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DSSC Sensitizers: A Panoramic Comparison

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Abstract: Currently, energy and greenhouse gas emissions are the biggest problems. As a result of overpopulation and high energy consumption, non-renewable energy sources are continuously depleting. Greenhouse gases are also being emitted at a very high rate. The modern world must use renewable energy sources, among which solar energy is safe and available everywhere. Solar energy is efficiently transformed into electrical energy by photovoltaics (solar cells). During the past decades, DSSC the type of thin-film photovoltaics, gained importance due to cost-effectiveness, durability, ease of fabrication, and low toxicity. These cells convert sunlight into electricity with a power conversion efficiency of approximately 20%. Glass substrate, photo-anode, sensitizer, electrolyte and counter electrode are the key components of DSSCs. Among these, sensitizers are the most important part of these cells that absorb photons, generate electrons, create electron-hole-pair and produce electricity. In the beginning, only ruthenium metal complexes were used as dyes, but now a large number of organic, inorganic and natural compounds are widely used to enhance the overall performance of these cells. This is an in-depth review on solar cells but mainly focuses on the construction, operating principle, and performance of DSSCs. In this review, we not only presented a library of sensitizers used in DSSCs but also gives a brief comparison between these sensitizers to help future research.

Keywords: Renewable energy, Solar energy, Photovoltaic, DSSC, Sensitizer.

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1. INTRODUCTION

Energy plays a vital role in the country's economic development, but with an increase in population, modernization and decreasing energy resources, its demand is constantly rising (1,2) Today, countries development is negatively affected by energy shortage (3). Nearly 80% of the world's energy demand is met by fossil fuels such as oil, gas, and coal (4). Using these resources to produce energy generates massive CO_2 emissions, which mainly contribute to global warming and climatic disturbances (1).

Energy resources are classified into two classes: renewable and non-renewable (5). Among them, non-renewable sources of energy, like fossil fuels (coal, gas, natural gas, and petroleum) are economically more important and depleting rapidly but import a negative role on the environment, producing a large amount of harmful gases (6), such as carbon dioxide (CO_2), methane or natural gas (CH_4), chlorofluorocarbons or CFCs (CCl_2F_2), nitrous oxide or laughing gas (N_2O), ozone (O_3) and peroxyacetyl nitrate (PAN) responsible for trapping heat radiated from earth's surface (7), ultimately raising the temperature of earth and causing photochemical smog (8). Around 60% of the world's population lives in Asia and faces environmental challenges due to the excessive use of fossil fuels. In China, Taiwan, Pakistan, India, Hong Kong, Macao, Nepal, Bangladesh, Indonesia, Malaysia and in other developing countries, carbon dioxide and other pollutants are causing serious ecological changes (9). In contrast, renewable energy sources include wind, solar, geothermal, and hydropower (10). Today, renewable energy is essential, clean, sustainable, fascinating and stabilizes modern energy demand (11).

2. SOLAR ENERGY

Earth receives solar radiations as light and energy. Due to its abundance and ease of availability, solar energy can meet the global energy demand. As energy demand grows in developing countries, they are seeking reliable sources of energy (12). A large portion of Europe's solar resources are located in Spain. In 2016, Spain led the PV market with 2.6 GW of grid-connected installations. In response, the global PV market has grown by around 5600 MW (13). After Spain, Germany ranked second in the world for PV installations. Approximately a third of all PV power installed globally is in Germany (14). In terms of energy production, China ranks second behind the United States. The solar energy potential of China is enormous (15). In 2010, energy production was 0.15GW. By 2020, it is projected to increase to 4-8 GW and in 2030, it is expected to reach 16.9TG (16,17). Solar radiation is most prevalent in Asian countries as compared to others because of long sunshine duration (12).

2.1. Solar Cell

Solar cells or photovoltaics convert sunlight directly into electricity by using the photovoltaic effect (12). The photovoltaic effect was discovered in 1839 by Alexandre Edmond Becquerel. The first silicon photovoltaic cells were created by Russell Ohl in 1946. Increasing the efficiency of solar cells is a major goal in solar cell development (18). Photovoltaic technology is currently based on the creation of electron holes in multiple layers (p-type and n-type materials) of semiconductor materials. The p-type and n-type junctions are arranged so that when light of sufficient energy strikes them, an electron is ejected and moves from one layer to the next. Electrons and holes are created in the process, which generates electricity (19). Solar cells convert solar energy into electricity as a function of the proportion of incoming solar output to the maximum electrical power produced by the cell under concentrated loads. Because it is so effective and thought to be so relevant, this predictable metric is now widely used for judging the worth of products (20).

