SRI VENKATESWARA INTERNSHIP PROGRAM FOR RESEARCH IN ACADEMICS (SRI-VIPRA)

SRI-VIPRA

Project Report of 2023: SVP2330

"Dye Sensitized Solar Cells"

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SRIVIPRA PROJECT 2023

Title : DYE SENSITIZED SOLAR CELLS

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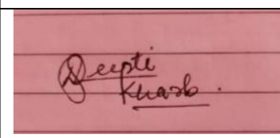
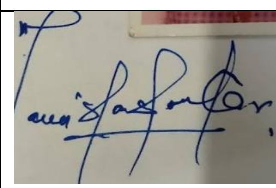
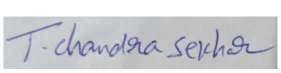
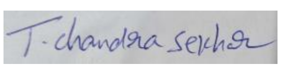
1		**Deepti Kharb**	**1121132**	**BSc.(P)Life Sciences**	
2		**Tanisha Sonkar**	**1121106**	**BSc.(P) Life Sciences**	



Signature of Mentor

Certificate of Originality

This is to certify that the aforementioned students from Sri Venkateswara College have participated in the summer project SVP-2330 titled "**DYE SENSITIZED SOLAR CELLS**".The participants have carried out the research project work under my guidance and supervision from 15 June, 2023 to 15th September 2023. The work carried out is original and carried out in an online/offline/hybrid mode.



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Acknowledgements

We would like to express our sincere gratitude to the Department of Chemistry of Sri Venkateswara college, for valuable contributions, guidance, and support in the preparation of this report. Their expertise and assistance have been instrumental in achieving the goals of this project. We are also thankful to **Chandra Shekhar Tekuri, Department of Chemistry, SVC** for their insightful feedback and input throughout the process. Their unwavering encouragement and assistance have been invaluable.

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Dye-Sensitized Solar Cells

Abstract

Dye-sensitized solar cells (DSSCs) have received great attention as efficient photovoltaic devices in the last decades. To achieve higher solar-to-electricity efficiency and improve long-term operating stability, the developing progress and the basic principles for DSSCs are necessary to be understood. In the last few years, India has witnessed tremendous research and development in solar energy, especially in the field of photovoltaics. This review not only covers the fundamentals of DSSC but also the related cutting-edge research and its development for industrial applications.

Introduction

Thin-film solar cells that produce electricity from sunlight include dye-sensitized solar cells (DSSCs), also called Grizel cells. They were developed at the École Polytechnique Fédérale de Lausanne (EPFL) in the 1990s by Michael Grätzel and Brian O'Regan, and they have attracted interest as a possible replacement for conventional silicon-based solar cells. Here are some salient characteristics and how DSSCs operate.

- **Working Principle**: The principle of photovoltaics governs how DSSCs operate, turning sunlight into electricity. Their mechanism, nevertheless, is distinct. A photosensitive dye, an electrolyte solution, and a semiconductor material (usually titanium dioxide, or TiO2) make up DSSCs.
- **Light absorption**: The photosensitive dye of DSSCs is responsible for the absorption of photons from sunlight, resulting in the formation of electron-hole pairs. This dye is responsible for the sensitivity of the cell to light and is commonly produced from organic and inorganic materials.
- **Electron transfer:** When the dye is exposed to light, it emits electrons. These electrons are then incorporated into the semiconductor material. The electrons are then transferred to the electrode, resulting in the generation of an electrical current.

- **Electrolyte:** DSSCs are characterized by their electrolyte solution, which facilitates the regeneration of dye molecules by absorbing and redistributing electrons to the dye molecules. This process of regeneration enables DSSCs to continue to generate electricity. Additionally, DSSCs offer a range of advantages, such as:

DSSCs are a cost-effective alternative to conventional silicon solar cells due to their use of cost-effective materials and simplified production processes. Furthermore, their flexibility allows them to be tailored to a variety of applications, such as curved surfaces and mobile devices. Furthermore, DSSCs are capable of generating electricity in indoor and low-light environments, making them ideal for use in areas with limited sunlight. Furthermore, the color variability of DSSCs due to their photosensitive dye allows them to be designed in a variety of colors, making them aesthetically pleasing.

