell, Photocatalysis [35]
2.	Chemical Bath Deposition Method	ZnS, PbS, ZnO	Solar cell, Optoelectronics, Photocatalysis [36-38]
3.	Successive Ionic Layer Adsorption and reaction (SILAR)	CdO, ZnO, CuO	Gas Sensing, Photocatalysis, Supercapacitor [39-41]
4.	Sol-gel Method	TiO_2, TiO_2-SiO_2, CZTS	Solar cell, Photocatalysis, Gas Sensing Self-Cleaning [42-45]
5.	Electrodeposition	Cu_2O, Ga:CdS, $Co(OH)_2$, WO_3	Optoelectronics, Solar cell, Supercapacitor, Photocatalysis [46-49]
6.	Chemical Vapour Deposition (CVD)	B: ZnO, F: Mn_3O_4	Solar cell, Optoelectronics, Photocatalysis, Gas sensing [50-51]
7.	Plasma enhanced-Chemical Vapour deposition	TiO_2, SiO_2	Antireflecting coating, dielectric and biomedical applications, Photocatalysis [52-55]
8.	Magnetron Sputtering	TiO_2-SiO_2, CdTe,	Photocatalysis, Solar cell [56-57]
9.	Triode Sputtering	AlN, In_2O_3	Surface acoustic wave application, photovoltaic and optoelectronic application [58-59]
10.	DC sputtering	TiO_2, ITO, Mn_3N_2	Photocatalysis, Photovoltaic, Supercapacitor [60-62]
11.	Flash evaporation	A-$FAPbI_3$, CdTe	Solar cells [63-64]
12.	Laser Evaporation	$NiMoS_2$, TiO_2/Au/TiO_2	Dye- sensitized solar cells, Photocatalysis [65-66]

Photocatalysis:

Photocatalysis refers to the acceleration of a chemical reaction through the absorption of light by a substance known as a photocatalyst. Photocatalysis is a process that involves the use of a catalyst to accelerate a photoreaction, typically driven by light. Efficiency of photocatalysts depends on various factors such as bandgap, charge carrier mobility, surface area, ability to suppress recombination Photocatalysis. In this process light is used to activate catalyst to speed up chemical reaction. Fujishima et al. use TiO_2 as a photocatalyst for the production O_2 and H_2 from water and discovered water photolysis [67]. For expansion in other potential application and to improve the photocatalytic efficiency the simple binary metal oxide or metal free semiconductor, such as ZnO, TiO2, WO3, etc have been widely studied as a photocatalyst [68-73]. The efficiency of photocatalytic method depends on properties of photocatalyst such as a) surface area material which includes adsorption phenomenon b) morphology of a material on which electron-hole recombination depends [74].

Some important Points about Photocatalysis:

1. **Semiconductor Catalysts:** Photocatalysis often involves semiconductor materials, such as titanium dioxide (TiO_2) or Zinc Oxide (ZnO). These materials can absorb light energy and generate electron- hole pairs, initiating chemical reactions.
2. **Absorption of Photons:** When photocatalyst is exposed to light, it absorbs photons. The energy from these photons is sufficient to excite electrons in the semiconductor material from the valence band to the conduction band and form electron-hole pairs.
3. **Generation of Electron-Hole Pairs:** The absorbed energy promotes electron from the valence band to conduction band and leave behind a positively charged hole in the valence band. The formation of these electron-hole pairs is a key step in the photocatalytic process.
4. **Redox Reactions:** Separated electrons and holes in the semiconductor can participate in the redox reactions.
5. **Reaction with target Molecules:** The excited electrons and holes migrate to the surface of the semiconductor and react with adsorbed molecules or contaminants.
6. **Regeneration of Catalyst:** Catalyst provide a pathway for electron-hole pairs. After the completion of reaction catalyst can return to its original state and cycle repeated as long as light is available. It does not take part in a chemical reaction; it only increases the rate or speed of chemical reaction.
7. **Applications:**
    - **Environmental Remediation:** To remove the pollutants from air and photocatalysis method is used. The reactive species generated by the catalyst can break down organic pollutants, toxins and pathogens.
    - **Water Purification:** It can be employed to disinfect water by killing bacteria and other microorganisms.
    - **Self-Cleaning surfaces:** Photocatalytic materials are used to create self-cleaning surfaces, as they can break down and remove organic contaminants when exposed to light.
    - **Hydrogen Production:** Photocatalysis is also investigated for its potential in generating hydrogen through water splitting, which is a clean and sustainable energy source.
8. **Challenges:** While photocatalysis holds promise for various applications, challenges include the need for efficient catalysts, optimization of reaction condition, and addressing issues related to catalyst stability and reusability.
9. **Research and Development:** Ongoing research aims to develop aims to develop new photocatalytic materials, improve the efficiency of existing catalysts, and explore novel

applications for this technology.

Fig No. 2 Basic Mechanism

Water pollution due to industrialization has grown to be a continuously growing trouble, which is affecting human lifestyles and the aquatic ecosystem international in all factors [75]. It is expected that over one thousand million humans dwelling in the arid areas could have a primary shortage of water via 2025 [76]. It's far, consequently, essential to treat waste water, in any other case they can pose both acute and persistent effect on human lifestyles and within the environment. Presently, there are four maximum popular strategies comprising physical adsorption, flocculation, chemical oxidation and photo-catalytic degradation, that have been followed to grid of natural contaminants from water [77-78]. The major drawback of those strategies is that they go way an expansion of chemical reagents and polymer electrolytes in water, which led to the era of unmanageable sludge and deposits. Photocatalysis then again, depends on in-situ image generated hydroxyl radicals (OH), superoxide radicals and positively charged (H^+) which completely decompose natural contaminants. For this reason, photocatalysis is an efficient, environmentally-friendly, low price and an easy operation for the elimination of contaminants [79]. To begin with, traditional porous cloth and nano based totally substances have been being used as adsorbents. The maximum usually used adsorbents for waste water treatment are activated carbon, zeolites, carbon nanotubes, mesoporous silica and chitosan beads [80]. However, they confronted technical obstacles including inefficiency, operational problems, excessive energy necessities, and lower financial gain. A perfect adsorbent ought to have high porosity and a big floor location with precise adsorbent web sites. Therefore, alternative photocatalytic materials have been extraordinarily suitable [81].

Metal oxide and Metal sulphide as a photocatalyst:

Metal oxide and metal sulphide skinny film photocatalysts can decompose an expansion of organic pollution into less dangerous response merchandise and the most common pollutant used for degradation exams are MB, RhB and MO dye. The development in thin film technology offers a wide commercial utility of steel oxide skinny movie photocatalysts. Even though TiO2 and ZnO are most studied and commercially a success material because of sure obstacles consisting of extensive band hole, lower efficiency, and so on, there's scope for different metallic oxides and metal sulphides. The surface morphology, electronic shape, crystalline length, thickness and deposition method of skinny film particularly in fluences its photocatalytic performance. In case of steel oxide, doing of steel or non-metal not handiest reduce the band hole electricity however additionally decreases the recombination of electrons and holes. Similarly, the photo electrocatalysis phenomenon determined to be efficient to make use electron mob present at the conduction band after irradiation. The degradation mechanism is related to the digital shape of the photocatalyst and bonding among pollutant species and catalyst. The addition of small amount of surfactant can be one of the methods to growth the surface vicinity of thin films. Further, utilization of a spread of substrate and modification in electronic shape can effectively decorate photocatalytic performance [82].

Here is a list of some metal oxides and metal sulphides which are commonly used as photocatalysts, along with their roles, efficiencies and band gap values are given in table. Depending upon the crystal structure, doping, and specific synthesis methods efficiency and band gap values are varied.

Table No.2: List of metal oxide and metal sulphides with role, efficiency and band gap.

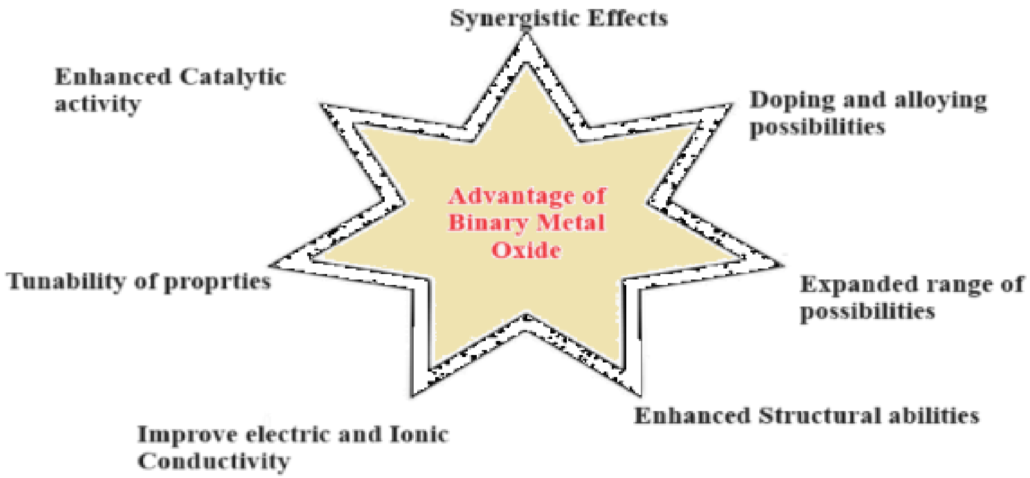
Sr. No.	Name of Metal Oxide	Role	Efficiency	Band Gap
1.	Titanium Dioxide (TiO2)	Water purification, air Purification, and self-cleaning surfaces	High efficiency in UV light and limited Efficiency in visible light	3.0-3.2eV
2.	Zinc Oxide (ZnO)	Water treatment and UV Filter in sunscreens	Moderate efficiency in UV and Visible light	3.3 eV
3.	Iron Oxide (Fe2O3)	Water oxidation and Pollutant degradation	Moderate efficiency in visible light	2.0-2.2eV
4.	Tungsten Oxide (WO3)	Water splitting and Environmental Remediation	Variable efficiency in Visible light range	2.4-2.8eV

Sr. No.	Name of Metal Sulphide	Role	Efficiency	Band Gap
1	Cadmium sulphide (CdS)	Hydrogen production and Pollutant degradation	High efficiency in Visible light range	2.4-2.5eV
2	Copper sulphide (Cu2S)	Solar energy conversion And environmental Applications	Variable efficiency In Visible light range	variable
3	Zinc sulphide (ZnS)	Hydrogen production And photocatalytic Degradation	Moderate efficiency In visible light range	3.5-3.8eV
4	Nickel sulphide (NiS)	Hydrogen evolution Reactions	Variable efficiency In Visible light range	Variable

These materials are actively researched, advancements in synthesis techniques and modifications continue to improve their efficiency and broaden their applicability in various photocatalytic process, but alone metal oxide and metal sulphide has some limitations, after 2009 maximum awareness is carried out to improve the possessions of nanomaterials such as chemical reactivity, optical, electrical and magnetic properties for better result [83], thus to increase the efficiency we need binary and ternary metal oxide as a photocatalyst.

Binary Metal Oxide as Photocatalysis:

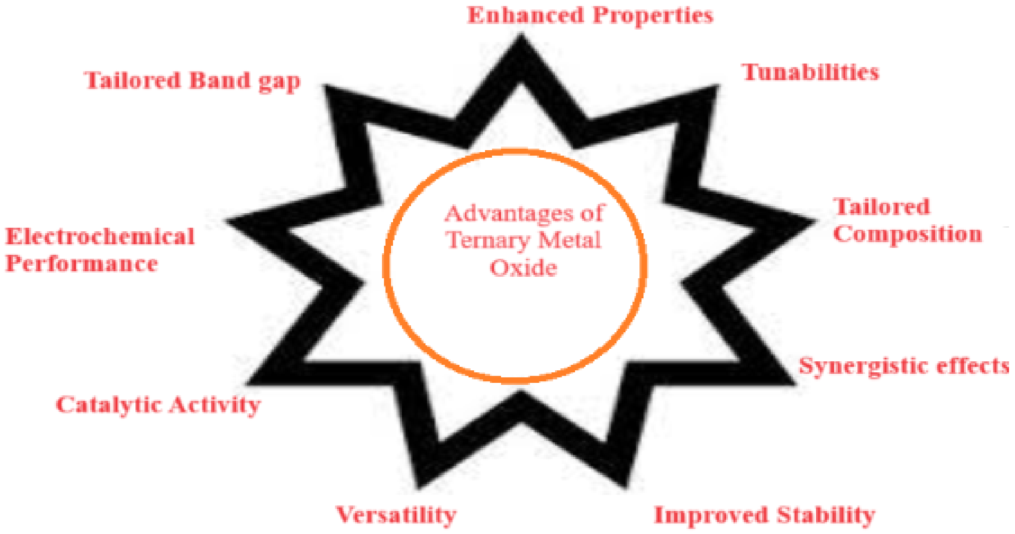
Binary metal oxides, which are compounds composed of two different metal elements and oxygen, can offer several advantages over single metal oxides. It's important that the specific benefits depend on the choice of metal elements, their ratios, and the intended application. Researchers often explore different combinations to discover new materials with optimized properties for specific technological needs.



As a promising compound, titania (TiO2) has been widely used in the photocatalytic degradation of natural pollution of water and air. Pure TiO2 has electricity hole of 3.2eV, hence UV mild is necessary to excite electrons on the TiO2 floor. To spark off the photocatalyst with better performance and longer wavelength, some of strategies have been added [84]. One strategy is put together TiO2/metallic oxide nanocomposites which include SiO2/TiO2 [85], CdS/TiO2 [86], ZnO/TiO2 [87], SnO2/TiO2 [88]. Lifetime of photo-brought about price consists of is a prime factor for improving photocatalytic interest. As for ZnO-TiO2 [89], the electron transfers from the conduction band of ZnO to that of TiO2 below illumination, and conversely, the holes switch from the valence band of TiO2 to that of ZnO. Accordingly, the life of photoinduced pairs increases because their recombination charge decreases. So that it will expand the range of excitation energies of TiO2 into the visible vicinity, materials of the slender band gap, such as ZnO, had been coupled with TiO2 [90]. The band gap of ZnO and TiO2 is quite massive so they are not capable of absorb the essential part of the sun spectrum i.e. the seen location efficaciously and may simply absorb a small range of the UV area this is why the highest quality and powerful utilization of sun radiations in this subject is still considered as a assignment. Numerous attempts have been made so that the absorption range of TiO2 and ZnO can be extended to the visible light region, which consist of deposition of noble metals, doping of transition metals and coupling of various semiconductor systems, etc [91]. Out of a majority of these available metal oxides, ZnO has demonstrated to be an fantastic and promising photocatalyst, because of its first rate characteristics find it irresistible less expensive price, precise oxidation potential, large free excitation binding strength, flexibility in fabrication, and many others. Moreover, every other critical issue is the rapid recombination charge of photo generated electron hole pairs inside TiO2 NPs. So, plenty of tries had been made to discover techniques facilitating the photoactivation of TiO2 below seen-mild. TiO2 doping with numerous materials could be taken into consideration as an easy approach to improve its photocatalytic overall performance [92]. substrate and the ratio TiO2/RhB were also investigated in the photocatalytic degradation of RhB. There may be a hinderance that limits using ZnO as a photoelectrode due to its n-kind behaviour, that doesn't permit ZnO to manipulate its electric conductivity [93]. Whilst transition metals like Ag, Mn, Fe, Co, Cr, Al and so forth are doped in ZnO there may be a alternate inside the electric, optical and magnetic residences with the changing of doping concentration [94]. surface defects create energetic sites and this is why analysing the effect of doped ZnO on its photocatalytic hobby turns into vital [95]. In current years, graphene oxide is referred to as a promising cloth to improve the structural stability and photocatalytic pastime of TiO2 NPs [96]. Alternatively, adheration of TiO2 NPs to head layers now not simplest prompted electrons for photovoltaic reactions but also prevented recombination with photo- generated holes [97]. In a single record, a simple solvothermal approach changed into used to graft TiO2 NPs on go (TiO2-pass as binary nanocomposite). Photograph- degradation interest of TiO2- pass nanocomposite became investigated on the degradation of MB and MO beneath UV-mild irradiation and in comparison, with pristine TiO2 NPs [98].

Ternary Metal Oxide as a photocatalysis:

Compared with the easy binary metal oxides, the TMOs possess a more complicated composition, chemical bonding among distinctive cations and oxygen atoms and bendy crystal structure [99]. Ternary metal oxides, which consist of three different elements, offer several advantages over binary metal oxides. It’s important that the advantages of ternary metal oxides depend on the specific elements chosen and their proportions. The selection of elements and their ratios plays a critical role in determining the material’s properties and performance in various applications.