2.1.1. Types of solar cells

Based on manufacturing material, cost, efficiency, size and life cycle, solar cell technologies can be roughly categorized as:

a) 1st generation solar cells: Silicon wafer based solar cells are “first-generation solar cells” made from single silicon crystals (monocrystalline) or many silicon crystals (poly-crystalline) (21,22) with efficiencies of 26.7% and 22.3%, respectively (23). Due to their rigidity, these cannot bend easily but covers 86% of the market with a maximum efficiency of 40%.

b) 2nd Generation Solar Cells: Thin-film solar cells are “second generation solar cells”, made of copper indium gallium selenide (CIGS) (24), cadmium telluride (CdTe), CZTs (25,26), Gallium Arsinide (GaAs) and amorphous silicon (a-Si) (27) having efficiencies of 23.4% (23,28), 21.0% (23), 37.4% (29) and 10.2-13.4% (23). Due to their flexibility, durability, stability, low cost, high optical absorbance, light weight, and portability, these are widely used in wearable electronic devices, agricultural infrastructure, space applications, and transportation but are extremely toxic because of the poisonous metals (30).

c) 3rd Generation Solar Cells: Unlike previous generations, third-generation solar cells are designed to improve efficiency, cost-effectiveness, and versatility while overcoming some limitations associated with previous generations. Third-generation solar cells encompass a number of different approaches, each with its own set of characteristics and potential applications. These includes, Nano crystal based SC (31), Polymer SC, Thermo-photovaltic (32), Dye sensitized SC (33), Graphene based SC (34), Quantum dots SC (35) and concentrated SC (22,36) with efficiencies of 5.14% (37), 18% (38), 40% (39), 11.1% (23) -15.4 (40), 14.1% (41), 12% (42), and 25% (43). These solar cells exhibit different efficiency with inexpensive material (44), and because of modernization and the increased demand for energy, researchers are always working to increase it.

3. DYE SENSITIZED SOLAR CELL

A DSSC is also known as Gratzel's cell, a thin-film solar cell that converts sunlight into electricity using a dye that can either be organic or inorganic (45). In 1991, Michael Grätzel and Brian O'Regan invented them. Due to their structure and materials, these are more suitable for certain applications than traditional silicon-based solar cells. Originally, DSSCs were a part of the second generation, but improvements in their design and materials contribute to their classification as third-generation solar cells (46). Due to their dramatic applications (47), like low cost (48), easy fabrication (49), flexibility (50), light weight, transparency (51), ease of manufacturing (52), efficiency (53), reuse of dyes and low toxicity, these are widely used nowadays (54).

Dye + Semiconductor + sunlight= Efficiency

3.1. Components of Dye Sensitized Solar Cell

Dye-Sensitized Solar Cells (DSSCs) comprise crucial elements, each playing a vital role in converting sunlight into electricity (55). The primary components include:

3.1.1. Glass-substrate

Glass substrate, the transparent and conducting surface on which the photo electrode is deposited (56). Mostly, FTO (Fluorine doped tin oxide) (57) and ITO (Indium tin oxide) (58) are used as conducting glass substrates. Conducting glass provides electrical conductivity necessary for shuttling electrons between anode and external circuit and allows sunlight to pass through photo-anode without significant absorption or reflection (59).

3.1.2. Photo-anode

Light absorption and electron generation in DSSC take on anode known as Photo-anode or photo-active electrode (60). Typically consists of nanocrystalline titanium dioxide (TiO_2) layered on a conductive glass substrate, with TiO_2 acting as the semiconductor. The nanocrystalline TiO_2 provides a large surface area for sensitizer, allowing sufficient light absorption (61,62). Except titanium oxide, other materials like ZnO (63), SnO (64), NiO (65), and CuO (66). The main function of photo-anode is to absorb light and facilitate electron injection into the semiconductor (51).