It is necessary to conduct research on dye-sensitive solar cells in order to unlock the potential of this cutting-edge solar technology, thereby increasing its efficiency, reducing its environmental impact, increasing its versatility, and making it more cost-effective while simultaneously broadening its scope of application for a sustainable solar energy future.

The use of organic dyes, synthesized from a variety of natural sources, has been the subject of intensive research in recent years due to their high coevolution rate, high harvest efficiency, biodegradation, low cost of production, and ease of processing. Natural dyes extracted from fruit, flowers, seeds, roots, or leaves of plants have been used as photosensitizers for DSSC. The most extensively studied photosensitizers are anthocyanins found in strongly colored fruits, flowers, and leaves. The strongly colored extracts from natural sources have been confirmed to contain high levels of anthocyanin, primarily cyanidin, and derivatives (cyanidin- 3-glucoside and cyanidin- 3, 5-5-glucoside). (Negese Yazie Amogne 2020).). Anthocyanin and Carotenoid are subjected to the coloring of natural sensitizers which enhance the absorption coefficient. The absorption spectrum of the sensitizer and its functional group upgrades the injection of exciting electrons into the nano porous semiconductor layer which enhances the efficiency of DSSC. DSSC fabricated using bracts of Poinsettia, Tamarillo, Annato seeds, Pungent Chilli, and a cocktail of these dyes were investigated in this article. The dye molecules absorb visible photons, which produce charge carriers (electric current) and transport electrons to the TiO_2 material. In India, Poinsettia is a popular garden plant known for its bright red bracts that resemble leaves and can be used to make a pH indicator due to its chemical composition. Tamarillo is rich in soluble fiber, energy, carbohydrates, anthocyanins (**Fig 1**), and carotenoids. Only tamarillo includes both polar (anthocyanins) and non-polar (carotenoids) colors among the fruits. The pigment bixin is found in Annatto, a small tree of the Bixaceae family. Annatto seeds produce a dark-red liquid that is commonly used as food coloring and flavoring. Carotenoids are abundant in the pericarp of the seeds, with cis-bixin accounting for up to 80% of the total and trans -and cisnorbixin accounting for the remaining 20%. The carotenoids capsanthin and capsorubin are responsible for the chili's bright red color. (Pooja Prakash 2023).

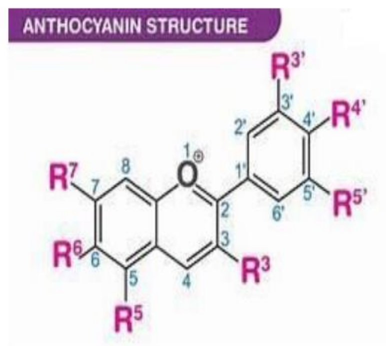


Figure 1. Structure of Anthocyanin

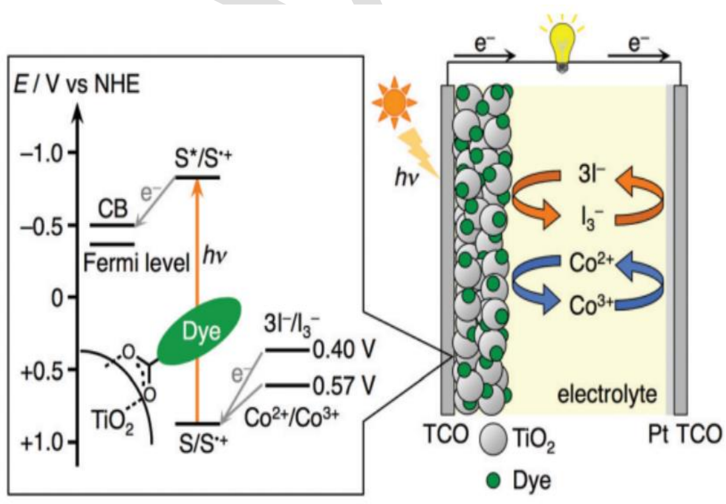
Porphyrins:

- All porphyrins reported so far from nature have their side chains substituted for the eight hydrogen atoms found in the four pyrrole rings that make up porphyrin. The common substituents present in natural porphyrins are acetate, propionate, methyl and vinyl groups. Porphyrin rings are numbered with Roman numerals I through IV, starting at the top and proceeding clockwise. The methane bridges are lettered with Greek letters, alpha through delta, again proceeding clockwise. Positions at which substituents could be attached are numbered 1-8, starting with the I ring, and proceeding clockwise. The structure is often represented in a cross-shaped shorthand form. The nitrogen atoms of a porphyrin occupy the four sites on the square plane of an octahedron, leaving two empty sites on the top and the bottom. These two sites are then filled by the axial ligands, which are known to react in special ways. By using them, biological systems carry out a wide range of chemical reactions. Porphyrins are stable compounds, red-violet to red-brown in color, that fluoresce red when excited by light near 400 nm. The reduced forms of porphyrins are termed porphyrinogens, the functional form of the compound that must be used in heme synthesis.

Are porphyrins an alternative to ruthenium(II) sensitizers for dye-sensitized solar cells?

- Typically, the device composed of a porous layer of TiO_2 nanoparticles covered with a molecular dye absorbs sunlight like chlorophyll in green leaves. The TiO_2 is immersed in an electrolyte solution, above which a platinum-based catalyst is placed. Similar to a conventional alkaline battery, an anode (the titanium dioxide) and a cathode (the platinum) are placed on either side of a liquid conductor (the electrolyte). Detailed device fabrication and the working principle of a DSSC are well documented in our earlier reports5,6. Since 1991 many efforts have been paid to improve the power conversion efficiency. Moreover, it did not take much time to prove that DSSCs are good a alternative for the conventional first and second generation silicon and other thin-film solar cells. Interestingly, the DSSC technology works well even in the diffused light conditions, unlike in the first and second generations of photovoltaic devices.
- Among various components of the DSSC device, the sensitizer is one of the key components in achieving high efficiency and durability. The most successful charge transfer sensitizers employed so far in DSSC are cisdithiocyanatobis-(2,2′-bipyridyl-4,4′-dicarboxylate)ruthenium(II) (together with its various protonated forms), its modified forms (N3 and N719) and trithiocyanate 4,4′4″- tricaboxy-2,2′ : 6′,2″-terpyridine ruthenium(II) (the black dye), which yield conversion efficiencies up to 11% under air mass (AM) 1.5 solar conditions with liquid redox electrolyte1,9. Nevertheless, studies are still needed to fill the gap between today's benchmark conversion efficiency of 32% (Shockley–Queiser10 limit predicted for a single junction cell). This can be achieved only through proper molecular designing of the sensitizer. A great variety of ruthenium(II) complexes have been reported in the literature in order to further improve the efficiency and durability of the device11–14. Even though the ruthenium(II) polypyridyl complexes are more dominant in today's DSSC research, they are expensive due to rarity of the metal. Moreover, they are less durable due to

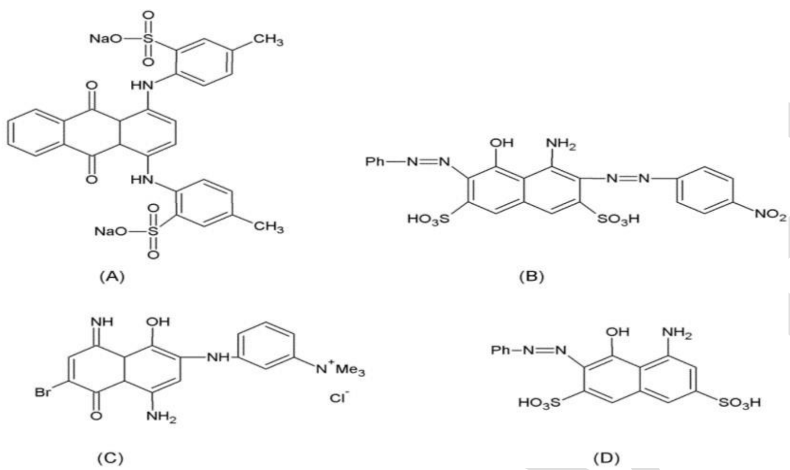
the presence of two or three –NCS groups, present in ruthenium(II) sensitizers. Another important drawback is that these complexes lack absorption in the red region of the visible spectrum and also have relatively low molar extinction coefficients above 600 nm. The next challenge is that the metal complex based sensitizers involve careful synthesis and tricky purification steps. Considering these drawbacks of ruthenium(II) sensitizers, metal-free sensitizers such as synthetic organic dyes and natural dyes have been thought of as alternatives for DSSC applications. As these sensitizers do not contain noble metals, there is no concern about resource limitation. However, the metal-free organic dye-based DSSCs are not useful for rooftop applications as these molecules are not durable due to instability. For a light-harvesting system, the essential requirements are that the sensitizing dye should have broad absorbing capability, preferably one that encompasses the visible spectrum to near-IR, binds strongly to the semiconductor surface (needs to have an anchoring group), has a suitably high redox potential for regeneration followed by excitation and should be stable over many years of exposure to sunlight. Based on chemical, thermal, photophysical and redox properties, porphyrins are found to be suitable low-cost alternative sensitizers for DSSC applications, even though the synthetic protocols of the porphyrins are tedious.