The complex shape gives vast benefits for TMOs as photocatalysts. First, the band aspects potentials for TMOs are appropriate for diverse photoinduced reactions. In addition, the presence of various metallic ions in the lattice of TMOs lets in for extra flexibility in designing and enhancing the band structure as well as other photophysical residences. Through band shape engineering, the capacity of sun harvesting and photon-excitation energy conversion may be optimized, inclusive of the fabrication of heterojunctions and the introduction of illness states [100]. Given that water photocatalysis changed into observed with the aid of Fijishima et al. with TiO2 as a photocatalyst for the manufacturing of O2 and H2 from water, many kinds of semiconductors have been fabricated and implemented as photocatalyst, especially for the broadly studied oxide materials. It’s far usual that the homes of substances significantly modified in keeping with their synthesis process, chemical additives, morphologies, floor amendment, elements doping and the formation of composites and so on [101-106]. The simple binary steel oxides or metal loose semiconductors, consisting of TiO2, ZnO, WO3 and C3N4, and so on., had been broadly studied as photocatalyst to understand the essential precept. The development of photocatalytic efficiency and the enlargement in different potential applications [107-112]. The ternary metal oxides (AxByOz) with extra flexible band structures own splendid capability to be carried out as photocatalysts. An extensive range of ternary metal oxides (TMOs) had been fabricated, and their photocatalytic pastime related to morphology, electronic, optical houses should be in addition investigated. The one-of-a-kind constituent factors within the AxByOz composition offer more than one alternative to alter the materials with tunning physical and chemical residence for an enhancement of photocatalytic performance [113].

Here is some ternary heterostructure metal oxide are listed with their role and band gap value,

Sr. No.	Ternary Oxide	Role	Band Gap
1.	TiO2/SnO2/ZnO [114]	Photocatalysis-Degradation of Water pollutants, Water splitting	TiO2-3.2eV SnO2-3.6eV ZnO-3.3eV
2.	MoS2/WS2/Graphene [115]	Catalysis, Electronic device Hydrogen Evolution reaction Pollutant Degradation	MoS2-1.8eV WS2-1.6eV
3.	Cu2O/ZnO/CuO [116]	Photocatalysis, Gas sensing Degradation of Organic pollutants, Hydrogen production	Cu2O-2.0eV ZnO-3.3eV CuO-1.2eV
4.	Bi2wO6/BiVO4/TiO2 [117]	Photocatalysis- Water oxidation, Pollutant degradation	Bi2WO6-2.8ev BiVO4-2.4eV TiO2-3.2eV
5.	CdS/ZnS/Ag2S [118]	Photocatalysis- Hydrogen Production, Degradation of Pollutants, Optoelectronics	Cds-2.4eV ZnS-3.7eV Ag2S-1.0eV
6.	Fe2o3/TiO2/Graphene [119]	Photocatalysis, Energy storage	Fe2o3-2.2eV TiO2-3.2eV
7.	CuIns2/CdS/ZnS [120]	Photocatalysis, Photovoltaics	CuInS2-1.5eV CdS-2.4eV ZnS-3.7eV
8.	ZnO/SnO2/In2O3 [121]	Gas sensing, Photocatalysis	ZnO-3.3eV SnO2-3.6eV In2O3-3.75eV
9.	Bi2MoO6/BiVO4/WO3 [122]	Photocatalysis, Water Treatment	Bi2MoO6-1.89eV BiVO4-2.4eV WO3-2.8eV
10.	TiO2/Fe2O3/SnO2 [123]	Photocatalysis, Solar cells	TiO2-3.2eV Fe2O3-2.2eV SnO2-3.6eV
11.	NiO/CdS/ZnO [124]	Photocatalysis, Optoelectronics	NiO-3.5eV CdS-2.4eV ZnO-3.3eV
12.	CuFeO2/Fe2O3/ZnO [125]	Photocatalysis, Energy Storage	CuFeO21.15eV Fe2O3-2.2eV ZnO-3.3eV
13.	Cu2O/ZnO/In2O3 [126]	Photocatalysis, Gas sensing	Cu2O-2.2eV ZnO-3.3eV In2O3-3.75eV

14.	MoS2/WS2/BN [127]	Electronic devices, Catalysis	MoS2-1.8eV WS2-1.6eV BN-2.44eV
15.	ZnO/CdS/Graphene [128]	Photocatalysis, Energy Storage	ZnO-3.3eV CdS-2.4eV

Efficiency and performance of these ternary heterostructures can be influenced by several factors, including synthesis methods, morphologies, and specific experimental conditions.

Conclusion:

In Conclusion, metal oxide represents key area of research for harnessing solar energy and mitigating environmental challenges. Binary metal oxide has been extensively studied, but their limitations have led to explore ternary metal oxide systems the diverse composition of ternary metal oxide photocatalysts have shown promising results in various applications, including water splitting, pollutant degradation, and hydrogen production. The understanding of underlying mechanisms, such as charge carriers, surface sates, and doping strategies, provides insights into optimizing the photocatalytic activity of both binary and ternary systems.

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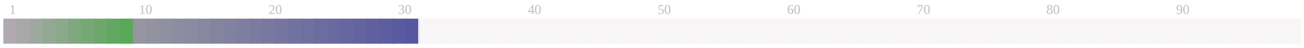

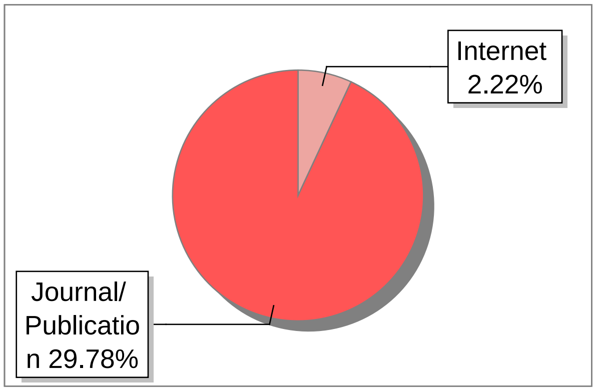

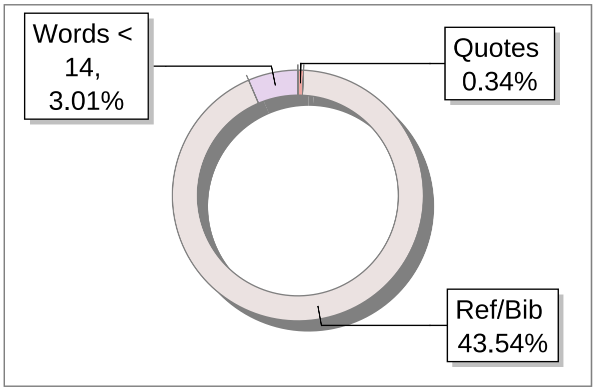

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First-principles DFT + U studies of the Nb-doped ZnO spray deposited thin films.

Experimental and Theoretical Study of Nb -Doped sprayed ZnO thin films.

The study of structural, and optical properties of sprayed Nb - doped ZnO: DFT + U and experimental approaches

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Abstract :

In present study ZnO, and Nb doped ZnO were synthesized on glass substrate by using chemical spray pyrolysis at suitable temperature. Zinc oxide (ZnO) is a n-type semiconductor material which has a wide direct band gap of energy ~3 eV. Dopant in ZnO nanostructures is an effective way to improve ZnO's structural properties in various applications. The concentration of impurities is varied from 1% to 4 mol% for (Nb-ZnO). The synthesized thin films are characterized by X-Ray diffraction method which shows hexagonal structure with 57nm crystalline size for optimized concentration of Nb and it optimized by JCPDS card number (01-079- 0208). Due to their excellent optical and electrical properties prepared films are used as a transparent window layer and electrodes in solar cell. For first principle study , We have performed PBE and PBE+U calculations to investigate the electronic structure of ZnO and Nb doped system . Firstly, it was found good correspondence for Hubbard parameter value using Ud,Zn = 0 to 12 eV and Up,O = 0 to 12 eV for undoped ZnO bulk system , and for Nb doped ZnO same range of Hubbard parameter value repeated with Ud (0 to 12 eV) for Nb.

Keywords: ZnO, , Nb, Structural and Optical properties, Chemical Spray Pyrolysis. DFT +U

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Introduction:

The ZnO materials follow the family of II-VI semiconductors and behave with a wide band gap having exciton binding energy around 60 meV [1]. ZnO has three different structures; those consist of rock salt, zinc blende, and wurtzite [2]. The semiconducting property of ZnO is used in optoelectronic applications [3]. ZnO can be used in gas sensing (4) , Furthermore, ZnO thin films are popular for use as thin film transistors. ZnO transistor thin films (TFT) work as channel layers to replace the amorphous silicon Journal Pre-proof 3 hydride in active-matrix liquid crystal displays [5,6]. ZnO thin films are used to upgrade the stability of the devices and circuits for high voltage operations when they are manufactured in the form of thin film transistors [7]. Zno based thin films can be used as Surface Acoustic Wave (SAW) [8]. Numerous scholars have studied the effects of dopants on ZnO thin films. When incorporated into the ZnO lattice, transition metal oxide dopants such as manganese (Mn [9]), chromium (Cr [10]), cobalt (Co [11]), iron (Fe) (12) and copper (Cu [13]) improve the magnetic properties. Titanium (Ti)-doped ZnO is used to improve electrical conductivity [14] because the radius of a Ti4+ ion is smaller than that of a Zn2+ ion by 30%. However, dopants like aluminium (Al [15]), magnesium (Mg [16]), tin (Ga [17]), and indium (In [18]) into ZnO films provide transparency and high conduction (TCO). Also, rare-earth elements like neodymium (Nd) and terbium (Tb) provide high clarity, high conductivity, and a luminescence trend [19 -20]. Lanthanium (La)-ZnO thin films act as photocatalytic materials [21]. Metallic Nb has an oxidation state of 0, which changes to +2 in the case of NbO; +4 in NbO2; and +5 in Nb2O5, each of which result in different electrical conduction behaviors [22]. The presence of Nb in ZnO thin films reduces the disorder and carrier scattering because of the substitution of Nb5+ with Zn2+ [23]. Moreover, Nb-doped ZnO can be used for TCO [23], gas sensing [24], solar cell applications [27], Efficiency of Nb-Doped ZnO Nanoparticles Electrode for DyeSensitized Solar Cells Application, [28] and photocatalystsis [29]. Magnetron Sputtered Nb-Doped ZnO Thin Films switching properties for RRAM Applications [30] , Nb doped ZnO thin films an be fabricated by different methods such as Magnetron Sputtering [31], Fabrication of chemically stable hydrogen- and niobium-codoped ZnO transparent conductive films Structure, optical and electrical properties of Nb-doped ZnO transparent conductive thin films prepared by co-sputtering method [32] , radio frequency magnetron sputtering [33-34] Niobium (Nb) doping (0 at.% to 3 at.%) in ZnO thin films prepared by the chemical spray pyrolysis method [35**] The NbZnO films were deposited using atomic layer deposition. [36-37],**ZnO nanostructures containing doped with different atom % of Nb are fabricated through ultrasound assisted hydrolysis in water [38]

Many fundamental physical properties of Nb -doped ZnO such as defect energy level and relationship between doping level and energy band gap, which are of important scientific and engineering interests, are unclear. In this work, theoretical studies are performed to understand the electronic properties of undoped and Nb -doped ZnO sysytem.[39]

There are several theoretical works that use the DFT method to study ZnO structures [40 - 45]. However, it is well known that the standard DFT method largely underestimates bandgap values [46], A density functional study for structural and electronic properties of

Zinc Oxide (ZnO), in wurtzite, rock salt and zinc-blende phases has been performed [47] The conventional Density Functional Theory (DFT) method based on exchange–correlation (XC) functionals of Local Density Approximation (LDA) and Generalized Gradient Approximation (GGA) produces underestimated value of energy band gap (~0.7–1.0 eV) compared with the energy gap value (~3.4 eV) measured in the experiment.[48-49] **This** is because the standard DFT is not able to properly take into account the exchange-correlation term. The bandgap underestimation results from the usage of grossly approximated potentials in the Kohn-Sham implementation.

There are three approaches to compensate for the bandgap underestimation of DFT: (1) the GW approximation [50] that takes into account the self-energy of a many-body system of electrons, (2) hybrid exchange-correlation functionals like HSE 51], PBE0 [52], and B3LYP [53] The two functionals assessed are the Tao-Perdew-Staroverov-Scuseria, a nonempirical metageneralized gradient approximation (meta-GGA) functional and the Heyd-Scuseria-Ernzerhof (HSE), a screened exchange hybrid functional.[54] and (3) the DFT+U formalism that includes the Hubbard on-site Coulombic U term [55- 60]. Among the three approaches, hybrid functionals and DFT+U are widely used in theoretical works. While hybrid functionals are computationally expensive, the DFT+U method is comparable to the standard DFT method in terms of the computational cost. In the following, we will present a summary of both approaches [60-61] Moreover, the DFT–LDA+U approach can significantly improve the calculation including transition metal localization [62] The obtained supercells of pure and Mn-doped ZnO materials are optimized using DFT. The generalized gradient approximation (GGA) in the scheme of Perdew–Burke–Ernzerhof (PBE) was used to treat the exchange-correlation function [63-64]

In this work we have performed PBE and PBE+U calculations to investigate the electronic structure of ZnO and Nb doped system . Firstly, it was found good correspondence for Hubbard parameter value using Ud,Zn = 0 to 12 eV and Up,O = 0 to 12 eV for undoped ZnO bulk system , and for Nb doped ZnO same range of Hubbard parameter value repeated with Ud (0 to 12 eV) for Nb.

Theoretical development of First principle Theory :

The foundation of first-principles method relied on quantum mechanics that describe the behavior of electrons and atomic nuclei in any situation [20]. The Schrodinger equation serves as the basic equation in this topic, which can be expressed as follows (Eq. (1)):

$$\hat{H}\,\Psi = E\,\Psi \text{ --(1)}$$

where Ĥ is the Hamiltonian operator, Ψ is the wavefunction, and E represents the energy of the system. The Hamiltonian operator consists of kinetic and potential energies due to the Coul

$$\hat{H} = \sum_{I=1}^{N} \frac{P^2(a)}{n!}(z-a)^n$$

Apparently, the Schrodinger equation is too complex to be solved and would lead to uncontrollable computation in a system containing more than one electron. This is largely due to the nature of electrons that strongly interact which each other, which leads to many-body problem [16,20]. Several approximations are then developed to solve the Schrodinger equation, of which the first useful one is the wellknown Born–Oppenheimer approximation

The idea in Born–Oppenheimer approximation is that the electron motion and nuclear motion are separated [16]. This is due to the fact that the mass of the nucleus is way larger than that of the electron, and the nuclei are principally fixed particles. By having this approximation in mind, the problem of interacting electron, ions and nuclei vanishes and eventually enables the possible application of the Schrodinger equation in a complex system

Density functional theory

In 1964, Hohenberg and Kohn [23] have developed a theorem that defined the electron density as a unique function for ground state energy of a system with N-electron. Later, a set of independent-particle equation has been established by Kohn and Sham [24]. They have introduced a Schrodinger-like equation with a modified effective potential that is much easier to calculate than the original Schrodinger equation.