3.1.3. Sensitizer

The most important component of DSSC is dye, also known as sensitizer or photosensitizer, that is responsible for the absorption of light, permute electrons to the excited states, and generating electron hole (67). This dye is usually naturally extracted from plants (68), inorganic metal ions (69), organic compounds (70) that are absorbed on titanium surface.

3.1.4. Electrolyte

Electrolyte in DSSC is a redox couple that shuttles electron between anode and cathode; it accepts electrons from phto-anode, regenerates sensitizer and completes the circuit, allowing the cell to convert sunlight into electrical energy continuously (33,71). Different electrolytes are used to increase the efficiency of cells, like I^-/I_3^- redox couple (71), Cu^+/Cu^{+2} (72), Co^{2+}/Co^{3+} (73), cobalt-polypyridine (74), Br^-/Br_3^- (62), LiI and N,N-methylpyrrolidinium dicyanamide (75).

3.1.5. Counter electrode

Counter electrode is a cathode, which is made from conducting material that collects and transfers electrons from external circuit (76) and also catalyzes the redox reaction of electrolyte or redox couple (77). Different types of counter electrodes are now used to improve efficiency, like Pt (78), carbon (79), black carbon (80), graphene (81), transition metals (82), conducting polymers (83), carbides, nitrides and charcoginides (77).

3.2. Working of DSSC

The working of DSSC is continuous and cyclic, and the main steps include (84,85).

- **a.** Dye adsorption: Nano-crystalline titanium oxide coated on conducting glass, on which dye is adsorbed.
- **b.** Excitation of Sensitizer: Dye becomes electronically excited by absorbing photons from sunlight.
- **c.** Electron-hole-pair creation: Electrons are injected into the semiconductor material by sensitizer, and electron-hole pairs are created.
- **d.** Electron transportation: Electrons moved through the semiconductor material towards the external circuit and generated the electric current.
- **e.** Redox reaction of electrolyte: By accepting electrons, the electrolyte is reduced, and electrons return to sensitizer for regeneration to its original state. As, electrolyte is redox couple, it oxidized to its original state by releasing electrons.
- **f.** Generation of electric current: Through the external circuit, the released electrons are directed to the counter electrode, where they generate an electric current.