Schematic illustration of components and operational principles of DSSCs. TCO denotes a transparent conducting oxide electrode.

CARBON DYES:

Dyes derived from carbon atoms, such as those found in the carbon nanotube or carbon quantum dot, have become increasingly popular as potential sensitizing agents in dye sensitive solar cells. Spectroscopic, electronic and electron injection properties of a new class of linear carbon chain (LCC) based organic dyes have been investigated, by means of density functional theory (DFT) and time dependent density functional theory (TDDFT), for application in dye-sensitized solar cells (DSSCs). The photophysical properties of LCC-based dyes are tuned by changing the length of the linear carbon chain; UV/VIS absorption is redshifted with increasing LCC length whereas oscillator strength and electron injection properties are reduced. (Giuseppe Consiglio 2023).



- Graphene: Graphene is a single layer of carbon atoms arranged in a hexagonal lattice. It possesses exceptional electrical conductivity and a high surface area. Graphene based dyes can efficiently capture and transport electrons, improving the efficiency of DSSCs.
- Carbon Nanotubes: Carbon nanotubes are cylindrical structures made of rolled-up graphene sheets. They exhibit excellent electrical conductivity and a large surface area. Carbon nanotube-based dyes have the potential to enhance light absorption and electron transport in DSSCs.
- Carbon Quantum Dots: Carbon quantum dots are nanoscale carbon particles with unique quantum properties. They have tunable optical properties, good electron mobility, and low toxicity, making them promising sensitizers for DSSCs.

Inkjet printed dyes:

- Development of novel dye designs for efficient light harvesting has always remained one of the major focus areas in DSSC research. However, less attention has been given to optimizing the traditional and time-consuming dye-sensitization process,[5,80] which may limit the rapid production of large area DSSC modules.
- In this regard, Hashmi and co-workers demonstrated rapid sensitization of TiO_2 photoelectrodes via printing dye inks through a scalable and established inkjet printing method. Considering the process where the dye molecules get adsorbed on the surface of the TiO_2 particles, the inkjet printing is in principle a similar process as the conventional soaking process. The only difference is that in the inkjet printing, a much more concentrated dye solution is applied on the film, and the position where the solution soaks the film can be precisely controlled by the droplet deposition. It must be that the diffusion of the dye molecules inside the nanopores is much faster than the drying of the macroscopic droplet, and for this reason, the dye molecules have enough time to get absorbed on the walls of nanopores before the solvent evaporates.
- This not only replaces the slow and dye bath-based conventional sensitization process of PEs, but also offers numerous opportunities. For example, multiple dyes can be printed with high precision over a solo TiO_2 photoelectrode, which enables for the first time the possibility to create a variety of colorful patterns, and greatly motivates the development of colorful photographs similar to digital pictures as functional solar cells.
- In addition, this method allows control over the transparency of a single TiO_2 electrode through depositing different amounts of dye in different parts of the electrode Previously, tuning the transparency of the DSSC has been possible only in a spatially uniform manner, by either adjusting the thickness of the TiO_2 layers or the conditions in the dye bath process (concentration, duration, temperature and pressure).[81–83] The spatial control of the dye loading of one or more dyes provides an interesting opportunity to design digitally printed color patterned DSSCs for use in design and architecture.
- Furthermore, inert environmental conditions for sensitizing TiO_2 electrodes may also be avoided if executed through the inkjet sensitization scheme. During the inkjet printing step, the dye ink remains preserved in the sealed cartridge and gets deposited from nozzles with a very small drop volume (1 or 10 picolitre), which minimizes the risk of direct exposure

to air and humidity. As a result, this contaminant-free dye solution can surely facilitate in achieving long-term photovoltaic performance stability of fabricated DSSCs in various stressful environmental conditions.