The Hohenberg–Kohn theorems

Kohn–Sham method

Exchange–correlation functional

Local density approximation

Generalized gradient approximation

Hubbard-U scheme

Experimental Methods:

1) Fabrication of Undoped and Nb doped ZnO thin films:
2) Computational :

The experimental structural parameters of wurtzite ZnO at $a = 3.2427$ Å and $c = 5.1948$ Å with wurtzite parameter $z = 0.3826$ as discovered by Sabine and Hogg [13] using X-ray crystallography method is used as the reference structural data in this work. A standard DFT geometrical optimization is first performed on the primitive wurtzite ZnO unit cell, followed by a self-consistent DFT calculation to study its electronic properties. Hubbard term Ud is then added to the d-orbitals of the Zn atoms, ranging from 2 eV to 14 eV in the interval of 2 eV. The second part of this research studies the effect of including both Hubbard term Ud to Zn d-orbitals and Up to O p-orbitals, where the Up values ranges from 5 eV to 9 eV. The changes to lattice constants and wurtzite parameter z as well as the band gap and valence band width are investigated. All calculations in this work are completed using the ABINIT electronic package [14] within the framework of projectoraugmented-wave (PAW) potentials [15] and LDA exchange correlation functionals. The PAW potentials used are from the datasets provided by Jollet et al. [16]. The plane wave basis sets are expanded to kinetic energy cutoff of 34 Hartree whereas the Monkhorst-Pack k-point mesh is set to an array of 8 8 6 at gamma centred grid. Cutoff energy is selected with convergence tolerance of 0.005 eV/atom whereas k-point mesh array is selected so that band gap is converged with 0.0004 eV tolerance. The LDA + U calculations are performed using full localized limit (FLL) double-counting correction [8]. The double-counting correction is necessary in a LDA + U calculation to avoid double counting of correlation part in localized electrons. The Hubbard term J is set to zero for all calculations; the rotationally invariant LDA + U form proposed by Dudarev et al. [9] is equivalent to the FLL method with J = 0 and U in place of U ————————————J [17]. **(E.S. Goh ⇑ , J.W. Mah, T.L. Yoon, Effects of Hubbard term correction on the structural parameters and electronic properties of wurtzite ZnO,** Computational Materials Science Volume 138, October 2017, Pages 111-116)

To simulate the doping effect in the system, a 32-atoms 2×2×2 supercell was used in our calculations, as shown in Fig. 1. Firstly, one Nb atom dopant is introduced to substitute one Zn atom, which yields to a dopant concentration of 6.25%. Secondly, to determine the magnetic ground state, a 32-atoms supercell with two replaced Zn atoms were constructed. This was necessary for calculations of the relative energies, the ferromagnetic (FM) and antiferromagnetic (AFM) spin alignments, the difference between these two energies per RE ion is defined as ΔE= EAFM–EFM, which indicates the magnetic stability in ZnO: Nb systems. However, the configuration with two dopants in the nearest neighbors called near configuration was evaluated. On the other hand, as the distance increased, far configuration was also considered. Finally, The Brillouin-zone integration was performed using a Mokhorst-Pack 2×2×2 (1/Bohr radius, a.u.) k-points mesh in the first Brillouin zone[22]. Thus, the computational scheme was appropriate for describing the electronic structure and the magnetic properties of Nb- doped ZnO.

Result and Discussion :

A) **Experimental**

B) **Theory**

BAND STRUCTURE OF ZINC OXIDE :

Experimentally, the electronic structure of zinc oxide has been investigated in some detail see Ref. 19 and references therein. Typically, the density of states reveals two primary bands between 0 and −10 eV measured from the valence band maximum. The upper band is primarily derived from O 2p and Zn 4s orbitals, while the lower band arises almost solely from Zn 3d electrons with a maximum between −7 and −8 eV. The measurements reveal a strong dispersion of the upper valence bands and a smaller dispersion of the Zn 3d levels. In general, DFT calculations yield too small band gaps compared to experiment. This effect is further enhanced in ZnO due to the underestimation of the repulsion between the Zn 3d and conduction band levels, which leads to a significant hybridization of the O 2p and Zn 3d levels and eventually to an overestimation of covalency. Schröer et al. have performed an analysis of the wave functions obtained from self-consistent pseudopotential calculations and determined a contribution of 20%–30% of the Zn 3d orbitals to the levels in the upper valence band to be compared with the experimental estimate of 9% covalency cited above. For zinc oxide the band gap calculated with LDA or GGA is about 0.7– 0.9 eV, which is just about 25% of the experimental value 3.4 eV. The insufficient description of strongly localized electrons such as those occupying the Zn 3d states in ZnO and the underestimation of their binding energies is a generic problem of DFT within the LDA or GGA, and at least partially a result of unphysical self-interactions. In fact, it has been found that calculations based on the Hartree-Fock or the GW approximation give much more tightly bound d-electrons and significantly larger band gaps. An alternative approach is the explicit correction of self-interaction.29 Vogel et al. have developed this idea further and devised a scheme, which allows one to incorporate self-interaction corrections SIC and electronic relaxation corrections SIRC already during the construction of pseudopotentials PP. 27 Thereby, they were able to reproduce the experimental band gap as well as the position of the 3d levels in several II-VI compounds with remarkable precision. In fact, the thus obtained band structure for ZnO compares better with experiment than calculations within the Hartree-Fock and GW approximations.21,28 SIC-PPs have also been used by Zhang et al. in the calculation of the formation enthalpies of a few neutral point defects in zinc oxide.3 Unfortunately, as they point out, the SIC scheme cannot be transferred unambiguously to charged defect calculations and is therefore not applicable in the present situation

Theoretical Approach and Computational Details:

32 we employed the rotationally invariant approach proposed by Dudarev et al. 33 The Hubbard U term corresponds to the mean-field approximation of the on-site Coulomb interaction, which is added to the exchange-correlation functional. We used an effective Hubbard parameter, i.e., the difference between the Coulomb U and exchange J parameters is

taken into account, $U_{eff} = U - J$. Among the U_{eff} combinations that could yield the correct description of the itinerant or localized behavior, we have also properly described the relative orbital positions with respect to the Fermi level. Thus, we have considered U_{eff} values from a self-consistent linear response procedure, 32 which describe the correct band gap value for ZnO (3.3 eV) and attend simultaneously the correct position of the d- and p-states in the valence band (VB). In this work, Firstly, it was found good correspondence for Hubbard parameter value using $U_{d,Zn}$ = 0 to 12 eV and $U_{p,O}$ = 0 to 12 eV for undoped ZnO bulk system , and for Nb doped ZnO same range of Hubbard parameter value repeated with Ud (0 to 12 eV) for Nb.

The calculations are performed using the plane-wave pseudopotential method as implemented in the Quantum ESPRESSO package 36. Electron-ion interactions were described using the projector-augmented wave (PAW) method37. A cutoff energy of 140 Ry and 1140 Ry were used for the plane-waves expansion and for the electronic density, respectively. For the Brillouin-zone integration, we have applied the Monkhorst-Pack method38, with a k-mesh of 6×6×6 and 6×1×6 k-points for the bulk and surface. The convergence criteria for the energy and force were 10^{-4} Ryd and 10^{-3} Ryd/Bohr, respectively

we have decided to benchmark our calculations using the band structure calculated by Vogel et al. employing their self-interaction and relaxation-corrected SIRC pseudopotentials, which reproduces the experimental band gap as well as the position of the Zn 3d levels.27 Values for $\bar{U} - \bar{J}$ between 0 and 10 eV were considered. As $\bar{U} - \bar{J}$ is raised the Zn 3d states are shifted downwards and the band gap increases. At the same time the equilibrium volume decreases while the bulk modulus varies only slightly. Eventually, we settled for $\bar{U} - \bar{J}$ = 7.5 eV. With this value the valence band energy levels as well as the (First-principles study of intrinsic point defects in ZnO: Role of band structure, volume relaxation, and finite-size effects Paul Erhart, Karsten Albe, and Andreas Klein, PHYSICAL REVIEW B 73, 205203 2006,)

Conclusion:

To perform this study, we have employed density functional theory (DFT) calculations, considering the Perdew-Burke-Ernzerhof (PBE) functional. However, it is well-known that the plain DFT fails to describe strong electronic correlated materials, where in general, the band gap underestimation is obtained. Thus, to the correct description of the electronic properties was employed a Hubbard correction, i.e., PBE+U calculations. The PBE+U methodology has provided the correct electronic structure properties for bulk ZnO in good agreement with the experimental values (99.4%) (Efracio Mamani Flores,∗a Rogério Almeida Gouvea,∗a Maurício Jeomar Piotrowskia and Mário Lucio Moreiraa, Band Alignment and Charge Transfer Predictions of ZnO/ZnX (X = S, Se, Te) Interfaces Applied to Solar Cells: A PBE+U Theoretical Study, : E. M. Flores, R. A. Gouvea, M. J. Piotrowski and M. L. L. Moreira, Phys. Chem. Chem. Phys., 2018, DOI: 10.1039/C7CP08177D)

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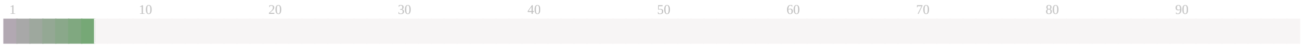

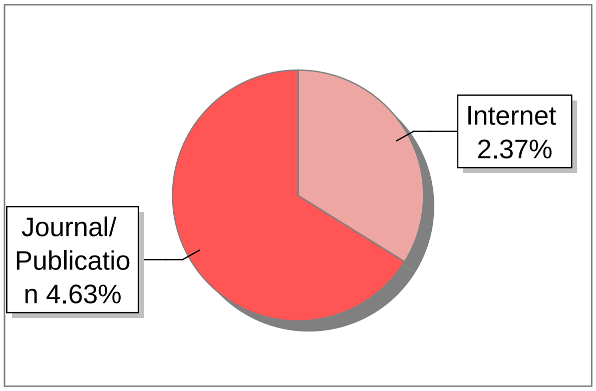

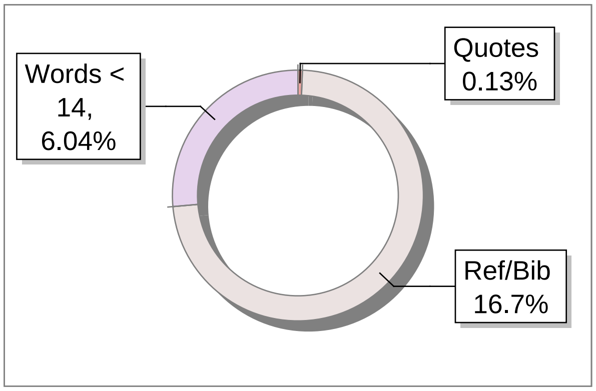

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Dye-Sensitized Solar Cells as Renewable Frontier: A Comprehensive Survey of Components, Mechanisms, and Advancements.

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Abstract: The global push towards renewable energy sources has led to a significant focus on the renewable energy revolution, with solar energy emerging as a prominent player. Within the realm of solar energy, Dye-Sensitized Solar Cells (DSSCs) have gained attention for their unique design and potential applications. This review article delves into the fundamentals of DSSCs, exploring key components such as the transparent conductive oxide electrode, semiconductor photoanode, dye molecules, electrolyte dispensation, counter electrode, and sealing layer. The working mechanism of DSSCs is elucidated, drawing parallels with the principles of photosynthesis in plants. Photovoltaic parameters such as open-circuit voltage, short-circuit current, fill factor, photo- conversion efficiency, and incident photon to current conversion efficiency are discussed for a comprehensive understanding of DSSC performance.

Historical advancements in DSSC components, including photoanodes, dyes, electrolytes, and photocathodes, are presented, highlighting innovations such as mesoporous TiO_2, RuBipy dyes, and iodide/ triiodide redox couples. Recent advances in DSSC technology are explored, and challenges faced in their development are discussed. The environmental and economic impacts of DSSCs are evaluated, emphasizing positive aspects such as low energy input in manufacturing and resource efficiency, as well as negative aspects like the presence of toxic materials and limited efficiency. The economic impact is analysed, considering lower manufacturing costs, job creation, market competitiveness, diversification of the solar industry, and potential effects on energy prices.

Finally, the future prospects of DSSCs are discussed, offering insights into ongoing research directions. In conclusion, this review provides a comprehensive overview of DSSCs, addressing their technological evolution, challenges, and potential contributions to a sustainable energy future.

Keywords: Renewable Energy; Dye sensitized Solar Cell (DSSC); Photovoltaic, Environmental and Economic impacts

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1. Introduction

Non-renewable energy sources such as Fossil Fuels (Coal, Petrol, Diesel, and Natural Gas) and nuclear power are major energy sources for the world today. The major concern about Non-renewable energy sources is that they are finite and do not replenish by nature, greenhouse gases are released during the process of burning Fossil Fuels which leads to climate change, the extraction process of non-renewable energy sources is very expensive. To overcome all these disadvantages of non-renewable energy sources we should find out an alternative source of renewable energy that fulfills our energy demand. Renewable energy refers to energy sources that are naturally replenished and have minimal impact on the environment [1]. Renewable energy sources such as solar energy, wind energy, hydroelectric energy, geothermal energy, and biomass energy are the best alternatives for non-renewable energy sources because they are clean, sustainable, and abundant [2].

1.1 Renewable Energy Revolution:

The global demand for renewable energy has reached a critical juncture in recent years, spurred by growing concerns about climate change and the finite nature of fossil fuel resources. This urgency has underscored the need for a swift transition towards cleaner and more sustainable energy sources. As of 2022, a significant portion of the world's electricity generation still relies on fossil fuels, highlighting the imperative for a substantial shift in the energy landscape. According to the latest report, a notable 29.55% of global electricity production in 2022 was derived from renewable sources. This diverse mix includes energy generated from hydropower, bioenergy, wind, solar, and other renewable sources. Figure 1 provides a visual representation of this distribution. The figures accentuate the increasing role of renewable energy in the global power supply, indicating a positive trajectory towards a more sustainable and environmentally friendly energy ecosystem. As the world grapples with the challenges posed by climate change and the finite nature of traditional energy resources, the focus on expanding and optimizing renewable energy production remains crucial for a resilient and sustainable future [3].

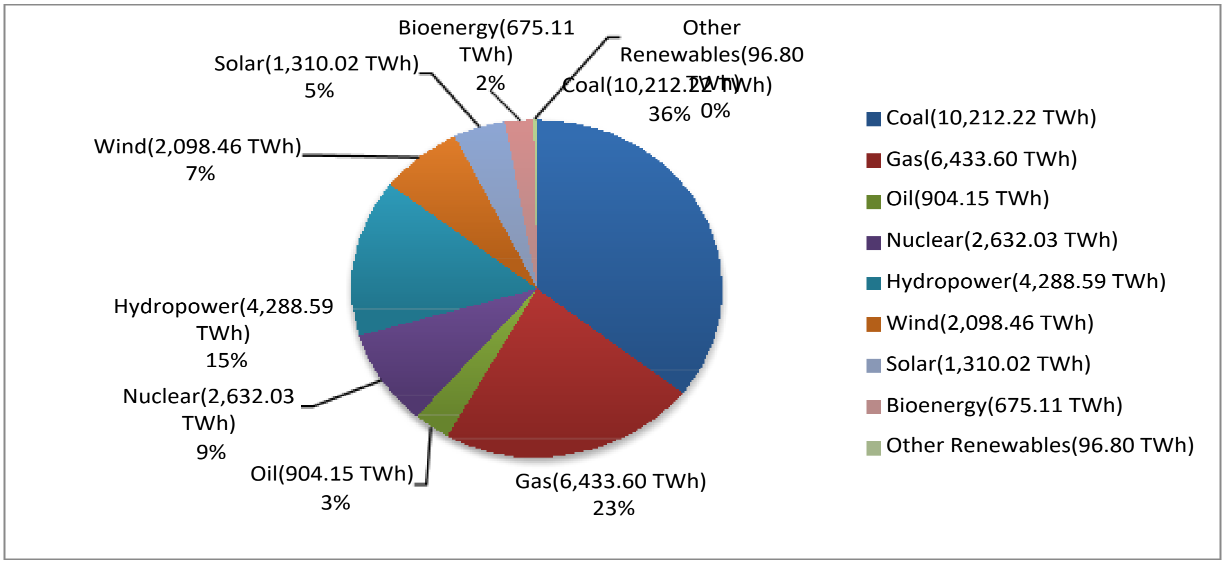

Figure 1: Global Electricity production by source, World in 2022

Moreover, the global spotlight on renewable energy development has intensified, making a substantial contribution to the overarching goal of sustainable development. Evidently, 169 countries, either at the national or state level, have embraced renewable energy targets. This widespread adoption underscores the universal acknowledgment of the critical significance of shifting towards renewable energy sources. These concerted efforts on a global scale signify a collective commitment to mitigating environmental impact, reducing carbon emissions, and fostering long-term sustainability. The integration of renewable energy targets into national and regional policies reflects a shared understanding of the pivotal role that renewable energy plays in addressing both environmental challenges and the broader agenda for sustainable development. As nations strive to meet these targets, there is a clear momentum towards building a more resilient, cleaner, and sustainable energy future for the benefit of current and future generations [4]. Over 130 national governments, including the European Union, committed to triple the world's installed renewable energy capacity to at least 11,000 GW by 2030 at COP28 in Dubai. Figure 2 shows electricity Generated by Renewable Energy sources from 2016 to 2023 year. Renewables 2023 covers policy trends, solar PV manufacturing, technology competitiveness, energy storage, hydrogen production capacity, prospects for renewable energy companies, and system integration, and includes a special section on biogas and bio methane forecasts [5].