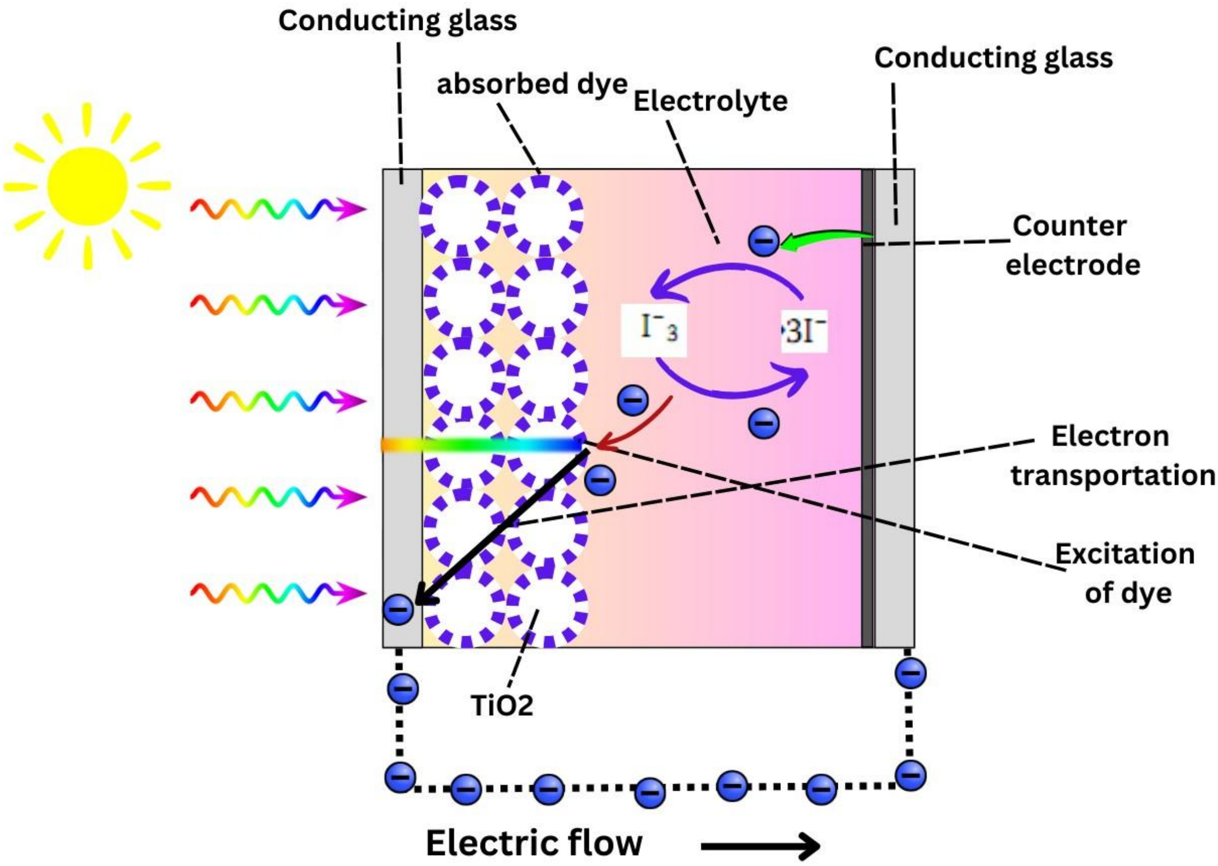

Figure 1: DSSC's working principle.

3.3. Efficiency of DSSC

Efficiency of DSSC was calculated by the given formula (68)

$$\eta = \frac{J_{ac} \times V_{oc} \times FF}{P_{in}} \times 100$$

J_{ac}= short circuit current; the largest current that may be drawn from solar cell (mA cm^{-2}); V_{oc}= open circuit voltage (mV), the maximum voltage available from solar cell; P_{in}= input power or power density of incident light, light power per unit area; FF= fill factor (It shows how effectively solar cells convert sunlight into electrical energy. The typical range is 0.5 to 0.85; represented in percentage, a high number denotes great efficiency (86) & can be calculated by the formula below (87).

$$FF = \frac{Pm}{(Jac \times Voc)}$$

Pm= maximum power output

3.4. Sensitizers/Dyes Used in DSSC's

Sensitizer is the most important part in DSSC, which absorbs photons and is responsible for injection of electrons (88). This sensitizer must have a) broad absorption spectra that cover the visible region and NIR b) anchoring groups that strongly bind with semiconductor layers like –COOH, –CN, $–NH_2$, $–PO_3H_2$, (89,90) c) cost-effectiveness (91,92), d) chemically compatible with all components like electrolyte and semiconductor material (93), e) stable (94), and f) non-toxic (95). A large number of sensitizers can be used in DSSC, and researchers are trying to synthesize dyes with maximum efficiency (96). Normally these dyes are categorized as:

Natural photosensitizers
Synthetic photosynthesizes

3.4.1. Natural sensitizers

Natural dyes offer a great potential for reducing the environmental impact of solar cell production and increasing sustainability due to their abundant affordability and eco-friendly nature. These dyes can be extracted from insects, plants, flowers, etc., and offer a wide range of colors like green, purple, blue, red, orange and many more. These natural dyes absorbing a broad range of light wavelengths makes them a viable option for improving the efficiency and performance of solar cells. many compounds like (97). In contrast to artificial dyes, natural dyes are readily available, less expensive, simple to make, non-toxic, eco-friendly, and completely biodegradable (95). Usually, they belong to the anthocyanin family, which can be found in red, blue, orange, purple, violet, and intermediate shades (95). As well as the purple-red color of autumn leaves, the red color of budding and young shoots is also due to anthocyanin (98). Anthocyanin is frequently used as sensitizer due to widespread availability, solubility in water, eco-friendliness and cost-effectiveness but mostly absorb visible light (95). Except for anthocyanin, chlorophyll, and carotenoids, extracted from plant leaves can also be used as dye sensitizers (68). However, chlorophyll alone is not favorable for DSSC and gives low efficiency due to the steric hindrance of its long chains (52). These natural photosensitizers showed different efficiencies summarized in Supplementary Table S1. Here, a total of 145 natural sensitizers with their efficiencies were summed up to show the importance of these natural sensitizers. These sensitizers are easy to extract but difficult to store, as they easily decompose with temperature change or light interaction.