- In general, executing the sensitization step with inkjet printing technology brings new possibilities, which may also impudence the overall manufacturing cost and the photovoltaic performance reproducibility in understanding the production of fully printable next-generation DSSC technology.

New opportunities for standardizing stability testing protocols of novel DSSCs for indoors applications and IoT devices

- Currently, the deployment of DSSCs outdoors or their integration in building integrated photovoltaics (BIPV) applications requires reliable certifications for their long-term photovoltaic performance stability under severely stressful conditions. On the other hand, the forecasted deployment of next generation DSSCs in IoT devices as efficient energy harvesting units indoors may relax the certification conditions, which could consequently lead to a commercial breakthrough. This is mainly due to different ecological conditions inside modern buildings, which not only maintain controlled environments but also remain far less stressful than simulated or natural climatic conditions outdoors. Mindful of the need for standardizing the set of testing protocols for the next generation of photovoltaic technologies based on emerging organic solar cells, DSSC or perovskite solar cells consensus statements have been recently reported to provide guidance for their reliable testing procedures and conditions for converting lab-sized solar cells into reliably integrable commercial products. With such previous practices, new consensus statements for standardizing new testing protocols seems logical, and can be predicted for various reasons, such as:
- The abundance of numerous light sources (including fluorescent lights, LEDs, sodium and halide lamps available with a wide variety of spectra) that have been installed in modern buildings. This makes an interesting situation for the prime selection of standard light sources for determining the reliable conversion efficiencies.

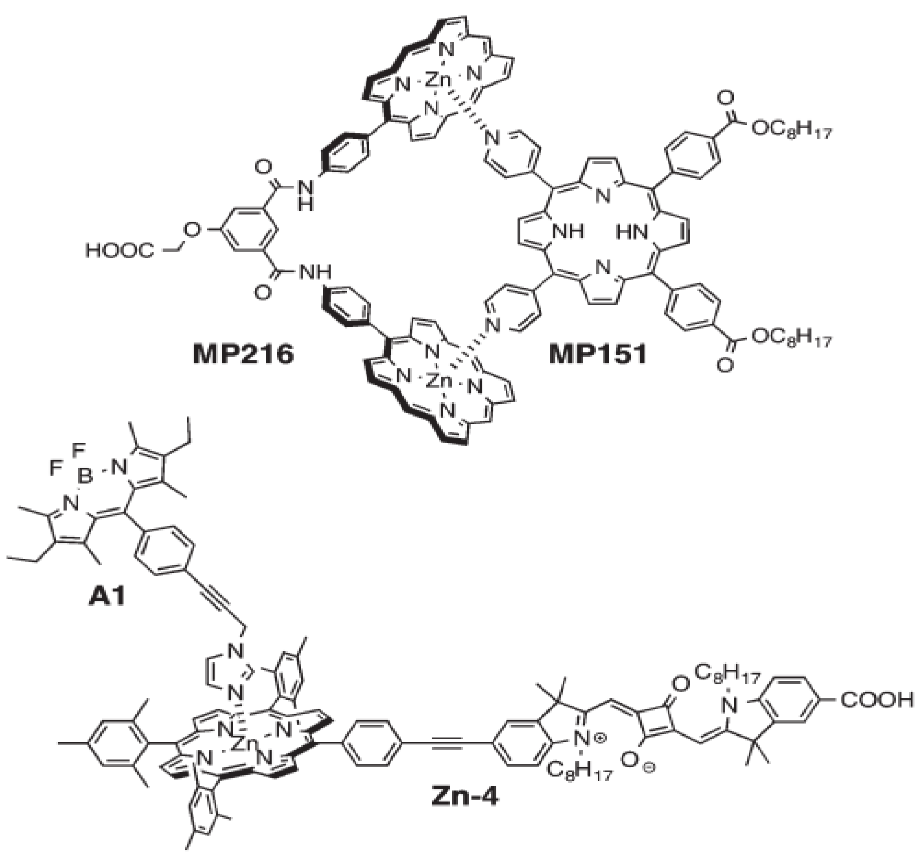
- Determining the standard temperature ranges for thermal stress testing, since the room temperature conditions remain far lower compared to the most demanding test (i.e. 85 C combined with 85% RH)105,106 needed to surpass in order to install the devices under natural climatic conditions outdoors. Nevertheless, the selection of temperature ranges for obtaining indoor installation certificates could remain influential from the perspective of transportation and storage of the fabricated solar cells or modules, where they could experience a wide range of temperatures before their final installations at the selected sites.
- An updated UV stress test for these advanced DSSCs could be adopted with a slight relaxation compared to the stressful UV stability tests aimed for their indoor deployment under modern LED light sources. These LED light sources have been widely deployed in current buildings as a low-cost, stable and energy efficient alternative to traditional lament-based light sources, and do not contain UV in their light spectrum. Therefore, such LED light sources gives a great possibility to next generation DSSCs for long-lasting and efficient power generation under their irradiation for longer periods if integrated in futuristic IoT devices.
- A possible reform in the traditional 1000 hours (6 weeks) of continuous stability tests may also be realized by further extending the exposure time to 2000 hours, since the rate of chemical reactions within the DSSCs could be far slower due to the less stressful conditions indoors. Hence, all these interesting possibilities motivate the development of a special set of stability tests to assess the reliable potential of next-generation DSSC devices to be operated under far more relaxed conditions than those used outdoors. Table 5 suggests several potential stability tests that may be adopted from previously established ISOS testing protocols to assess the photovoltaic performance stability of these next-generation DSSC devices, for their deployment as energy harvesting units in the futuristic IoT devices and portable electronics.