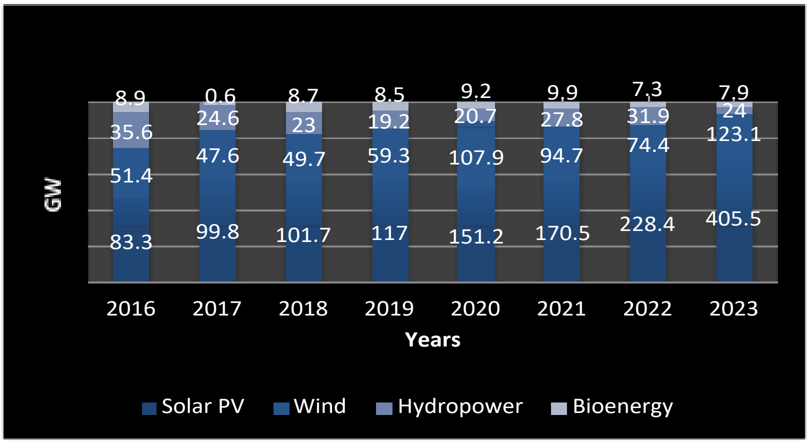

Figure 2: Electricity Generated by Renewable Energy sources from 2016 to 2023 year

The global trajectory in renewable energy is poised for a historic leap in the next five years, surpassing the cumulative capacity installed since the inception of the first commercial renewable energy power plant over a century ago. This surge is underpinned by supportive policies embraced by more than 130 countries, paving the way for an impressive addition of almost 3,700 gigawatts (GW) of new renewable capacity from 2023 to 2028. Anticipated milestones in the upcoming five years mark a transformative era for renewable energy. By 2024, the combined power generation from wind and solar photovoltaic (PV) sources is projected to eclipse that of hydropower. A ground-breaking shift is expected in 2025 when renewables outpace coal, establishing itself as the predominant source of electricity generation. Following suit, 2025 and 2026 are earmarked for wind and solar PV, respectively, to surpass nuclear electricity generation. Looking ahead to 2028, renewable energy sources are predicted to contribute to over 42% of global electricity generation, with the tandem growth of wind and solar PV doubling their share to 25%. Figure 4 illustrates the evolving landscape, depicting the share of renewable electricity generation by technology from 2000 to

2025. This comprehensive shift towards renewable energy signals a remarkable turning point in the global energy landscape, driven by a convergence of technological advancements and supportive policy frameworks. As the world strives towards these milestones, the vision of a more sustainable and resilient energy future comes into clearer focus [5].

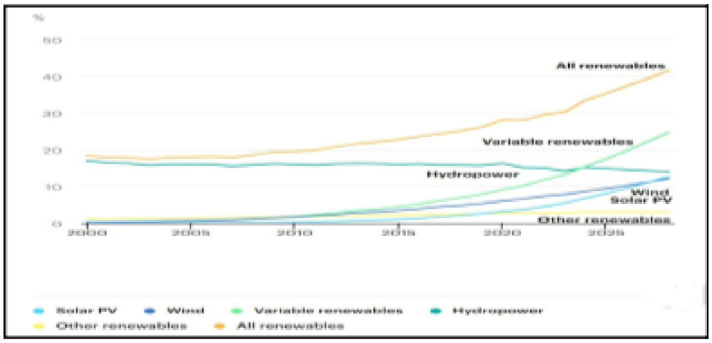

Figure 3: Share of renewable electricity generation by technology, 2000-2028[5].

According to a study conducted by Sharma et al, 111 countries have implemented feed-in value for renewable energy projects, while some countries have transitioned to more liberal and market-based competition strategies, such as auctions [6].

Our focus centres on the examination of solar energy as a primary renewable resource within the context of our investigation, delving into its intricate facets and implications within the broader framework of sustainable energy utilization.

1.2 Solar Energy:

The sun is a prominent source of renewable energy known as solar energy, which is abundant on planet Earth. At present, advanced technologies are being used to convert harvested solar energy into electricity. These technologies have been extensively tested and are now widely used around the world as sustainable alternatives to non-hydro renewable energy technologies [7].

Solar energy plays a pivotal role in advancing sustainable development, acting as a catalyst for progress across environmental, economic, and social dimensions. From an environmental standpoint, solar power plays a crucial role in reducing reliance on fossil fuels, thereby control greenhouse gas emissions and lessening the environmental impact associated with conventional energy sources. This shift toward solar energy represents a significant step in fostering a cleaner and more sustainable energy landscape. On an economic front, the solar industry emerges as a key player, generating job opportunities and fostering economic growth. This not only stimulates innovation in technology and manufacturing but also contributes to the overall diversification and resilience of the economy. Furthermore, solar projects often prioritize extending energy access to underserved communities, promoting social equity and elevating living standards. In essence, the adoption of solar energy aligns seamlessly with a comprehensive approach to sustainable development, addressing imperatives related to environmental preservation, economic prosperity, and social inclusivity. Solar energy can be harnessed and converted into electricity or directly utilized for various purposes. The two primary technologies for capturing solar energy are photovoltaic systems, which convert sunlight into electricity through solar cells, and solar thermal systems, which utilize sunlight to generate heat for electricity production or other applications. Photovoltaic systems are commonly observed in the form of solar panels on rooftops or expansive solar farms, while solar thermal systems find application in concentrated solar power plants [8].

This multifaceted integration of solar energy into various aspects of human life reflects its potential to drive positive change on a global scale. As we leverage solar technologies, we not only make strides towards a cleaner environment and sustainable economic growth but also contribute to fostering social equity and inclusivity.

1.3 Solar Cell:

At the heart of the photovoltaic (PV) principle lies the distinctive capability of specific materials, known as semiconductors, to generate an electrical current upon exposure to light. This crucial phenomenon, identified as the photovoltaic effect, serves as the fundamental mechanism governing the operation of photovoltaic cells, commonly referred to as solar cells. These solar cells constitute the foundational components of a photovoltaic system, acting as integral units responsible for capturing sunlight and converting it into electricity.

Typically crafted from semiconductor materials, with silicon being a prevalent choice, solar cells are meticulously designed to harness the energy from sunlight and transform it into electrical power. Silicon-based solar cells have historically dominated the photovoltaic landscape. However, this status quo is undergoing a transformation with the advent of a third generation of solar cells, challenging the supremacy of traditional silicon-based devices. This new wave includes innovations such as Dye-Sensitized Solar Cells (DSSCs), Quantum Dot Solar Cells (QDSCs), Organic Solar Cells, and Perovskite Solar Cells, introducing in a diverse range of materials and technologies that hold promise for advancing the efficiency and applicability of solar energy conversion [9].

Various generations of SC are listed is as shown in figure 4. The first generation of SC is silicon-based, more than 90% of solar cells are used in the world is silicon sandwiches. There are mainly four types of silicon SC. Classification is based on the basis, of which type of silicon is used in production. The mono-crystalline silicon-based cell gives higher efficiency (up to 25 %) But growing large crystal of silicon is a very energy-intensive process. So the production cost is the highest of all the solar cell panel types [10].

The second generation of SC is based on the cadmium telluride (CdTe), copper indium gallium diselenide (CIGS), and amorphous silicon it also called a thin-film solar cell. Both Converging efficiencies of the cell are 10 to 15% in the second-generation solar cell. As compared to the first generation CdTe/CIGS solar cell is more flexible. However, has the production of cells requires high vacuum pressure, high heat treatment energy consumption is larger. A second-generation solar cell is based on scarce elements and this causes increasing price [11].

The third generation of SC is very different from the first and second generation SCs because the novel semiconductor materials were used which includes polymer SC, organic SCs, Dye-sensitized solar cell (DSSC) and Quantum Dot solar-sensitized cell (QDSSC). The third generation of solar cells is a step forward from the traditional ones we commonly see. In this phase, scientists are exploring new materials and designs to make solar cells more efficient.

One key feature is the use of multi-junction cells, which stack different layers to capture a wider range of sunlight and boost overall efficiency. The goal of this generation is to make solar energy more effective and affordable, encouraging its use in various applications. Researchers are actively experimenting with different materials to enhance performance and address environmental concerns, marking a significant phase in the ongoing evolution of solar cell technology [12].

Fourth-generation solar cells are like upgraded versions of traditional solar panels. They use different materials to make them more efficient and flexible. These cells can be lighter and bendable, making them suitable for various applications. Scientists are working on making them cost-effective and environmentally friendly, aiming to make solar energy more affordable and sustainable. Even though these solar cells are still in the research stage, they have the potential to improve how we capture and use solar power in the future [13].

This classification reflects the continuous progress in solar technology, with each generation building upon the achievements of the previous ones to make solar energy more efficient, affordable, and adaptable to various applications. The categorization of solar cells based on their respective generations is visually depicted in the accompanying figure 4.

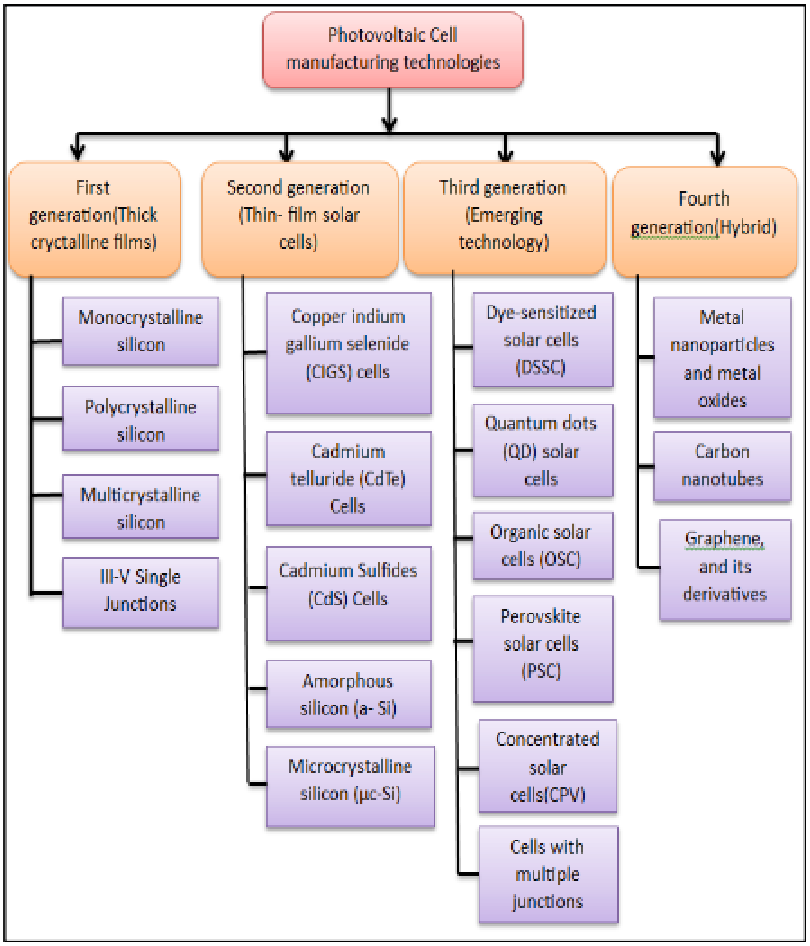

Figure 4: Various Generations of Solar Cells and Their Types

2. Dye Sensitized solar cell:

Dye-sensitized solar cells offer a promising frontier for renewable energy. These solar cells have several advantages including low cost, the simple procedure of Fabrication, higher plasticity, higher transparency, a great variety of colors, low toxicity, and ease of production. Furthermore, DSSCs have the potential to achieve high efficiency in converting sunlight into electricity. One promising area of research in DSSCs is the use of different materials for the photoanode and counter electrode [14]. Researchers have been able to improve the efficiency of Dye-Sensitized Solar Cells (DSSCs) by studying different types of counter electrodes based on transparency, flexibility, and conductivity. Additionally, modifications to the photoanode have also been explored to enhance the performance of DSSCs. These modifications include introducing blocking and scattering layers or using 1-D or 2-D nanostructures. In recent years, researchers have also focused on improving the stability of DSSCs for their commercial viability. The long-term durability of these devices is crucial. Furthermore, the development of new materials and dyes with improved absorption properties and stability is another area of active research in DSSCs. Overall, DSSCs offer a promising and exciting avenue for renewable energy generation, and their unique characteristics and potential have garnered significant attention in the field of renewable energy [15]. The overarching goal of this review is to provide a thorough and insightful examination of the current state of research in Dye-Sensitized Solar Cells (DSSCs), positioning them as a cutting-edge frontier within the realm of renewable energy.

2.2 Fundamentals of DSSC:

Understanding more briefly the structure of Dye- sensitized solar cell with various components: The main parts of a dye-sensitized solar cell (DSSC) are usually arranged in a certain way to help to convert sunlight into electrical energy. Figure 5 shows architecture insights of DSSC with the appropriate components.

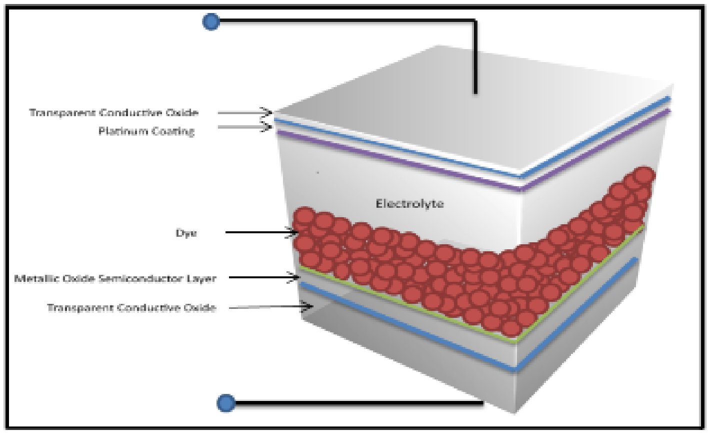

Figure 5: Architectural Insights of DSSC

2.2.1 Transparent Conductive Oxide (TCO) Electrode and Substrate:

The glass or plastic substrate that forms the basis of the DSSC is frequently covered in a transparent conductive oxide layer, such as indium-doped tin oxide (ITO) or fluorine-doped tin oxide (FTO) [16]. These FTO and ITO substrates provides platform for the deposition of semiconductor materials. The substrates essentially have high transparency so that to allow light pass through to reach the photosensitive dye. For better result, light absorption transparency should be greater than 80%. The substrate should be highly conductive, to get maximum charge transfer and reduction of energy loss. The attainment of total efficiency is mostly dependent on the DSSC substrates. The substrates conductivity and transparency dictate the cell's efficiency. Substrates are coatings with thinner layers that support the semiconductor layer of the DSSC structurally and act as a current collector. Low resistivity substrates are essential to promote electron transmission and reduce energy losses [17].

2.2.2 Layer of Semiconductors (Photoanode):

Semiconductor metallic oxides are use as photoanode. Usually, titanium dioxide (TiO2), a thin layer of a wide-bandgap semiconductor material, is placed on the TCO electrode. This layer offers a high surface area for light absorption and functions as the photoanode [18]. A productive dye absorber must have high photocorrosion resistance, rough surface, and a large surface area, as well as the capacity to accept electrons. Good adhesion to substrates is also very important. The band-gap of photoanode materials affects overall efficiency, so it is important to optimize it. TiO_2, NiO, ZnO, Cu_2O, SnO_2, $SrTiO_3$, Zn_2SnO_4, WO_3, $BiVO_4$, V_2O_5 and Nb_2O_5 are examples of popular metal oxides with higher band gaps (> 3 eV) [19].

Metal Oxide	Advantages	Disadvantages	Reference
TiO_2	High electron mobility, photostability, wide band gap, biocompatibility, abundance.	Limited absorption range, dye adsorption challenges, hysteresis effect, electron trapping.	[20]
ZnO	High electron mobility, transparent conductive properties, versatility in nanostructure, ease of fabrication, broad absorption spectrum.	Reduced stability, electron trapping, material compatibility, cost implications, toxicity concern.	[21]
SnO_2	High transparency, good electron mobility, enhanced stability, potential for dye compatibility, ease of fabrication.	Electron trapping, limited band gap, material defects, cost implication, sensitive to processing conditions.	[22]

NiO	P-type semiconductor, ease of doping, visible light absorption, compatibility with hole transport materials, chemical stability.	Challenges in fabrication, potential for recombination, cost implication, narrower band gap, lower electron mobility.	[23]
WO_3	Wide absorption range, high electron mobility, photostability, improved light harvesting.	Complex fabrication, limited conductivity, sensitive to processing condition, electron trapping.	[24]
Cu_2O	P- Type semiconductor, ease of synthesis, potential for tandem cells, compatibility with hole transport, visible light absorption.	Limited stability, complex fabrication, reduced absorption efficiency, lower electron mobility, potential for recombination.	[25]
V_2O_5	High electron mobility, wide absorption range, chemical stability, tenability.	Limited conductivity, cost implication, potential for recombination, sensitive to processing condition.	[26]
$SrTiO_3$	Excellent electron mobility, potential for enhance efficiency, stability, wide band gap, versatility.	Limited light absorption, potential for recombination, cost implication.	[27]
Zn_2SnO_4	High electron mobility, tandem cell potential, chemical stability, tenability.	Complex fabrication, limited conductivity, sensitive to processing condition, potential for recombination.	[28]

Table 1: Advantages and disadvantages of metal oxides used as photo anode

2.2.3 The Dye Molecule:

The sensitizer plays a crucial role in Dye-Sensitized Solar Cells (DSSCs), serving as a vital component responsible for capturing light across the visible to near-infrared spectrum. Its key features include a broad spectrum range and high molar extinction coefficients. Additionally, the sensitizer must facilitate effective charge separation, minimizing electron recombination, and ensuring efficient electron injection into oxide semiconductors. The photosensitive dye, typically organic or a ruthenium-based complex, is adsorbed onto the semiconductor layer. This dye becomes the catalyst for the initiation of the electron excitation process upon absorbing sunlight. This series of events is essential for the overall functionality and efficiency of DSSCs in harnessing solar energy [29]. The metal complex sensitizer synthesized from complex fabrication method while natural sensitizers are prepared from different parts of plant like flowers, leaves, bark and roots etc. using simple ethanol, methanol or water extraction process thus less costly as compared to synthetic dyes. Types of Dyes used in DSSC are shown in figure 6 [30].