3.4.2. Synthetic sensitizers

Today, a variety of synthetic sensitizers are used, including organic and inorganic compounds.

I. Organic sensitizers: Furthermore, organic dyes are now a practical alternative to inorganic dyes, which are perceived to be hazardous, costly, and difficult to synthesize (99). Researchers are investigating a wide range of organic compounds because of their benefits, which include low cost, ease of synthesis, environmental friendliness, stability, co-sensitization, a broad absorption spectrum, and redox mediators that enhance injection as well as electron transport (70). These compounds include carboxylic acids (100), indoles (101), hydrazones (102), pyridines (103), phorphyrins (104), Schiff bases (105), and aromatics that are currently used as sensitizers in DSSCs (70,106). The first usage of organic compounds as DSSC dyes occurred in the 2000s. Initially, DSSCs use eight organic dyes—methyl orange, crystal violet, fast green, aniline blue, alcian blue, methyl orange, and carbolfuchsian—as dye sensitizers. Eosin Y was expected to be the best among all of them, with the maximum efficiency of 0.399 (Voc = 0.671, Jsc = 1.02, and FF = 58.1) (107). Due to pi-conjugation, donor electrons and heteroatoms, these metal-free organic sensitizers exhibited high efficiency (52).

As a result of ongoing research, a wide variety of organic compounds are currently employed as DSSC sensitizers. To aid in comprehension, the material is summarized in Supplementary Table S2. During the past 15 years, organic sensitizers gained importance due to high yield, easy storage and reuse sensitizers.

II. Inorganic Sensitizers: In DSSCs, metal complexes, particularly transition metal complexes, show better photovoltaic performance and higher stability than organic and natural dyes due to their unique optical and electrical properties (108). Once photons are absorbed, they effectively transfer electrons into the semiconductor material, which is usually titanium dioxide, to initiate the production of an electric current. The long-term performance of DSSCs depends on the greater stability and lifespan provided by certain metal-based dyes. In DSSC, ruthenium-based complexes are most extensively used; for over 30 years, they exhibited high efficiency of up to 80% due to their versatility, high absorption, and ability to form stronger bonds with donor nitrogen of ligands (52) but are costly, toxic, and decompose with the passage of time (109).

Copper complexes not only act as sensitizers but also work as redox mediators (110). Except these, nickel (111), iron (112), zinc (113), osmium and many other transition metal complexes are also used as sensitizers. Some metal-based sensitizers are summarized in Supplementary Table S3.

It is expected that the DSSC innovation will be used to fulfill many prospective power requirements like economic growth, energy sustainability, and the conservation of the environment. Furthermore, DSSC is one of the most prominent renewable technologies that help reduce environmental problems. Globally, researchers are focusing on improving dye-sensitized solar cells' efficiency. To improve DSSC performance, a variety of strategies are being explored, and dye material is one of them. As DSSC's performance is directly affected by sensitizers as they are the most prevalent component. Sensitizers mentioned above are some of the reported metal-free, natural, and metal-based sensitizers. Scientists are constantly working to synthesize/modify the reported sensitizers to enhance their efficiency, flexibility, and environmental compatibility.

4. DETAILED COMPARISON (DISCUSSION) OF PHOTOSENSITIZERS USED IN DSSC

To gain a deeper insight into DSSCs, it is essential to explore the various types of photosensitizers, the heart of DSSC. These sensitizers are key to the efficiency, stability, and overall performance of DSSCs, as they facilitate light absorption and electron transfer to the semiconductor. In this section, we will present a comprehensive comparison of the main categories of photosensitizers—natural dyes, organic (metal-free) dyes, and metal-based dyes—based on literature. By exploring their mechanisms, efficiencies, absorption spectra, as well as their advantages and challenges, we aim to provide a detailed understanding of each type. This comparison will not only shed light on the potential of these photosensitizers but also highlight how ongoing innovations could shape the future of DSSCs, positioning them as a leading technology in the pursuit of sustainable energy solutions.

I. Natural photosensitizers

As these are plant-based dyes extracted from plants like chlorophyll, anthocyaninand, carotenoid, as well as natural materials like animal-based ones like blood, meat or coal.