Further improvement of DSSC performance

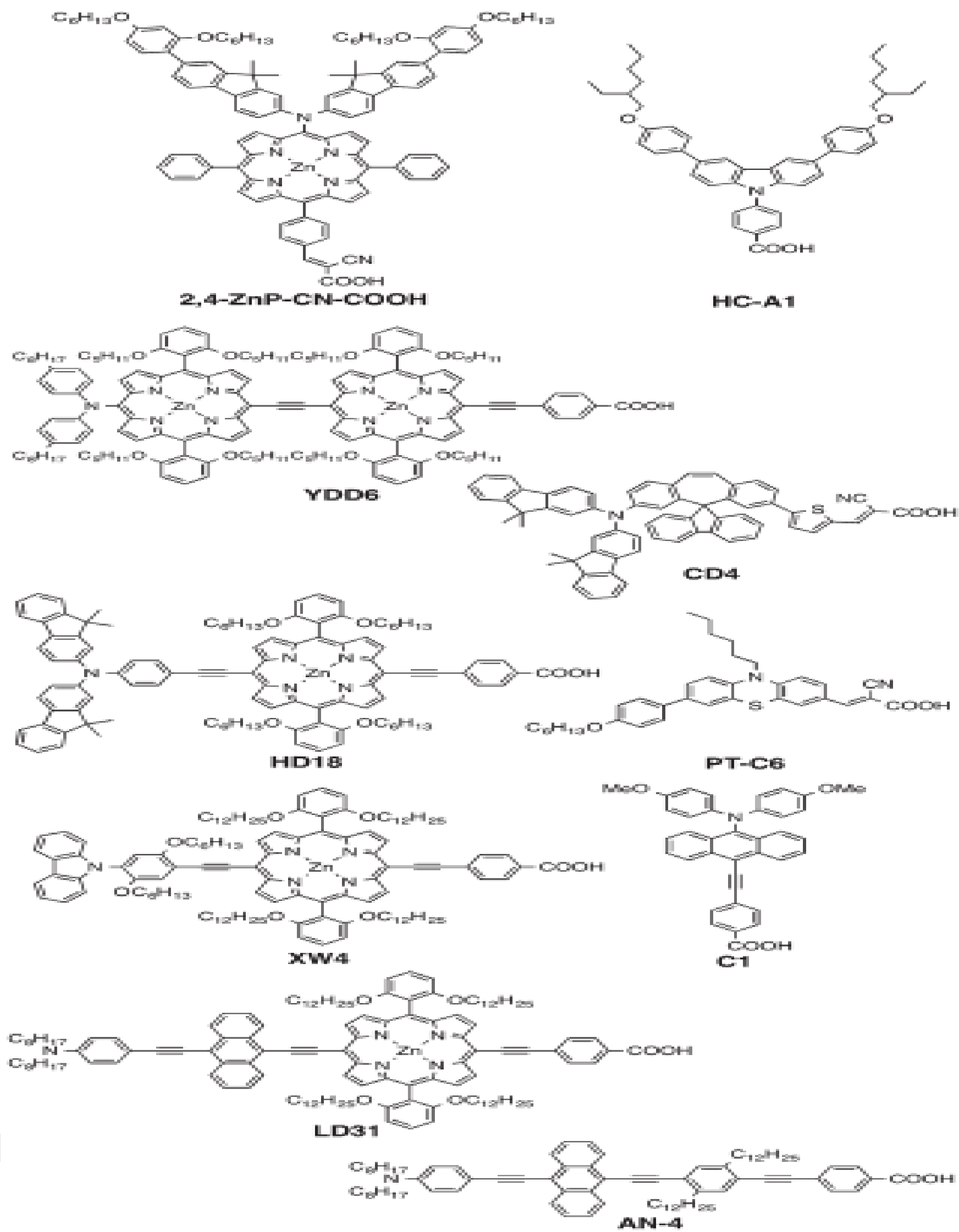
- Co-sensitization

1. Co-sensitization is an effective approach to enhance the cell performance through a combination of two or more different dyes exhibiting complementary absorption in the visible and NIR regions (Fig. 23). Dye aggregation on TiO2 may be inhibited by mixing the dyes with different shapes and sizes. Kim and co-workers reported a DSSC with push–pull porphyrin 2,4- ZnP-CN-COOH co-sensitized with HC-A1. 78–80 While an η-value of 4.9% was obtained in the absence of a co-sensitizer, a DSSC with HC-A1 as the co-sensitizer displayed a remarkably improved η value of 8.4%.79 Co-sensitization not only increases JSC, but also VOC, because of an enhancement of the light-harvesting ability as well as suppression of CR. Yeh and Diau et al. used a cocktail of YD2-o-C8 (vide infra), CD4, and YDD6 with different absorption profiles for DSSCs. An η-value of 10.4% was achieved under the optimized cell conditions.81 The IPCE values of 75–80% and 40–60% were obtained in spectral regions of 400–700 nm and 700–800 nm, respectively, giving a high JSC value of 19.28 mA cm−2 . Chen and co-workers applied a combination of HD18 and PT-C6 to DSSCs.82 Since the phenothiazine molecule PT-C6 can act as both co-adsorbent and sensitizer upon co-adsorption, the DSSCs displayed an η-value of 10.1% under their optimized conditions. Xie