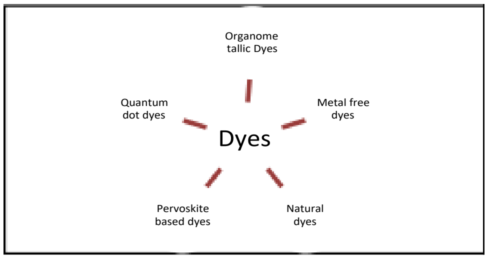

Figure 6: Types of Dyes Used in DSSC

i. Organometallic Dyes:

Organometallic dyes are distinct molecules that are utilize in dye-sensitized solar cells (DSSCs) to boost light absorption and enable efficient electron transfer. These dyes consist of a metal-ligand complex with a central metal ion, like osmium, or ruthenium, which is coordinated to ligands. Organometallic dyes have adaptable electronic properties, thanks to their chromophore that takes in radiation across the entire solar spectrum, specifically in the visible range. When these photons are absorbed, electrons in the metal-ligand complex become excited and are later injected into the conduction band of the semiconductor material, usually titanium dioxide (TiO2), generating an electric current. Organometallic dyes are highly versatile, and their design flexibility allows for specially crafted absorption profiles, optimizing their performance in converting sunlight into electrical energy within the unique environment of DSSCs. This characteristic flexibility is vital in adapting DSSCs to varying light conditions and enhancing their overall efficiency [31].

ii. Metal Free Dyes:

Metal-free dyes represent a category of light-absorbing molecules distinguished by the absence of any metal components. In contrast to their metal-containing counterparts, these dyes offer a cost-effective, easily synthesizable, and environmentally friendly alternative. They emerge as a compelling choice, providing an eco-conscious option distinct from traditional organometallic dyes. Typically composed of organic compounds featuring conjugated π-electron systems, metal-free dyes include structures like porphyrins or organic dyes such as indoline or squaraines. The absorption of photons by these π-electron systems plays a pivotal role in initiating the flow of current within Dye-Sensitized Solar Cells (DSSCs), generating crucial electron-hole pairs that contribute to the overall efficiency of the solar cell. While metal-free dyes may exhibit a potentially lower light absorption efficiency compared to their organometallic counterparts, ongoing scientific efforts are dedicated to enhancing their performance and expanding their applicability in solar cell technology. This underscores the broader commitment to leveraging sustainable and readily available materials in the realm of renewable energy systems, emphasizing the importance of ecological considerations in the pursuit of cleaner and more efficient energy solutions [32].

iii. Natural Dyes:

Natural dyes stand out as a sustainable and eco-friendly option in the realm of dye-sensitized solar cells (DSSCs). Derived from plant sources, microbes, or other biological materials, these dyes harness pigments like chlorophyll, anthocyanins, or betalains to absorb sunlight and generate electricity, mirroring the functionality of synthetic dyes. In a DSSC, the interaction between natural dyes and light initiates the generation of electron-hole pairs within the semiconductor material, typically titanium dioxide (TiO2), leading to the flow of current.

While natural dyes may exhibit lower efficiency compared to their synthetic counterparts, ongoing research endeavours focus on optimizing extraction methods and enhancing their performance. This concerted effort aims to pave the way for the development of greener and more sustainable solar energy technologies. Noteworthy attributes of natural dyes include their renewability, biodegradability, and often cost-effectiveness, aligning seamlessly with the principles of sustainable solar energy technologies. In the following discussion, we delve into a few natural dyes that researchers worldwide have explored, shedding light on their potential contributions to the evolution of sustainable solar energy solutions [33].

- **Chlorophyll:**

Chlorophyll is an essential pigment found in plants, responsible for the process of photosynthesis. Chlorophyll is obtained from green leaves and is most efficient in absorbing light in the blue and red regions of the electromagnetic spectrum. It is also used as a natural dye in various applications, including dye-sensitized solar cells (DSSCs). There are four types of chlorophyll: chlorophyll a, chlorophyll b, chlorophyll c, and chlorophyll d. Chlorophyll a and chlorophyll b have slight differences in the composition of a side chain - chlorophyll a has a composition of $C_{55}H_{72}O_5N_4Mg$, while chlorophyll b has a composition of $C_{55}H_{70}O_6N_4Mg$. The most efficient derivative of chlorophyll 'a' is methyl trans-32-carboxy-pyropheophorbide.

In DSSCs, chlorophyll acts as a light-absorbing agent, capturing photons and generating electron-hole pairs when excited. The electrons then help to create an electrical current flow in the semiconductor material, such as titanium dioxide (TiO2), enabling solar energy conversion. The use of chlorophyll in DSSCs aligns with eco-friendly practices and emphasizes the potential for biomimicry. By drawing inspiration from nature's photosynthetic processes, scientists can advance solar cell technology. Researchers are still working to optimize the integration of chlorophyll and improve the overall efficiency of DSSCs, highlighting the importance of harnessing the inherent capabilities of natural pigments for renewable energy solutions [34].

- **Flavonoids:**

Flavonoids are pigments found in various plant tissues that contribute to the vibrant colors of flowers, fruits, and vegetables. Flavonoids are the most widespread and physiologically active group of biological pigments present in bryophytes, gymnosperms, angiosperms, and ferns. Their organic structure is based on 15 carbon atoms with 2 phenyl rings, connected by a basic C_6-C_3-C_6 skeleton. They efficiently absorb light in the visible region [35].

Flavonoids are sustainable alternatives for natural dyes and offer biodegradable options for solar energy conversion. These pigments are used as colorants in natural dyes due to their light-absorbing properties. Flavonoid pigments such as anthocyanins, quercetin, and kaempferol are extracted from plant sources like berries, citrus fruits, and tea leaves. They can be used in dye-sensitized solar cells (DSSCs) due to their ability to absorb sunlight efficiently. These pigments generate electron-hole pairs within the semiconductor material, often titanium dioxide (TiO_2), leading to the production of electrical current in DSSCs. Researchers are trying to optimize flavonoid-based natural dyes to improve their performance in DSSCs and expand their use in renewable energy technologies [36].

- **Anthocyanins:**

Anthocyanins are a type of flavonoids that are natural pigments present in different fruits, vegetables, and flowers. These pigments give red, purple, and blue colors to these plant tissues and can display unique color changes depending on pH levels. Anthocyanins are glycoside salts of phenyl-2-benzopyrilium based on a C15 skeleton with a chromane ring bearing a second aromatic ring of C in position 2 (C_6-C_3-C_6). Anthocyanin molecules have carbonyl and hydroxyl groups that can bind to the surface of TiO_2 semiconductors. This helps in the excitation and transfer of electrons from the anthocyanin molecules to the conduction band (CB) of metallic oxides. Anthocyanins are gaining attention as natural dyes for use in dye-sensitized solar cells (DSSCs). They are extracted from sources like berries, grapes, and red cabbage and can efficiently absorb light across the visible spectrum, making them ideal for capturing sunlight and generating electron-hole pairs in the semiconductor material, typically titanium dioxide (TiO_2), used in DSSCs. This property makes anthocyanins promising candidates for sustainable and eco-friendly solar energy conversion. Researchers are working on refining the integration of anthocyanin-based natural dyes to improve their performance in DSSCs. They are contributing to the development of renewable energy technologies inspired by nature [37], [38], [39].

- **Carotenoids:**

Carotenoids, a family of tetraterpenoids, are natural pigments widely distributed in plants, algae, and photosynthetic bacteria. These pigments impart colors spanning from yellow and orange to red in various fruits and vegetables. Despite being less explored as natural dyes in dye-sensitized solar cells (DSSCs), certain carotenoids have demonstrated the ability to absorb light and generate electrons in semiconductor materials, such as titanium dioxide (TiO_2), a common component in DSSCs.

Noteworthy carotenoids like beta-carotene and lutein can be extracted from readily available sources such as carrots, tomatoes, and sweet potatoes. Their absorption characteristics within the visible light spectrum make them particularly suitable for solar energy conversion. Ongoing research is dedicated to optimizing the incorporation of carotenoid-based natural dyes into DSSCs, aiming to maximize their potential contribution to sustainable and environmentally friendly solar energy solutions.

This continuous investigation reflects a commitment to harnessing the unique properties of carotenoids for solar energy applications. By expanding our understanding and refining integration methods, we strive to unlock the full potential of carotenoids in DSSCs, paving the way for a more sustainable and eco-friendly future in solar energy utilization [40], [41], [42].

- **Betalains:**

Betalains, distinguished by their vibrant red and yellow hues, are pigments found in select plants, notably within the Amaranthaceae and Caryophyllaceae families. These compounds lend their striking colors to specific flowers and fruits, including beets and cacti. In contrast to more familiar pigments like anthocyanins and chlorophylls, betalains form a distinct class. Their water-solubility sets them apart, and unlike some counterparts, they maintain color stability across varying pH levels [43]. The potential of betalains as natural dyes has been extensively explored, with applications spanning the realms of food and textiles. Their vivid and enduring colors make them particularly attractive for such uses. While betalains are not as prevalent in dye-sensitized solar cells (DSSCs) as other natural pigments like chlorophyll or anthocyanins, researchers are actively investigating their suitability for solar energy conversion. Leveraging the light-absorbing properties of betalains holds promise in this context, even though further research is required to optimize their integration into DSSC technology [44]. Betalains are categorized into betacyanins and betaxanthins based on their pigments, each offering antioxidant properties and light absorption. Notably, these pigments exhibit stability in acidic environments, adding to their versatility. The ongoing exploration of betalains in various applications underscores their potential as an eco-friendly and sustainable option for coloration, contributing to a broader initiative towards environmentally conscious practices in diverse industries [45].

iv. Quantum dot Dyes:

Quantum dots (QDs) have emerged as promising semiconductor particles for consideration in dye-sensitized solar cells (DSSCs), drawing attention due to their distinctive optical and electronic characteristics. Unlike conventional organic dyes, quantum dots are exceptionally small, exhibiting quantum confinement effects that enable tunable absorption across a wide spectrum [46]. In the realm of DSSCs, quantum dots serve as efficient light harvesters. Upon absorbing photons, they elevate electrons to higher energy states, generating electron-hole pairs. These excited electrons can be injected into the semiconductor material, typically titanium dioxide (TiO_2), initiating a current flow and contributing to the conversion of solar energy into electricity. The merits of employing quantum dots in DSSCs encompass their capacity to absorb various wavelengths of light, the potential for multiple exciton generation (yielding multiple electron-hole pairs from a single photon), and enhanced stability compared to certain organic dyes [47]. While the advantages are noteworthy, practical applications present challenges that demand attention. Concerns include toxicity, production costs, and the achievement of optimal quantum dot coverage on the semiconductor surface. Researchers remain engaged in persistent exploration of quantum dots' potential in DSSCs and other solar cell technologies, driven by the goal of leveraging their unique properties to amplify efficiency and performance in renewable energy systems. This ongoing investigation underscores the commitment to advancing solar cell technology through the nuanced understanding and strategic application of quantum dots, paving the way for enhanced sustainability and efficacy in harnessing solar energy [48].

v. Perovskite base Dyes:

Perovskite materials are currently under extensive investigation as a potential substitute for traditional organic dyes in dye-sensitized solar cells (DSSCs), marking an exciting frontier in photovoltaic research. These materials are renowned for their remarkable power conversion efficiencies, and offer a promising avenue in the field of solar energy. In DSSCs, perovskite materials serve dual roles as both a sensitizer and semiconductor, owing to their distinctive crystal structure that facilitates efficient light absorption and charge carrier generation.

The utilization of perovskite materials in DSSCs presents a range of advantages, including a broad absorption spectrum, a tunable bandgap, and high charge carrier mobility. Despite these merits, challenges persist in optimizing their stability, scalability, and fabrication processes. Issues pertaining to material degradation, toxicity, and long-term stability require careful consideration. Nevertheless, perovskite-based DSSCs have demonstrated tremendous potential in achieving high efficiency, capturing interest as a promising next-generation solar cell technology [49].

Ongoing research endeavours are focused on surmounting the current challenges associated with perovskite materials in DSSCs. The overarching goal is to fully unlock and leverage the inherent benefits of perovskite materials, contributing to the development of solar energy solutions that are not only efficient but also commercially viable. This commitment to ongoing exploration reflects the collective effort to propel solar cell technology forward, striving for advancements that can significantly impact the renewable energy landscape [50].

❖ Comparison between Synthetic dyes and Organic dyes [51], [52].

Sr. No	Parameter	Synthetic Dye	Organic Dye
1	Cost	Complex fabrication method involve since results in high cost	These dyes are extracted from different parts of plants such as leaves, stem, bark, flowers, fruits etc. This results low cost
2	Effects on Environment	Due its chemical nature it hazardous to environment	It is environmental freely because of its natural occurrence
3	Availability	Not readily available	Readily available
4	Fabrication Process	It requires variety of solvents and time consuming purification	Requires simple and direct chemical procedure
5	Stability	It shows high stability because it degrades slowly in presence of sunlight	It shows low stability because it degrades rapidly in presence of sunlight
6	Absorption on solar spectrum	N3 dye has absorption up to 800 nm	Natural dyes ha absorption range of 400- 700 nm. This is visible region of solar spectrum.
7	Efficiency	It provides high efficiency For DSSC	Compare to synthetic dyes it provides low efficiency for DSSC

Table 2: Comparison between Synthetic dyes and organic dyes

2.2.4 Electrolyte Dispensation:

The semiconductor layer is treated with a redox electrolyte solution, typically made up of a solvent and a redox pair (such as iodide/triiodide). Liquid electrolyte is mostly preferred for DSSC application. Liquid electrolyte are classified into organic electrolyte and ionic electrolytes. By facilitating the movement of ions and electrons, this solution keeps the cell's overall efficiency high and aids in dye regeneration. For efficient and stable DSSC's, the electrolyte must possess following properties

I. The redox potential should be highly positive, For high voltage, high electrical conductivity.
II. The viscosity of an electrolyte must be low so that electron can be transferred quickly.
III. Good interfacial contact with semiconductors, counter electrodes and nano-crystalline.
IV. Absorbance should not be in the range of visible spectrum. [53]

2.2.5 Counter Electrode (Photocathode):

The electrolyte layer is topped by a counter electrode, which is usually composed of platinum or a conductive carbon substance. The electrical circuit is completed by this electrode's catalysis of the redox couple's reduction. The CE is formulated by applying a catalytic layer of platinum on the conducting glass substrate. Platinum (Pt) catalyst provides good catalytic activity, high exchange current density, and transparency. But there are several disadvantages of platinum such as:

I. High cost and limited availability.
II. Platinum might be dissolved in electrolytes containing the I^-_3 /I^- redox couple, producing PtI_4.
III. It shows poor corrosion resistance against iodide/tri-iodide (I^-_3/I^-).

All this disadvantages led to the development of other alternative such as metals, carbon materials, organic polymer, Inorganic compounds, Nitrides, Oxides, sulphides and phosphides, composites etc. [54].

2.2.6 Sealing Layer:

A sealing layer, commonly composed of glass or a polymer substance, is applied to enclose the cell and shield its components from the elements [55].

With this fundamental design, solar energy can be efficiently captured and transformed into electrical energy in DSSCs, which makes them a potential technology for photovoltaic applications.