Mechanism of Natural Sensitizers: Natural dyes, like anthocyanins and chlorophyll, are effective due to their broad absorption range, capturing sunlight by their chromophoric structures, which absorb visible light through conjugated systems. When these dyes absorb photons, their electrons get excited and move to the conduction band of a semiconductor. The dyes are anchored to the semiconductor, allowing electron transfer and oxidation. The dye is then regenerated by accepting electrons from a redox mediator in the electrolyte, restoring it for more light absorption. Meanwhile, the electrons travel through the semiconductor to an electrode, generating electric current, while the mediator recharges the dye.

Efficiency of Natural Photosensitizers: The efficiency of natural photosensitizers varies but has significant promise for efficient light absorption and energy conversion, particularly chlorophyll, a widely studied natural pigment that has PCE up to 2%. Similarly, anthocyanins, derived from fruits like blueberries, exhibit PCE of about 5%, carotenoids from pumpkin and carrots have an efficiency of 1%, while curcumins from turmeric have an efficiency of up to 2%. Besides these, sensitizers derived from animal sources like fish scales and hair have high efficiency, up to 8%, while coal is also a natural material that exhibits PCE of about 5%.

Stability of Natural Sensitizers: Natural dyes are less stable, as these are easily affected by sun exposure or environmental conditions, pH, humidity, and temperature as well. However, extra care, modifications or addition of stabilizers, preservatives can increase their life spam.

Absorption Spectrum of Natural Photosensitizers: Natural sensitizers generally have a broad absorption spectral range from UV to visible, like anthocyanin (400-800nm), chlorophyll (400-450nm & 650-700nm), betalains and carotenoids (400-550nm), curcumins (400-500) and flavonoids (250-500nm).

Advantages of Natural Photosensitizers: Natural dye sensitizers offer a range of compelling advantages that significantly enhance both their environmental and economic benefits.

a. *Renewability & Sustainability:* Derived from renewable materials, these dyes are more eco-friendly compared to synthetic alternatives. For example, anthocyanins from blueberries and red cabbage are not only abundant but also biodegradable, reducing environmental impact and supporting sustainability in solar technology.
b. *Simple Extraction & Cost-effective:* The extraction process for natural dyes is often simpler and more cost-effective, like betalains from beets exemplify this with their affordable extraction methods. *Broad Absorption Spectra:* Natural dyes have broad absorption spectra, such as chlorophyll from green plants, which efficiently captures light across both blue and red wavelengths.
c. Biocompatible & Non-toxic: Natural dyes, like carotenoids from carrots and pumpkins, are biocompatible and non-toxic.
d. *Diverse Color Change:* The diverse color properties of natural dyes, like curcumin from turmeric, which change color depending on pH (yellow in acidic and red in basic conditions), can be optimized for light absorption and efficiency.
e. *Low Carbon Footprints:* Natural dyes generally have a lower carbon footprint, as their extraction and processing consume less energy compared to the production of complex synthetic dyes.

***Disadvantages of Natural Photosensitizers**:* Despite their ecological benefits, natural dye sensitizers have several disadvantages.

a. *Lower Stability:* One of the primary challenges is their limited stability; natural dyes like anthocyanins from blueberries and betalains from beets are prone to degradation under continuous light exposure and oxidative conditions, which can diminish their performance over time. For example, chlorophyll, although efficient in light absorption, often suffers from degradation and reduced efficacy in DSSCs due to its sensitivity to environmental factors.
b. *Low Efficiency & Performance:* Additionally, natural dyes generally exhibit lower quantum efficiency compared to synthetic dyes such as ruthenium complexes, which can achieve efficiencies above 10%. This lower efficiency, coupled with issues related to dye solubility and charge transfer, can limit the overall performance of DSSCs utilizing natural dyes.
c. Change Transfer Issues: The production and processing of natural dyes can sometimes be inconsistent, not always facilitating electron transfer, leading to variability in their quality and effectiveness.

Future prospects of Natural Photosensitizers: As the world is facing an energy crisis, it is today's requirement to develop or use such material that is more environmentally friendly. Researchers are continuously trying to increase the life span, stability and efficiency of natural sensitizers through chemical modifications.

II. Organic (Metal-Free) Dyes

The unique nature (donor-π-acceptor) of organic sensitizers makes them more feasible and attractive as photosensitizers for DSSC with high efficiency and non-toxic nature.