and coworkers presented the co-sensitization of XW4 by C1 for DSSCs.83 An η-value of ca. 8% for a DSSC with only XW4 was increased to ca. 11% for a DSSC by the co-sensitization. Diau and Lin et al. demonstrated that LD31 co-sensitized with AN-4 extended the light-harvesting ability up to ca. 800 nm and an η-value of 10.3% was attained in an iodine-based electrolyte.84 However, since LD31 has already achieved an outstanding light-harvesting ability, the co-sensitization with AN-4 resulted in only a 0.3% increase in the η-value compared to that of a DSSC based on LD31 alone (10.0%). These excellent works indicate that organic dyes possessing absorption bands around 500 nm are useful for the co-sensitization with porphyrin sensitizers that lack intense absorption around 500 nm. Additionally, relatively rigid and bulky structures would be favorable for the suppression of dye aggregations. Interestingly, the η-value of DSSCs using the cosensitizer alone seems to have no relationships with the η-values of DSSCs with the corresponding porphyrin sensitizer together with the co-sensitizer. For instance, DSSCs based on PT-C6, C1, and HC-A1 attained η-values of 8.2%, 5.7%, and 0.37%,80 respectively. At least co-sensitizers should reveal a high IPCE value at a specific wavelength region that compensates the moderate IPCE by porphyrins. Meanwhile, HC-A1 possesses the hole-conducting function because of a low