2.3 Working Mechanism of DSSC:

2.3.1 The working design of DSSC is replicated from the principle of photosynthesis in plants:

The working mechanism of DSSC resembles with the photosynthesis of plant. During photosynthesis light energy is converted into chemical energy by complex biochemical process. Chlorophyll plays pivotal role in the process of absorption of light. Chlorophyll pigment consists of prophyrin ring. When light (Visible spectrum) incident on chlorophyll pigment in the leaves, it excites electrons in the prophyrin ring. A photosystem is made up of a bigger protein complex that includes the chlorophyll pigment. Through a process known as photolysis, oxidizing water molecules take the place of the released electrons within this complex. Protons (H+ ions) and electrons are released as a result of this oxidation of water. The excited electrons, now derived from water, are passed through a series of protein complexes known as the electron transport chain. As these electrons move through the chain, they release energy, which is used to actively transport protons across the thylakoid membrane. The accumulation of protons in the thylakoid space creates an electrochemical gradient, which is harnessed by an enzyme called ATP synthase. This enzyme facilitates the synthesis of adenosine triphosphate (ATP), a molecule crucial for cellular energy storage and utilization. As the electrons move through the electron transport chain, they eventually reach an electron carrier, which accepts them and becomes reduced. This reduced carrier then plays a crucial role in another process known as the Calvin cycle. During this process, carbon dioxide (CO2) is fixed and used to create sugars, including glucose [56].

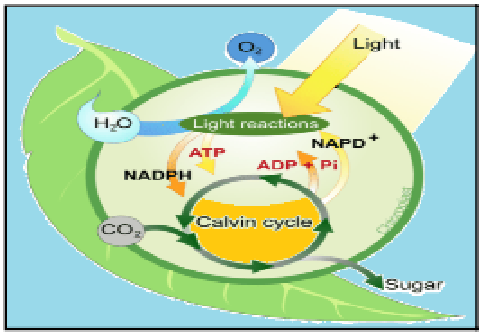

Figure 7: Photosynthesis process in plants

The Working Mechanism of DSSC is shown in fig. It involves several steps as follows.

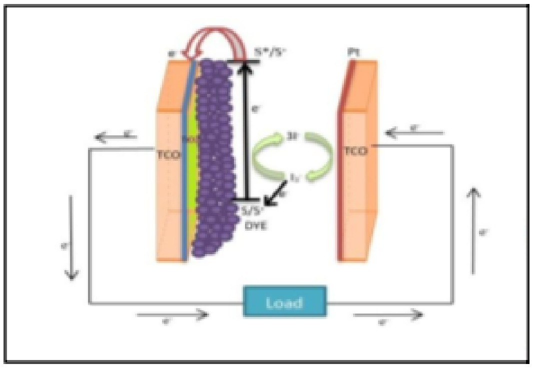

Figure 8: Working Mechanism of DSSC

i. **Sensitizer Molecule (Dye Molecule) Photoexcitation**: The dye-sensitized solar cell (DSSC) consists of semiconductors such as TiO2, ZnO, SnO2, WO3, NiO, Nb2O5, Cu2O, etc. The dye (S) is applied to a thin layer of semiconductor material. During solar cell energy conversion, this excited state is crucial for initiating the process of photoexcitation of the sensitizer molecule when it absorbs sunlight [57].

ii. **Electron-Hole Pair Generation and Separation**: An electron is transferred to the semiconductor material by the photoexcited sensitizer, resulting in the formation of an electron-hole pair. Positive and negative charges are successfully separated by this method, avoiding recombination.

iii. **Electron Injection into Semiconductor**: The conduction band of the semiconductor is then traversed by the injected electrons.

iv. **Electrolyte Redox Couple:** The cell contains an electrolyte solution, which usually contains a redox pair (I_3^-/I^-, for example). By absorbing the supplied electrons, the redox pair helps the sensitizer regenerate.

v. **CE, or counter electrode**: The electron collector is a counter electrode, which is frequently covered in a catalyst such as platinum. The counter electrode is reached by the semiconductor's electrons via an external circuit.

vi. **Counter-Electrode Redox Reactions**: The circuit is completed at the counter electrode where the electrons are employed in redox processes to decrease oxidized substances. This procedure keeps a potential difference and guarantees an ongoing electron flow.

vii. **Return of Electrons to Semiconductor**: The cycle is restarted when electrons from the external circuit return to the dye-sensitized semiconductor and replenish the dye molecules [58].

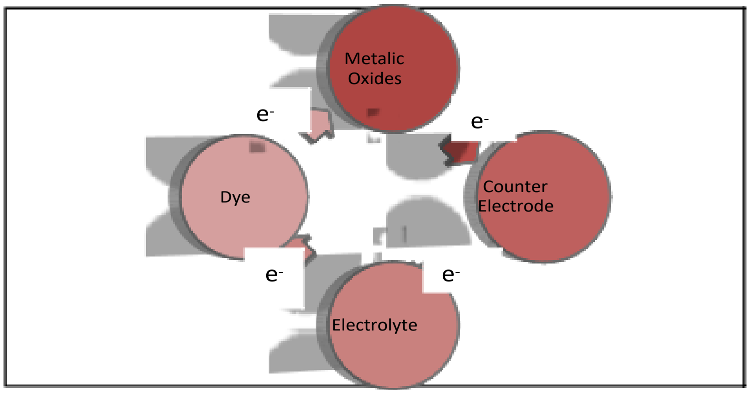

Figure 9: The Cyclic movement of electron in working mechanism of DSSC

2.3.2 Commonalities between working mechanism of DSSC and photosynthesis in plants:

Dye-Sensitized Solar Cells (DSSCs) and photosynthesis in plants exhibit several common elements in their working mechanisms:

- **Light Absorption by Pigment:** Both DSSCs and photosynthesis involve the absorption of light by a pigment.
- **Electron Excitation and Charge Separation:** In both processes, the excitation of electrons and subsequent charge separation are crucial steps.
- **Electron Transport through a Medium:** A key component in both mechanisms is the transport of electrons through a medium, whether it's a semiconductor material in DSSCs or the thylakoid membrane in photosynthesis.
- **Regeneration of Components:** Both systems require the regeneration of components, such as the dye in DSSCs or chlorophyll in photosynthesis, to sustain their functionality.

While DSSCs and photosynthesis have their distinct characteristics, the fundamental principles underlying their utilization of sunlight for energy conversion share similarities. These commonalities serve as a source of inspiration for the development of sustainable energy technologies, highlighting the intricate interplay of light, chemical reactions, and electrons [59].

3. Photovoltaic parameters and their estimation [60].

The performance of DSSCs is typically estimated by the open-circuit voltage (V_{OC}), the short-circuit current (I_{SC}), the fill factor (FF), and the PCE. These parameters are determined by I-V Plot. Figure 10 shows a typical I–V plot for photovoltaic cells. Below are details of these parameters.

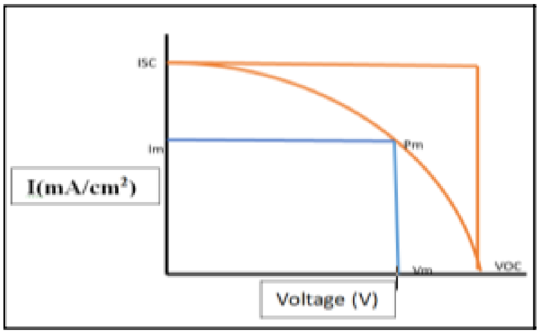

Figure 10: Typical I- V characteristics of Photovoltaic cell.

3.2 Open- circuit voltage (V_{OC}):

The open-circuit voltage in a solar cell denotes the voltage across its terminals when no current is flowing. This specific voltage signifies the maximum potential achievable from the cell under the condition where the resistance between the working and counter electrodes is infinite. It essentially represents the difference between the redox potential of the electrolyte and the Fermi level of the semiconducting oxide. In essence, the open-circuit voltage serves as a crucial parameter in understanding the performance of a solar cell. It provides insights into the maximum voltage that can be harnessed from the cell in ideal conditions, offering a key metric for assessing the efficiency and functionality of solar energy conversion systems.

3.3 Short- circuit current density (J_{SC}):

The short-circuit current in a solar cell is defined as the output current when there is no voltage difference across its electrodes. In simpler terms, it represents the current generated by the cell under the condition where the load resistance is reduced to zero. This is commonly expressed as the short-circuit current density (J_{SC}), which is calculated as the ratio of the measured short-circuit current to the active area of the cell. In essence, the short-circuit current provides valuable information about the maximum current that a solar cell can deliver when its terminals are effectively shorted. This parameter is crucial in assessing the performance and efficiency of a solar cell, offering insights into its capacity to generate electrical current under optimal conditions.

3.4 Fill Factor (FF):

The Fill Factor (FF) in the context of solar cells is defined as the ratio of the maximum power output (Pm) to the product of the short-circuit photocurrent (I_{SC}) and the open-circuit photovoltage (V_{OC}). Figure 10 visually illustrates that the maximum power (Pm) is achieved through the multiplication of Im (photocurrent) and Vm (photovoltage), pinpointing the optimal operating point known as the maximal power point. The Fill Factor serves as a crucial metric, quantifying the impact of electrical and electrochemical losses within Dye-Sensitized Solar Cells (DSSCs). In essence, the FF provides a quantitative measure of how efficiently a solar cell converts sunlight into electrical power. It sheds light on the effectiveness of the cell in harnessing the generated current and voltage to produce maximum power, offering valuable insights into the overall performance and potential improvements of DSSCs.

$$\mathrm{FF} = \frac{\mathrm{Pm}}{\mathrm{Isc} \times \mathrm{Voc}} = \frac{Im \times Vm}{(Isc \times Voc)} \qquad (1)$$

3.5 Photo Conversion Efficiency (PCE):

The overall Power Conversion Efficiency (PCE) serves as a crucial metric, gauging the effectiveness of converting light into electrical energy within a solar cell. The calculation of PCE involves utilizing parameters obtained from the current-voltage (I-V) plot, as illustrated in Figure 10. The formula for calculating PCE is typically expressed through Equation (2), where specific parameters extracted from the I-V plot are incorporated. This equation encapsulates the comprehensive evaluation of the solar cell's performance, taking into account factors such as short-circuit current (I_{SC}), open-circuit voltage (V_{OC}), fill factor (FF), and the maximum power output (Pm). The resulting PCE value provides a quantitative measure of how efficiently the solar cell transforms incident light into usable electrical energy. In essence, PCE stands as a pivotal indicator of the overall effectiveness of a solar cell, guiding researchers and engineers in the quest for continual improvements and advancements in solar energy conversion technologies.

$$\eta = \frac{Jsc \times Voc \times FF}{Pin} \qquad (2)$$

Where, Jsc= Short- circuit current density, Voc= Open circuit voltage, FF= Fill Factor, Pin= Incident power.

3.6 The Incident Photon to Current Conversion Efficiency (IPCE):

The Incident Photon to Current Conversion Efficiency (IPCE), also referred to as Quantum Efficiency, serves as a critical measure of how efficiently a solar cell converts incident light into electrical energy. This metric is particularly insightful as it quantifies the generation of electrons based on the wavelength of the incoming light, providing a wavelength-dependent assessment of a solar cell's performance. Essentially, IPCE reveals the amount of photocurrent a solar cell can generate when exposed to monochromatic light. To experimentally estimate IPCE, the following equation is commonly employed. This equation involves parameters derived from experimental data, providing a quantitative and wavelength-specific evaluation of the solar cell's ability to convert photons into electrical current. This characterization is valuable for researchers and engineers aiming to understand and optimize the performance of solar cells under different light conditions [61].

$$IPCE = \frac{1240 \times Jsc}{\lambda \times \mathrm{Pin}} \qquad (3)$$

4. Historical Advancements in different components of DSSC

4.2 Historical Advancement in Photoanode:

4.2.1 TiO2 photoanodes:

In a ground-breaking development in 1991, Brian O'Regan and Michael Gratzel proposed the concept of Dye-Sensitized Solar Cells (DSSCs), utilizing dye-sensitized colloidal TiO_2 films. This innovative approach laid the groundwork for the creation of solar cells characterized by both low cost and high efficiency. O'Regan and Gratzel's research marked a pivotal moment in solar cell technology, opening avenues for the development of more accessible and effective solutions for harnessing solar energy [16].

4.2.2 Mesoporous TiO_2 photoanodes:

In 2005, Wang, Moser, and Gratzel significantly advanced our understanding of Dye-Sensitized Solar Cells (DSSCs) by employing electrochemical impedance spectroscopy in their examination. Their research played a crucial role in enhancing our insights into the internal charge transfer mechanisms of the cell, specifically highlighting the importance of mesoporous TiO_2 structures. By delving into the intricacies of DSSCs using this sophisticated technique, the team contributed valuable knowledge that aids in optimizing the performance and efficiency of these solar cells [62].

4.2.3 NiO- Based Photoanodes:

In 2010, Nattestad, Mozer, and Bach conducted impactful research on highly effective photocathodes for dye-sensitized tandem solar cells. Their investigation centred on the utilization of NiO-based materials to enhance the performance of Dye-Sensitized Solar Cells (DSSCs), with a specific emphasis on tandem configurations. This work contributed valuable insights into the potential of NiO as a key component in tandem setups, furthering the understanding of materials that could optimize the efficiency of DSSCs in tandem solar cell applications [63].

4.2.4 ZnO Photoanodes:

In 2011, Yella and colleagues significantly advanced the field with their work on porphyrin-sensitized solar cells, achieving impressive efficiencies exceeding 12 %. Their ground-breaking study utilized a cobalt-based redox electrolyte, highlighting the significance of diverse materials, including ZnO, in the development of high-performance Dye-Sensitized Solar Cells (DSSCs). This research not only demonstrated the potential of porphyrin sensitizers but also underscored the importance of innovative materials and redox systems for enhancing the efficiency of DSSCs [64].

4.2.5 Photoanodes based on Perovskite:

In 2013, Xing and collaborators achieved significant progress by introducing perovskite-based photoanodes, showcasing extensive and balanced electron- and hole-transport lengths. This breakthrough has garnered substantial interest in the field due to the exceptional optoelectronic properties exhibited by perovskite materials. Their work highlighted the potential of perovskites for advancing the performance of solar cells, particularly in terms of efficient electron and hole transportation, contributing to the ongoing evolution of photovoltaic technologies [65].

4.2.6 3D Hierarchical Photoanodes:

In 2016, Chen and colleagues employed radially grown SnO2 nanotubes within three-dimensional hierarchical TiO2 nanotube arrays, introducing a novel approach to enhance the photoanode's capabilities for light harvesting and charge transport in dye-sensitized solar cells (DSSCs). This innovative strategy aimed to uplift the overall performance of DSSCs by improving the photoanode's efficiency in capturing light and facilitating the transport of charges, contributing to advancements in solar cell technology [66].

4.2.7 Black TiO_2 Photoanodes:

In 2016, Liu and collaborators presented ground- breaking evidence regarding the potential application of black titania for solar hydrogen conversion. Black TiO_2, a modified version of titanium dioxide, exhibited enhanced capabilities in light absorption and catalysis, opening new avenues for improving the efficiency of dye-sensitized solar cells (DSSCs). This discovery highlighted the promising role of black titania in advancing solar energy conversion technologies [67].

4.2.8 Carbon-Based Photoanodes:

In 2017, Zhang and colleagues focused their efforts on flexible dye-sensitized solar cells (DSSCs), employing a composite photoanode composed of graphene sheets and hierarchical TiO_2 spheres. This study systematically explored the synergistic effects of integrating diverse materials to enhance the overall performance of DSSCs. The research emphasized the necessity for flexibility in solar cell applications, underlining the importance of adaptability and versatility in advancing solar energy technologies [68].

4.3 Historical Advancement of Dyes:

Dyes play an important role in dye-sensitized solar cells (DSSCs) in the generating electron-hole pairs by absorbing light. Here are some historical advancements in dyes for DSSCs, along with relevant research papers:

4.3.1 RuBipy Dyes:

In the 1990s, O'Regan and Grätzel conducted research that led to the development of Dye-Sensitized Solar Cells (DSSCs). They discovered that ruthenium-based dyes, particularly Tris (bipyridine) ruthenium (II), held great promise for this purpose. To create a sensitization layer, they applied this complex to a semiconductor material like titanium dioxide. When exposed to sunlight, the dye absorbed light and produced an excited electron, which was then injected into the semiconductor. This initiated the flow of electrons, which generated electricity. The redox mediator played a crucial role in regenerating the ruthenium dye by accepting and transferring electrons, ensuring continuous operation. This pioneering work laid the groundwork for DSSCs, demonstrating the effectiveness of ruthenium-based dyes in converting solar energy into electrical power [16].

4.3.2 Porphyrin- Based Dyes:

Porphyrin dyes are renowned for their robust absorption capabilities in the visible spectrum, making them ideal for solar cell applications. In a notable study by Yella and colleagues in 2011, they successfully developed porphyrin-sensitized solar cells utilizing a cobalt-based redox electrolyte. This innovation capitalizes on the efficient light-absorbing properties of porphyrin dyes, while the incorporation of a cobalt-based electrolyte enhances the redox processes essential for sustained energy conversion in the solar cell. This research contributes to advancing the effectiveness of porphyrin-based sensitization in solar cell technologies, showcasing the potential for harnessing visible light for renewable energy generation [69].