Mechanism of Organic Photosensitizers: In organic compounds, conjugate systems facilitate light absorption. Generally, these compounds have donor groups (D-π-A system), like thiophene and carbazole, and acceptor groups, like cyanoacrylic acid. Sometimes, these have extended conjugated systems like vinyl groups, conjugated chains, rings, and anchoring groups that strongly bind with titanium oxide. After absorption, electrons are promoted from ground state to excited state. This excitation usually occurs as the electron moves from π (lower energy orbit) to π* (high energy orbit).

Efficiency of Organic Photosensitizers: The efficiency of organic sensitizers is much higher than the natural dyes. Their efficiency increased with an increase of conjugate systems (ring/chain), donor groups. Thiophene-based derivatives have high efficiency up to 9% while cyanoacrylic acid derivatives have PCE more than 12%.

Stability of Organic Sensitizers: Organic sensitizers are durable, stable and resistant in normal conditions. However, these sometimes show *photo-degradation* (loss of activity or color via light exposure), *thermal degradation* (damage due to heat), and *oxidative degradation* (damage due to oxidative environment). But modifications can enhance their lifespan and longevity.

Absorption Spectrum of Organic Sensitizers: Organic sensitizers show variable absorption spectral ranges like coumarins 450-470 nm, anthraquinones 400-500 nm, thiazines 300-400nm, conjugate polymers 450-550 nm, aniline derivatives 200-300 nm, and azo dyes 400-500 nm.

Advantages of Organic Photosensitizers: There are several advantages to using them as sensitizers.

a. *Flexibility:* The main advantage of organic sensitizers is their flexibility; can undergo structural modifications to enhance their performance, like D-π-A system.
b. *Cost-Effective:* Thiophene derivatives are normally low-cost as compared to metal complexes and easy to store natural ones.
c. *Low Toxicity:* Another main advantage is low toxicity; these do not contain any toxic metals and are therefore supposed to be environmentally safe.
d. *Easy Modifications:* As these contain different functional groups that are easily modified to increase efficiency, like cyano- or carboxylic derivatives.
e. *Broad Absorption Spectrum:* These also have broad absorption spectra and the ability to absorb light of a long range of wavelengths, like squaraine dyes. 600-850 nm.

***Disadvantages of Organic Sensitizers**:* With several advantages, organic sensitizers also have some disadvantages.

a. *Photostability:* The main disadvantage is their photostability like cyanine dyes that decompose when in contact with UV light.
b. *Electrolyte interaction:* Sometimes, these dyes react with electrolytes, especially when iodine-based electrolytes are used.
c. *Purification challenges & Efficiency:* Another notable disadvantage is their purification after synthesis; efficiency of organic dyes normally decreases in such cases with impurity.

Future prospects for Organic Sensitizers: Organic photosensitizers offer promising potential for energy development in the modern era. However, to fully realize their capabilities, improvements are needed through green synthesis methods, the incorporation of functional groups to broaden the absorption range, and the development of hybrid systems to enhance both efficiency and stability.

III. Metal-Based Dyes

Due to high efficiency and excellent stability, metal-based photosensitizers play a pivotal role. These dyes are normally complexes of ruthenium, platinum, palladium, iron, zinc or cobalt that exhibit broad absorption spectra.

***Mechanism of Metal-based Photosensitizers*:** Transition metals like ruthenium or osmium, which are essential for effective light absorption and electron transfer, are used for metal-based dye sensitizers in DSSC. In these dyes, the transition metal center serves as the primary photoactive site, responsible for absorbing light and exciting electrons. Meanwhile, the surrounding ligands play a dual role: they enhance light absorption by extending the dye's absorption spectrum and anchor the dye to the semiconductor surface, ensuring stable and efficient charge transfer.

Efficiency of Metal-based Sensitizers: The efficiency of metal-based dyes is highest among all the sensitizers used in DSSC, like zinc complexes (13%), ruthenium complexes (13%), iron complexes (7%), and cobalt (10%).

Stability of Metal-based Photosensitizers: Among all the photosensitizers, ruthenium metal-based photosensitizers are good photostable, chemically stable and have the highest lifespan, while iron exhibits lower. Sometimes, these metal-based sensitizers exhibit ligand loss, react with electrolyte or oxidize.

Absorption Spectrum of Metal-based Photosensitizers: Normally, ruthenium-based complexes exhibit a 400-700 nm spectral range, while iron and cobalt are 400-600 nm.