oxidation potential. Thus, the use of co-sensitizers with multiple functions, such as efficient light-harvesting around 500 nm, suppression of dye aggregation, and excellent hole-conducting character, would be a potential option for improving the cell performance of porphyrin DSSCs. Another concept derives from the use of an energy relay with additional photoactive dye in supramolecular assemblies.85–8 While the electron and energy transfer processes of supramolecular systems have been studied in great detail, the utilization of supramolecular interactions in solar cells is scarce. Ballester, Palomares and co-workers designed the self assembled trisporphyrin complex MP216 + MP151. 86 The pyridyl group of porphyrin MP151 coordinated to the zinc atom of porphyrin MP216 adsorbed on a TiO2 surface. The DSSC performance was obtained with a 100% increase in η-value for the supramolecular trisporphyrin MP216 + MP151 assembly (2.9%), compared to a plane zinc bisporphyrin MP216 (1.5%). Not only did the improved light-harvesting ability attain a higher photocurrent generation, but also the blocking effect of the supramolecular assembly retarded the CR process. Odobel et al. utilized a boron dipyrromethene (BODIPY) dye bearing an imidazole moiety A1 as a light-harvesting antenna for a supramolecular assembly with zinc porphyrin dye Zn-4. 87 The action spectra clearly displayed that the IPCE value in the 450–550 nm region was strongly enhanced when the porphyrin dye Zn-4 was connected to the antenna dye A1. For a DSSC based on this supramolecular array, an η-value of 4.6% was remarkably higher than that based on Zn-4 alone (3.6%) due to an increase of JSC by 25%. On the other hand, BODIPY dye lacking the imidazole moiety displayed no enhancement, highlighting the importance of the supramolecular assembly for efficient energy transfer. These approaches can be extended to other pigments possessing substituents coordinating to zinc metal, such as a pyridine and imidazole moiety. To extend this concept and achieve higher cell performances, optimization of additional dyes and supramolecular architecture is required.



Supramolecular assemblies of MP216 + MP151 and Zn-4 + A1



Molecular structures of porphyrins and co-sensitizers

Advantages of Dye Sensitized Solar Cells

- Since, nanoparticles are used these can absorb almost all the photons from the sunlight. Further, dyes used in the solar cells convert photons into electrons efficiently
- They are cost effective as compared to other semiconductor cells,
- DSSC can absorb diffuse sunlight and fluorescent light. Thus these can work efficiently in cloudy weather. These have low cutoff and therefore, are suitable for running small devices indoor
- They last long thereby reducing frequent replacements
- Mechanically robust which makes them easy to use and handle?
- As these are composed of thin layers heat is easily radiated to reduce the internal temperature. This helps in increasing the excellency of the cells.

Applications

- The first commercial application of DSSC created by G24 innovations was in 2009 where these were used in backpacks and bags in Hong Kong. The solar panels built into these backpacks and bags could harvest energy to repower mobile electronic devices such as mobile phones, e-books, cameras, and portable LED lighting systems. He portable electronics, cellphones and cameras could be recharged. The modules could also be cheaply incorporated into powergenerating windows and billboards.

Conclusion

Dye-sensitive solar cells (DSSCs) are a promising renewable energy technology that is in line with sustainability objectives. DSSCs are cost-effective and offer the potential to use sustainable and eco-friendly materials. Research is currently being conducted to address efficiency issues and enhance their commercial viability, making them an attractive choice for renewable energy production in a variety of applications. Their inexpensive and abundant materials, along with our ability to fabricate them as thin and light-weight flexible solar panels makes them well-suited for producing low-cost indoor solar panels, provided that the cell manufacturing methods can be scaled to industrial production with high cell efficiency and long-term indoor durability. The research trends discussed in this work related to the production of next-generation DSSCs show that important progress has been made with new and optimized materials, ultimately increasing the photovoltaic performance of these photovoltaic devices. These alternative materials offer new possibilities for fabricating advanced DSSC designs such as mechanically contacted liquid junction or solvent free solidstate zombie DSSCs. Moreover, the process now suggested in this work offers a more economical approach to producing an advanced DSSC device structure on a single glass substrate, which may significantly influence the overall production costs. Producing solid-state DSSC architecture with the suggested process now on single substrates with printed dyes and a Cu redox based solid-state hole conductor will further increase the robustness of DSSCs under natural and simulated environmental conditions, and will provide new opportunities for portable electronics and internet-of-things devices.

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