4.3.3 Dithieno[3,2-b:2',3'-d] pyrrole (DTP) Dyes:

In a significant development, Feldt and collaborators in 2010 achieved the creation of dye-sensitized solar cells by utilizing dye-based sensitizers and cobalt polypyridine redox mediators. The incorporation of dye-based dyes is notable for their effective light-absorbing properties, optimizing sunlight capture for energy conversion. The inclusion of cobalt polypyridine redox mediators is crucial in facilitating the regeneration of the dye molecules, a key step for the sustained functionality of the solar cells. This research contributes to the advancement of dye-sensitized solar cell technology, showcasing the potential of combining specific dyes and cobalt-based redox mediators to enhance the efficiency of solar energy conversion [70].

4.3.4 Metal-Free Organic Dyes:

In 2010, Wu and colleagues addressed concerns regarding the cost and scarcity of ruthenium in solar cell technology by shifting their focus to metal-free organic sensitizers. Their research aimed to explore alternatives to ruthenium-based dyes, which are often expensive and limited in availability. The key breakthrough was the confirmation that metal-free organic dyes could be effectively employed in the development of Dye-Sensitized Solar Cells (DSSCs) capable of water-splitting. This finding opens up new possibilities for more sustainable and cost-effective solar cell technologies, paving the way for advancements in harnessing renewable energy through the use of organic sensitizers without the reliance on scarce and costly materials like ruthenium [71].

4.3.5 Perovskite-Based Dyes:

In 2013, Burschka and collaborators presented a significant advancement in the field of solar cell technology by showcasing the application of perovskite-based dyes. Perovskites, hybrid organic-inorganic materials, were utilized in their study, introducing a novel direction for creating efficient and stable Dye-Sensitized Solar Cells (DSSCs). This research marked a breakthrough in the quest for improved solar cell performance, as perovskite materials demonstrated the potential to enhance both the efficiency and stability of DSSCs. The use of perovskite-based dyes represents a promising avenue for advancing the development of more reliable and effective solar energy conversion technologies [72].

4.3.6 Indoline Dyes:

In 2014, Mathew and collaborators achieved a noteworthy advancement in Dye-Sensitized Solar Cells (DSSCs) by employing molecular engineering techniques on porphyrin sensitizers, particularly indoline dyes. Through meticulous design at the molecular level, they were able to enhance the efficiency of DSSCs, achieving an impressive 13% efficiency. This breakthrough underscores the critical role of molecular design in optimizing the performance of solar cells. The focus on indoline dyes within the porphyrin sensitizers illustrates the impact of precise molecular engineering on improving the conversion of sunlight into electricity. Mathew et al.'s work highlights the significance of tailoring molecular structures for enhanced device efficiency, contributing to the ongoing advancements in solar cell technology [73].

The provided information underscores significant milestones in the evolution of dyes for Dye-Sensitized Solar Cells (DSSCs), tracing a trajectory from the initial use of ruthenium-based sensitizers to the exploration of various alternatives. Researchers have progressed from relying on ruthenium, which can be expensive and scarce, to investigating organic, metal-free, and perovskite-based dyes. This shift has been driven by a pursuit of enhanced efficiency and stability in DSSCs. The ongoing exploration of novel dye materials signifies a continuous commitment to improving the performance of these solar cells, reflecting a dynamic and evolving landscape in the quest for more efficient and sustainable solar energy conversion technologies.

4.4 Historical Advancement in Electrolyte:

Development in electrolytes for dye-sensitized solar cells (DSSCs) is pivotal for improving their efficiency, stability, and overall performance. Below are some historical advancement in DSSC electrolytes.

4.4.1 Iodide/Triiodide (I-/I3-) Redox Couple:

The pioneering work of O'Regan and Grätzel laid the foundation for Dye-Sensitized Solar Cells (DSSCs) by introducing the I-/I3- redox couple into the electrolyte. This innovation marked a crucial step in developing a low-cost and efficient solution for charge transport within DSSCs. The I-/I3- redox couple involves the use of iodide (I-) and triiodide (I3-) ions, creating a dynamic exchange of electrons that facilitates the flow of electrical charge. This redox couple serves as an integral component in the electrolyte of DSSCs, contributing to the effective conversion of solar energy into electricity. O'Regan and Gratzel's early contributions paved the way for the advancement of DSSC technology, offering a cost-effective and viable solution for efficient charge transport in these solar cells [16].

4.4.2 Polyiodide/Iodide Redox Couples:

In 1993, M. K. Nazeeruddin conducted ground-breaking research that delved into the realm of polyiodide/iodide redox couples within the electrolyte of Dye-Sensitized Solar Cells (DSSCs). This study significantly expanded the range of available redox mediators, exploring diverse polyiodide/iodide combinations. By investigating various redox couples, Nazeeruddin aimed to identify optimal configurations that would enhance the efficiency of charge transfer in DSSCs. The research not only contributed to the understanding of redox mediation in these solar cells but also offered a broader spectrum of choices for designing electrolytes, paving the way for advancements in DSSC technology and the potential for improved solar energy conversion [29].

4.4.3 Cobalt-Based Redox Couples:

In 2010, Feldt and collaborators conducted a pivotal study that showcased the utilization of cobalt-based redox couples in the electrolyte of Dye-Sensitized Solar Cells (DSSCs). This research marked a significant exploration into the potential of cobalt-based compounds to serve as redox mediators, with the aim of improving the overall performance of DSSCs. By integrating cobalt-based redox couples into the electrolyte, the study sought to enhance the efficiency of charge transfer within the solar cells, ultimately contributing to the advancement of DSSC technology. The findings of Feldt et al. provided valuable insights into the role of cobalt-based redox mediators in optimizing the functionality of DSSCs, thereby influencing the ongoing efforts to refine and improve the efficiency of these solar energy conversion devices [74].

4.4.4 Cobalt Polypyridine Redox Mediators:

In 2010, Feldt and colleagues made a significant contribution to the field of Dye-Sensitized Solar Cells (DSSCs) by concentrating on the design of organic dyes and cobalt polypyridine redox mediators. Their research provided valuable insights into optimizing two critical components of DSSCs: the dye responsible for light absorption and the redox mediator essential for facilitating electron transfer. By focusing on cobalt polypyridine redox mediators, the study aimed to enhance the efficiency of charge transfer within DSSCs, thereby improving overall performance. Feldt et al.'s work emphasized the importance of a synergistic approach to both dye and electrolyte design, offering a pathway for achieving high-efficiency DSSCs. These findings have implications for the ongoing refinement of solar cell technologies, contributing to the quest for more effective and sustainable energy conversion methods [75].

4.4.5 Ionic Liquid-Based Electrolytes:

In 2003, Wang and collaborators made a noteworthy contribution to the advancement of Dye-Sensitized Solar Cells (DSSCs) by introducing ionic liquid-based electrolytes. Their research focused on developing stable quasi-solid-state DSSCs, addressing challenges associated with the volatility and leakage of traditional liquid electrolytes. By incorporating ionic liquids, which are salts in a liquid state at relatively low temperatures, Wang et al. aimed to enhance the stability and durability of the solar cells. The introduction of ionic liquid-based electrolytes not only mitigated concerns related to electrolyte leakage but also provided a more reliable and robust alternative, contributing to the development of DSSCs with improved performance and longevity. Wang's work played a crucial role in expanding the possibilities for stable quasi-solid-state DSSCs, offering a solution to enhance the practical viability of this solar cell technology [76].

4.4.6 Organic Solvent-Free and Aqueous Electrolytes:

In 2004, Wang and colleagues achieved a significant advancement in Dye-Sensitized Solar Cells (DSSCs) by introducing a stable quasi-solid-state system that eliminated the use of organic solvents. Their research utilized an amphiphilic ruthenium sensitizer and a polymer gel electrolyte, marking a departure from traditional organic solvents. This innovation not only improved device stability but also addressed environmental and safety concerns associated with solvent use. The quasi-solid-state DSSC developed by Wang et al. represented a more sustainable and practical approach, showcasing the potential for organic solvent-free and aqueous electrolytes in enhancing the overall performance and reliability of DSSCs. This work contributed to the ongoing efforts to make solar cell technologies more environmentally friendly and accessible [77].

These above information mark key milestones in the evolution of electrolytes for DSSCs, from the starting use of I-/I3- redox couples to the expansion of alternative redox mediators, ionic liquids, and stable quasi-solid-state electrolytes. In progress research continues to explore new electrolyte formulations to improve DSSC efficiency and stability.

4.5 Historical Perspective of Photocathode:

Dye-Sensitized Solar Cells (DSSCs) generally comprise two essential components: a photoanode and a photocathode. Traditionally, a significant portion of research efforts has been directed towards improving the performance of the photoanode. However, it is crucial to emphasize that advancements in the photocathode also play a pivotal role in determining the overall efficiency and functionality of DSSCs. Both the photoanode and photocathode contribute to the process of harnessing solar energy, and innovations in either component can have a profound impact on the cell's performance. Recognizing the significance of enhancing both electrodes is essential for achieving comprehensive progress in the development and optimization of Dye-Sensitized Solar Cells.

4.5.1 Pt Counter Electrode as Photocathode:

In 1991, O'Regan and Grätzel laid the foundational work for Dye-Sensitized Solar Cells (DSSCs) by featuring a Pt (platinum) counter electrode as the photocathode in their primary DSSC fabrication. This early research marked a crucial step in the inception of DSSCs, showcasing the viability of platinum as a material for the photocathode. The choice of Pt as the counter electrode was pivotal for its catalytic role in facilitating the reduction of the redox couple in the electrolyte, a fundamental process for converting sunlight into electricity. O'Regan and Gratzel's pioneering work not only established the Pt counter electrode as an integral component in DSSC fabrication but also set the stage for subsequent advancements and innovations in the development of efficient and sustainable solar cell technologies [16].

4.5.2 Platinum-Free Catalysts:

In 2005, Wang and collaborators conducted a significant survey that explored the use of platinum-free catalysts for the counter electrode in Dye-Sensitized Solar Cells (DSSCs). This research marked a notable shift in the approach to DSSC fabrication by investigating alternatives to platinum, a material often associated with high cost and limited sustainability. By examining various catalysts that didn't rely on platinum, Wang et al. aimed to demonstrate the feasibility of replacing Pt with more cost-effective and environmentally friendly materials. This work not only highlighted the importance of seeking alternatives to platinum but also contributed to the ongoing efforts in making DSSCs more economically viable and sustainable, paving the way for advancements in the field of solar cell technology [18].

4.5.3 Carbon-Based Photocathodes:

In 2009, Kuang and collaborators made a significant discovery by identifying highly ordered TiO2 nanotube arrays as a promising photocathode material for Dye-Sensitized Solar Cells (DSSCs). This finding offered valuable insights into the potential benefits of nanostructured carbon materials in improving the flexibility, efficiency, and overall performance of DSSCs. The use of highly ordered TiO2 nanotube arrays as a photocathode introduced a structured and organized approach, enhancing the light-absorbing capabilities of the solar cell. Kuang et al.'s research contributed to the exploration of innovative materials, shedding light on how nanostructured carbon materials could be harnessed to advance the design and functionality of DSSCs, ultimately influencing the ongoing development of more efficient and flexible solar energy conversion technologies [78].

4.5.4 Cu$_2$O Photocathodes:

In 2010, Zhang and Wang made a noteworthy exploration into the application of copper oxide (Cu2O) as a photocathode material, presenting a viable alternative to the conventional platinum-based counter electrodes in Dye-Sensitized Solar Cells (DSSCs). This research marked a departure from the reliance on platinum, which is often expensive and less sustainable. The study demonstrated the potential of Cu2O as an effective material for the photocathode, showcasing its ability to serve as a catalyst for the reduction reactions in the electrolyte. By offering a feasible alternative to Pt-based counter electrodes, Zhang and Wang's work contributed to the diversification of materials used in DSSC fabrication, potentially enhancing cost-effectiveness and sustainability in solar cell technology. This research played a crucial role in expanding the possibilities for more accessible and environmentally friendly components in DSSC design [79].

4.5.5 Nickel Oxide (NiO) Photocathodes:

In 2010, Nattestad and colleagues showcased the effectiveness of nickel oxide (NiO) photocathodes, emphasizing the exploration of alternative materials for enhanced performance, particularly in the context of tandem Dye-Sensitized Solar Cells (DSSCs). This research marked a significant step in the search for materials beyond conventional choices, offering insights into the capabilities of NiO as a photocathode. By demonstrating the effectiveness of NiO, the study suggested the potential for improved efficiency and functionality in tandem DSSCs. This work contributed to the broader exploration of diverse materials, providing valuable knowledge for the development of advanced solar cell technologies that prioritize performance and versatility. Nattestad et al.'s findings played a crucial role in expanding the options for materials used in tandem DSSCs, fostering innovation in the pursuit of more efficient and adaptable solar energy conversion systems [80].

4.5.6 Inorganic Compounds:

The year 2009 marked a significant surge in research focusing on photocathode catalysts for Dye-Sensitized Solar Cells (DSSCs). Notably, Grätzel and collaborators made a groundbreaking contribution by introducing an inorganic compound, cobalt sulphide (CoS), as a novel catalyst for the counter electrode in DSSCs. This innovation represented a departure from conventional catalyst materials and opened up new possibilities for enhancing the efficiency and performance of DSSCs. By incorporating CoS as a counter electrode catalyst, the study explored the unique properties of inorganic compounds, potentially offering improved catalytic activity and stability. Grätzel et al.'s work in 2009 played a crucial role in diversifying the range of materials considered for photocathode catalysts, laying the groundwork for further advancements in solar cell technology [54].

5. Recent Advances in DSSC:

In recent years, dye-sensitized solar cells have experienced substantial advancements, resulting in improved performance and efficiency in converting solar energy through photoelectrochemical processes. One notable breakthrough involves the creation of highly efficient organic dye-sensitized solar cells utilizing copper electrolyte. These cells have achieved remarkable conversion efficiencies, reaching up to 34%, particularly through the implementation of co-sensitization strategies. These developments showcase the progress in harnessing solar energy through innovative technologies, offering promising prospects for more effective and sustainable solar cell solutions [81].

In a recent study conducted by Cao and colleagues, there was a significant modification in the design of Dye-Sensitized Solar Cells (DSSCs), specifically incorporating a copper-based electrolyte. This alteration resulted in an impressive energy conversion yield of approximately 32% under moderate light conditions equivalent to 1000 lux. The findings highlight a remarkable improvement in the efficiency of DSSCs, showcasing the potential of the copper-based electrolyte to enhance energy transition in response to moderate light exposure. This research contributes to the ongoing advancements in solar cell technology, demonstrating the feasibility of innovative designs for more effective energy conversion in varying light conditions [82].

In 2017, a research study explored the use of natural extracts, including black currant, plum, Indian jamun, and berries, for sensitizing Dye-Sensitized Solar Cells (DSSCs). The investigation revealed that anthocyanin extracts from mixed berry juice and black currant resulted in the highest power conversion efficiencies (PCEs) of 0.53% and 0.55%, respectively. Boyo et al. also examined a flavonoid dye derived from the Jatropha curcas Linn plant in the context of DSSCs. The obtained results showed an efficiency (η) of 0.12%, with a current density (JSC) of 0.69 mA/cm2, a voltage (VOC) of 0.054 V, and a fill factor (FF) of 0.87. These findings underscore the potential of natural extracts as sensitizers for DSSCs, offering insights into diverse sources for efficient solar cell technology [83].

In recent years, scientists have been actively exploring methods to enhance charge transport in Dye-Sensitized Solar Cells (DSSCs) by focusing on the design of electron transport layers (ETLs). Their efforts involve experimenting with innovative materials and deposition techniques to elevate the overall performance of these solar cells. A study conducted by Liu P. W.-S. in 2017 delved into these advancements, shedding light on the ongoing initiatives to improve the efficiency of DSSCs through thoughtful modifications in the composition and structure of electron transport layers. This research reflects the collective pursuit of developing more effective and sustainable technologies for harnessing solar energy [84].

In recent studies, researchers have achieved notable strides in the development of perovskite-based dye-sensitized solar cells, achieving impressive conversion efficiencies exceeding 25%. This breakthrough in utilizing perovskite materials has opened up new avenues for cost-effective and highly efficient solar cell technology. The work conducted by Devender Singh in 2018 highlights the promising advancements in incorporating perovskite compounds into the design of dye-sensitized solar cells, showcasing their potential to revolutionize the field and pave the way for more accessible and efficient solar energy solutions [85].