Advantages of Metal-based Sensitizers: Metal-based complexes exhibit impressive advantages.

a. *High Efficiency:* Ruthenium- and osmium-based photosensitizers exhibit high efficiency up to 13%.
b. *Broad Absorption Range:* Ruthenium complexes with their broad absorption range of 400-700 nm.
c. *Excellent stability:* Metal-based dyes show excellent photostability and chemical stability as compared to organic dyes.
d. *Low toxicity:* Certain metals like copper, cobalt and zinc complexes are less toxic and eco-friendly with high efficiency.
e. *Flexible nature:* Metal complexes have a flexible nature due to their bonding atoms, ligand modifications, metal combination and ligand variation.

Disadvantages of Metal-Based Photosensitizers*:* Despite their high efficiency, metal-based dyes have some disadvantages.

a. *Toxic nature:* Ruthenium-based sensitizers are toxic and raise environmental issues.
b. High Cost: Some metals like osmium, ruthenium, and palladium are expensive and need high costs for commercialization.
c. Decomposition: Some metal-based sensitizers decompose and undergo ligand-dissociate or ligand-exchange reactions in the presence of electrolytes, like cobalt complexes, that can easily react with electrolytes.

Future prospects for Metal-Based Photosensitizers: The future of metal-based sensitizers for dye-sensitized solar cells (DSSCs) looks very promising. Advancements are being made in developing new metal complexes that enhance efficiency by extending light absorption into the infrared spectrum. Efforts to reduce costs include using more abundant and affordable metals like iron and copper, along with optimizing production methods. Key improvements are also focused on enhancing the stability of these sensitizers, increasing their photostability, and ensuring compatibility with various electrolytes. With a growing emphasis on sustainability through eco-friendly and recyclable materials and the integration of DSSCs with technologies such as hybrid systems and flexible substrates, these advancements are set to make metal-based DSSCs more efficient, cost-effective, and commercially viable, leading to broader adoption in the renewable energy sector.

Based on the above data, a brief comparison between these sensitizers is presented below for better understanding.

Property	***Natural***	***Metal-free***	***Metal-based***
Source	Extracted from plant or any living material	Synthesized	Synthesized, often used transition metal complexes
Light absorption range	Limited	Broad	Broad
Toxicity	Non-toxic	Vary, low as compared to metal-based	High due to presence of heavy metals
Cost	Low	Low but vary	High/expensive
Bio-degradability	High	Vary	Low/none
Eco-friendly nature	High	Differ	Very low/none
Stability	Low, normally decompose on exposure to light	Moderate, sometimes decompose on exposure to light	High
Sensitivity	Low	High as compared to natural	High
Flexibility & modification	None	High due to tailored structure	High
Efficiency	~10	~11	~14
Example	Chlorophyll, anthocyanin etc.	Indole, imidazole, hydrazone, aromatics, pyridines etc.	Ruthenium, osmium, cobalt etc., metal complexes

5. CONCLUSION

Currently, the world is facing a serious energy crisis. Increasing consumption has led to the depletion of non-renewable energy resources. Solar energy is considered to be the most efficient renewable resource due to its abundant supply. One of the most promising energy sources for the future of our planet is solar energy, which plays a crucial role in meeting the global energy challenge. Compared to other forms of energy, solar energy is inexpensive and continuous. In recent years, solar and photovoltaic cells have become a hot topic. These cells convert sunlight directly into electricity via photovoltaic effect. Among all the solar cells, dye-sensitized solar cells are the thin-filmed, 3^{rd}-generation solar cells and are widely used due to easy fabrication, a large number of sensitizers, inexpensiveness, and broad EM spectra. Photosensitive dyes absorb sunlight, generating electron-hole pairs. A photosensitive dye can be extracted from living organisms or synthetics, e.g., metal-based or metal-free compounds. Researchers are exploring novel sensitizers to improve DSSC performance, but the efficiency of these devices is less than 20%. During the past few years, the energy crisis has become the most potent problem. The current review summarized all possible dye sensitizers (natural and synthetic) used/synthesized during the last 15 years with 310 references, 145 natural sensitizers, 275 organic-based (metal-free) and 115 metal-based photosensitizers, and hope that it will be a potential increment in future research.

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