In their recent work, Naik and colleagues have introduced a novel dye for Dye-Sensitized Solar Cells (DSSCs) by combining simple aniline-based dyes (A1-4) with an N3 dye for co-sensitization. These co-sensitizers incorporate an N, N-dimethylaniline ring as the donor scaffold, coupled with electron-withdrawing functionalities like barbituric acid (A1), N, N-dimethyl barbituric acid (A2), thiobarbituric acid (A3), and N,N-diethyl thiobarbituric acid (A4) as acceptor/anchoring units. The resulting solar cell employing this dye demonstrated a noteworthy power conversion efficiency (PCE) of 7.02%. Naik et al.'s research underscores the successful synergy of different dye components in enhancing the efficiency of DSSCs, offering a promising avenue for advancing solar cell technology [86].

Beyond the strides in materials, notable breakthroughs have occurred in enhancing the stability and durability of dye-sensitized solar cells (DSSCs). Researchers have successfully tackled the persistent challenge of device degradation, making significant strides in prolonging the lifespan of these solar cells. Moreover, progress in fabrication processes has played a crucial role in making dye-sensitized solar cells commercially viable, opening the door for large-scale production and widespread adoption as a clean and sustainable energy solution. This work, highlighted by Jayatissa in 2018, reflects the collective efforts to overcome hurdles in DSSC technology, advancing its reliability and practicality for a broader application in the renewable energy landscape [87].

Tandem solar cells, a technology that combines various cell technologies to enhance efficiency, have gained attention in recent research. One particular avenue of investigation involves integrating Dye-Sensitized Solar Cells (DSSCs) with silicon-based solar cells. This approach is aimed at leveraging the complementary strengths of both technologies to achieve improved overall efficiency in solar energy conversion. The study by Chen B. R. in 2019 sheds light on these efforts, emphasizing the potential synergy between DSSCs and silicon-based cells for more effective and versatile solar power generation. Such endeavors represent a step forward in optimizing solar cell systems for enhanced performance and broader applicability in the renewable energy landscape [88]

Kalaiyar and collaborators have introduced a novel dual-anchored Ru (II) complex termed RNPDA, which they synthesized. This unique complex was developed using a Schiff base derived from 4-nitro-phenylenediamine (NPD-PC) as a ligand. Schiff-based metal complexes are gaining attention for their potential as sensitizing materials, attributed to their favourable photo physical properties. The RNPDA dye consists of two key components: electron-withdrawing pyridines and an anchoring unit featuring a nitro group. When employed as a photosensitizer for Dye-Sensitized Solar Cells (DSSCs), the RNPDA complex demonstrated a noteworthy overall power conversion efficiency (PCE) of 3.42%. The study by Subramaniam K. in 2019 highlights the promising potential of this newly developed complex in enhancing the efficiency of DSSCs, contributing to the ongoing exploration of innovative materials for solar energy conversion [89].

6. Challenges in Dye- Sensitized Solar cells:

Numerous studies have focused on enhancing the efficiency and stability of Dye-Sensitized Solar Cells (DSSCs). However, their efficiency falls behind that of synthetic DSSCs for several reasons. While the efficiency of DSSCs is currently lower than that of silicon crystalline solar cells, it can be improved by choosing suitable materials such as substrate, dye, and electrolyte. The application of graphene in DSSCs has notably contributed to advancing cell efficiency.

The initial step in DSSCs involves the excitation of dye molecules by sunlight. However, the dyes commonly used are often inadequate for absorbing the entire solar spectrum, resulting in a deficiency in the generation of photoexcited electrons. The most effective sensitizers identified so far are Ru-based synthetic organometallic dyes, known for their efficiency. However, they come with a high cost and toxicity. On the other hand, abundant natural dyes extracted from plants and vegetables have not proven promising in achieving reasonable PCEs [76].

These challenges emphasize the need for further research and innovation to overcome limitations and enhance the practicality of DSSCs, making them more competitive in the field of solar energy conversion.

After the dye molecules are excited by sunlight in Dye-Sensitized Solar Cells (DSSCs), the photoexcited electrons move to the conduction band (CB) of the metal oxide, which forms the photoanode in DSSCs. Popular choices for DSSC fabrication include TiO2- and ZnO-based photoanode materials. However, challenges such as limited electron mobility, high recombination in TiO2, and low chemical stability in ZnO contribute to the degradation of DSSC performance [90].

The electrons from the photoanode then travel to the counter electrode through the transparent conducting oxides (TCO) substrate and the external circuit. Counter electrodes made of Pt and carbon, although popular, face challenges related to optical transparency, increased corrosion from the electrolyte, and contact resistance to the TCO substrate. These issues can lead to a decrease in the Fill Factor (FF) [91].

The physical state of the electrolyte plays a crucial role in DSSC performance, where the renewable cycle is completed through the redox process utilizing electrons. Challenges associated with liquid-phase electrolyte leakage often contribute to the degradation of DSSCs.

Stability issues arise from the degradation of the dye in the presence of sunlight radiation. This challenge can be addressed by selecting sensitizers that demonstrate stability at varying temperatures. Synthetic dyes, like ruthenium complexes, exhibit greater stability than natural dyes, making them a preferable choice. Additionally, using mixed dyes may contribute to increasing cell efficiency.

The use of liquid electrolyte in Dye-Sensitized Solar Cells (DSSCs) introduces temperature instability, freezing at low temperatures and expanding at elevated temperatures, posing potential harm to the cells. Consequently, there is ongoing investigation into solid electrolyte-based DSSCs, although this approach tends to result in lower cell efficiency.

Similar to traditional silicon solar cells, DSSCs face challenges of poor absorption in the red part of the solar spectrum, limiting electric current generation. However, these challenges can be mitigated through advancements in sensitizers. Natural dyes, while less efficient in absorption compared to synthetic dyes, have hindered the mass production and widespread application of DSSC technology. The developmental cycle for DSSCs is still in its early stages, demanding further advancements to enhance efficiency.

Despite these challenges, DSSCs have pioneered the development of new sensitizer-based solar cells. Scientists are hopeful that suitable photovoltaic devices will eventually overcome the limitations of DSSCs. A positive trend in research is now focusing on the development of new perovskite-based solar cells, demonstrating promising outcomes as alternative photovoltaic devices to traditional silicon-based p-n junction solar cells. It is noteworthy to emphasize that the discovery of Perovskite Solar Cells (PSCs) has been influenced by the operating principles of dye-sensitized solar cells, marking them as upgraded versions of DSSCs.

7. Environmental and Economic Impacts [59]:

7.2 Positive Environmental Aspects:

7.2.1 Low Energy Input in Manufacturing:

Dye-Sensitized Solar Cells (DSSCs) offer a notable advantage in terms of low energy input during the manufacturing process when compared to traditional silicon-based solar cells. This efficiency stems from the utilization of less energy-intensive materials, such as titanium dioxide and organic dyes. The incorporation of these materials not only enhances the overall environmental sustainability but also contributes to a reduction in the carbon footprint associated with solar cell manufacturing [16].

7.2.2 Resource Efficiency:

DSSCs demonstrate the potential for greater resource efficiency compared to their silicon-based counterparts. The materials employed in DSSCs are characterized by their abundance and widespread availability, alleviating the reliance on rare and expensive resources. This inherent resource efficiency in DSSC technology holds the promise of fostering a more sustainable and accessible production process for solar cells[16].

7.2.3 Flexible Design and Aesthetics:

One of the distinctive features of DSSCs lies in their flexible design capabilities and aesthetic adaptability. These solar cells can be crafted in various shapes and sizes, and their flexibility allows seamless integration into diverse surfaces. This design versatility opens the door to creative and aesthetically pleasing solar solutions. The ability to customize DSSCs for different applications not only enhances the visual appeal of solar technology but also promotes its acceptance and integration into a myriad of environments. This characteristic positions DSSCs as innovative and adaptable contributors to the landscape of sustainable energy solutions [92].

7.3 Negative Environmental Aspects:

7.3.1 Toxic Materials:

A notable drawback of Dye-Sensitized Solar Cells (DSSCs) lies in the potential presence of toxic materials, specifically in the liquid electrolytes commonly used. These electrolytes often contain organic solvents that can pose environmental hazards. The risk of leakage, particularly during the disposal phase, raises concerns about the potential for soil and water contamination. Addressing the issue of toxic materials is crucial to ensure the environmentally responsible deployment and disposal of DSSCs [93].

7.3.2 Durability and Longevity:

DSSCs face challenges regarding their durability and longevity in comparison to traditional solar cells. Factors such as the degradation of organic dyes and the vulnerability of certain components to environmental elements, including moisture, can impact the overall lifespan of DSSCs. The potential for shorter lifespans may necessitate more frequent replacements, resulting in increased waste generation and posing challenges for sustainable life cycle management [94].

7.3.3 Limited Efficiency:

Despite their advantages in lower manufacturing costs, DSSCs currently exhibit lower conversion efficiencies compared to some alternative solar cell technologies, notably silicon-based solar cells. This limitation means that a larger number of DSSCs may be required to generate the same amount of electricity, potentially offsetting some of the environmental benefits associated with their lower manufacturing energy requirements [94].

7.3.4 Energy-Intensive Recycling:

The recycling process for DSSCs can be both energy-intensive and complex due to the diverse range of materials used in their construction. While efficient recycling methods are essential to mitigate the environmental impact of spent DSSCs, developing such processes poses significant challenges. Striking a balance between the benefits of recycling and the energy intensity of the process is crucial for minimizing the overall environmental footprint of DSSC technology [94].

Dye-Sensitized Solar Cells (DSSCs) present a nuanced environmental profile with both potential advantages and challenges. On the positive side, DSSCs offer notable benefits such as lower energy input during manufacturing and enhanced resource efficiency compared to traditional solar cells. These characteristics contribute to a reduced overall carbon footprint and a more sustainable production process. However, it is crucial to acknowledge and address concerns associated with toxic materials, durability, and recycling in DSSCs. The presence of potentially harmful organic solvents in liquid electrolytes raises environmental risks, especially during the disposal phase, posing threats of soil and water contamination. Additionally, the durability of DSSCs and their susceptibility to environmental factors may lead to shorter lifespans, necessitating more frequent replacements and potentially resulting in increased waste generation. The recycling process for DSSCs is another area of concern, marked by its energy intensity and complexity due to the diverse range of materials used in these solar cells. Efficient recycling methods are essential for minimizing the environmental impact of spent DSSCs, but the development of such processes presents notable challenges. As technology advances and research efforts continue, there is optimism that these challenges can be effectively addressed. Ongoing innovations and improvements in DSSC technology may lead to enhanced environmental sustainability. By mitigating concerns related to toxic materials, improving durability, and developing more efficient recycling methods, the environmental profile of DSSCs can be further optimized, making them a more eco-friendly choice in the landscape of solar energy technologies.

7.4 The Economic Impact of DSSCs:

7.4.1 Lower Manufacturing Costs:

Dye-Sensitized Solar Cells (DSSCs) hold a potential economic advantage through their ability to be manufactured at a lower cost when compared to traditional silicon-based solar cells. The incorporation of these economical components has the potential to significantly reduce overall production costs, making DSSCs an attractive option for solar energy applications from the utilization of less expensive materials, such as titanium dioxide and organic dyes [16].

7.4.2 Job Creation:

The growth and expansion of the DSSC industry have the potential to spur job creation across various sectors. This includes manufacturing, research and development, and installation, offering employment opportunities in different regions. As the demand for DSSCs rises, a corresponding increase in workforce needs could contribute to job creation and economic development.

7.4.3 Market Competitiveness:

The lower manufacturing costs associated with DSSCs can enhance their competitiveness in the solar energy market, particularly in applications where cost plays a crucial role. This increased cost-effectiveness could lead to a higher adoption rate and an expanded market share for DSSCs. The competitiveness of DSSCs may drive innovation and affordability, making them a compelling choice in the broader solar energy landscape.

7.4.4 Diversification of the Solar Industry:

DSSCs present a unique technological approach to harnessing solar energy, setting them apart from traditional solar cells. The development and commercialization of DSSCs have the potential to contribute to the diversification of the solar industry. This diversification fosters innovation and healthy competition, propelling advancements in solar energy technologies and expanding the range of available options.

7.4.5 Impact on Energy Prices:

While not a direct consequence of DSSCs alone, the widespread adoption of various solar technologies, including DSSCs, could play a role in reducing dependence on conventional energy sources. This shift has the potential for long-term effects on energy prices and the dynamics of energy markets. The integration of solar technologies contributes to a more sustainable energy mix, influencing market forces and potentially leading to more stable and competitive energy prices over time.

8. Future Prospect:

Dye-sensitized solar cells (DSSCs) are considered to be the power source of the future due to their cost-effectiveness and improving converter performance standards. DSSCs are easy to fabricate and manipulate and perform well in scattered light and at increased temperatures compared to conventional solar cell techniques. With a single major interface DSSC, transformation rates of above 13% have been achieved. However, to reach maximum commercialization, production standards must approach 15%. Besides productivity, other issues involve improving system reliability and lowering component and production expenditures. Dyes, as the photosensitive element, have a significant impact on DSSC optical absorption and illumination transformation. Despite the fact that much effort has gone into generating multispectral dye photosensitizer over the last two decades, additional advances in the affordability and functionality of artificial ruthenium-based dyes are becoming highly improbable [16].

Hybrid halogen perovskite, combining inorganic and organic components, exhibits superior absorbance efficiency compared to standard dyes, making it a promising photo catalyst for

Dye-Sensitized Solar Cells (DSSCs). The use of perovskite ($CH_3NH_3PbI_3$) nanostructures as sensitizers in DSSCs was first explored in 2009, but the initial attempt showed low performance (4%) due to the rapid dissolution of perovskite in a liquid electrolyte. Subsequent research revealed that perovskite can function as both hole and electron conductors, with the crystalline perovskite layer maintaining charge creation and transportation. Etgar et al. (Etgar, 2012) developed a $CH_3NH_3PbI_3/TiO_2$ heterostructure system, where $CH_3NH_3PbI_3$ serves as both a photon generator and a hole transportation substance. Over the past six years, solid-state perovskite photovoltaic cells have witnessed a remarkable increase in efficiency from 3% to 22%, according to the United States National Rechargeable Energy Laboratories (NREL), marking a ground-breaking phase in solar cell development [95].

Besides boosting efficiency, other major topics that require to be handled in forthcoming studies are how to increase cellular durability over a lengthy operational period. The loss of electrolyte solution and deteriorated Pt catalyst are the major causes of destabilization in DSSCs. To avoid spillage, solid-state hole transportation materials (HTM) should be used instead of electrolyte solution. Graphene compounds, which have better electrochemical endurance with extended prospective switching, can also be used to substitute Pt catalyst. Milic JV and his colleagues calculated a lifecycle of 20 years for DSSC components by tackling these difficulties [96].

Perovskite photovoltaic cells face a limitation in their activity, lasting only about 100 hours without functionalization. The quick disintegration of perovskite substances, particularly when exposed to environmental humidity and sunlight, contributes to the breakdown of perovskite crystalline structure. This issue poses a challenge for the long-term stability and durability of perovskite-based solar cells [97].

Despite more than 15 years of intense research, the physical chemistry behind several basic operations in the DSSC device is not yet fully understood. While there is a detailed understanding of energetics and kinetics for specific model and reference systems under controlled conditions, it remains difficult to predict how even minor changes to the system, such as replacing one component or changing the electrolyte composition, will impact DSSC performance. The chemical complexity of DSSCs has become clear over time, and the primary challenge for future research is to master this complexity, particularly at the oxide/dye/electrolyte interface. Therefore, it will be important for future research to carefully select several reference systems that emphasize different key aspects of the device and to thoroughly characterize these systems using all available techniques. By comparing and modelling these reference systems, we may improve our fundamental understanding of the DSSC device [98].

9. Conclusion:

In response to the environmental challenges posed by fossil fuel emissions and the finite nature of traditional energy resources, there is a global shift towards integrating renewable energy sources into the energy landscape. Renewable energy, offering innovative alternatives for electricity generation, holds immense potential to meet global energy demands sustainably. Among these, solar energy technology stands out as a promising solution to address future energy needs. The electrochemical photovoltaic system, utilizing dye-sensitized nanocrystalline technology, has proven to be a reliable contender compared to traditional solid-state junction devices. This system effectively converts solar energy into electricity, demonstrating its viability in the renewable energy sector. While Dye-Sensitized Solar Cells

(DSSCs) present a cost-effective option, their practical efficiency falls short, prompting extensive research across various aspects of DSSCs. The exploration of diverse electrodes, electrolytes, and dyes is proposed to enhance their performance.

The review provides a valuable compilation of findings for scientists aiming to advance the field. Notably, organic dye sensitizers emerge as a cost-effective and environmentally friendly choice, with ruthenium dyes currently recognized as the most efficient. Addressing the limited lifespan of DSSCs is crucial for their widespread adoption, necessitating ongoing research to improve both efficiency and longevity.

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