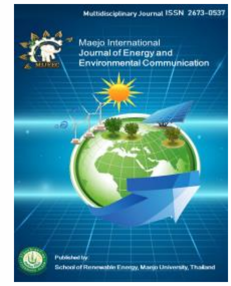
Maejo International Journal of Energy and Environmental Communication

Journal homepage: https://ph02.tci-thaijo.org/index.php/MIJEEC



ARTICLE

A comprehensive review of the evolution of dye-sensitized solar cells from ruthenium dyes to organic pigments with the influence of graphene nanoribbons

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ARTICLEINFO

Article history:
Received 23 March 2023
Received in revised form
19 May 2023
Accepted 21 May 2023

Keywords:
Dye-sensitized solar cells
Organic pigments
Light-harvesting prowess
Electron mobility
Solar energy technologies

ABSTRACT

Dye-sensitized solar cells (DSSCs) have emerged as a significant advancement in renewable energy, rivalling traditional silicon-based photovoltaics. The dye in these cells has transitioned from costly ruthenium-based compounds to cost-effective, natural organic pigments. This shift has enhanced DSSCs' efficiency and stability, with their flexibility positioning them as potential alternatives to conventional rigid solar panels. Yet, there remains the hurdle of plastic substrates' temperature limitations, especially when DSSC production often requires much higher temperatures. Innovations to address this include electrophoretic deposition, pulse laser deposition, and the titanium tetraisopropoxide process. In addition, the potential of materials, particularly titanium dioxide and the influential graphene nanoribbons, in photoanode applications has been at the forefront of recent research. While DSSCs boast of transparency and economic benefits over their conventional counterparts, they still grapple with metal complexes and sustainability issues. The shift towards organic, eco-friendly dyes has been significant considering this. This review delves into DSSCs' development, mechanics, challenges, and solutions, highlighting their integration with devices like supercapacitors for promising renewable energy prospects.

1. Introduction

As the global population expands and urbanization accelerates, leading to a commensurate rise in energy demand for needs, the burgeoning industrial growth in developing nations and technological advancements further emphasize this upward trajectory (Whangchai et al., 2021). This surge in energy use, largely driven by fossil fuels, is concerning due to the rapid depletion of these resources and the associated environmental and health risks (Dussadee et al., 2022; Trejo et al., 2022). Consistent use of fossil fuels contributes to increased emissions of greenhouse gases like methane, carbon dioxide, and nitrous oxide, which exacerbate global warming and climate change (Kongchan et al., 2022; Palanisamy et al., 2022).

Since the world's population and industrial needs grow, the debate intensifies about our rising energy consumption, environmental impact, and the search for alternative energy sources (Ratchawet and Chaiworn, 2022). Renewable energy is at

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the forefront of this debate, especially when balancing environmental health with economic growth (Dussadee et al., 2016; El-Agez et al., 2022). Many countries are now re-evaluating their energy policies to improve existing technologies, promote green innovations, and shift to renewable energy (Unpaprom et al., 2021). Among these, solar energy stands out due to its abundance and sustainability (Li et al., 2023). Solar panels generate electricity without greenhouse gas emissions, combating climate change. They also reduce pollutants harmful to our health. Though its intensity may vary due to weather and seasons, the sun is a consistent energy source. Solar energy, the earth's most abundant renewable resource, offers a sustainable solution to the escalating global energy demand (Khammee et al., 2023). Hence, the growing popularity of solar cells and solar panels in the energy market. Provides an insightful projection into the global solar energy market in Figure 1, emphasizing the growing importance of solar technologies and the data source provided by the IEA Statista 2018 (International Energy Agency (IEA), 2020).

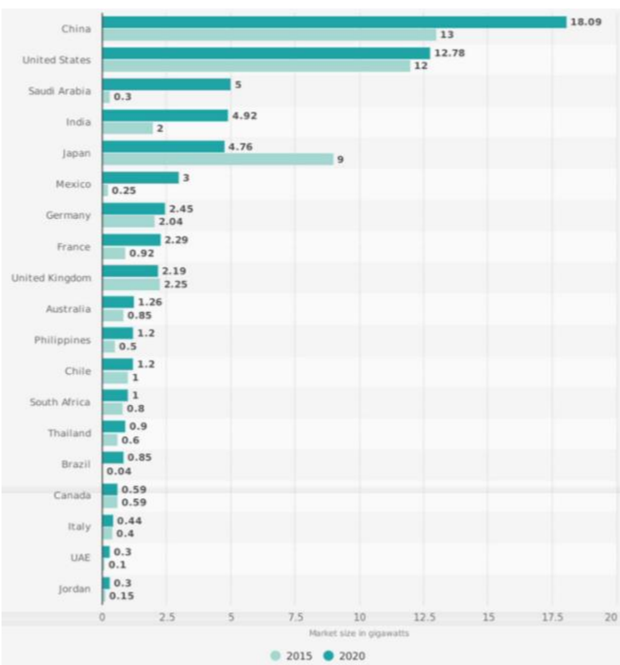

Figure 1. Provides an insightful projection into the global solar energy market, emphasizing the growing importance of solar technologies

Harnessing this infinite power of the sun has taken various forms, with Nano thin-film solar cells emerging as a notably promising avenue. DSSCs, a subset of these thin-film cells, have garnered attention for their cost-effectiveness, ease of fabrication, flexibility, and adaptability. However, a prevailing challenge with DSSCs lies in the traditional use of ruthenium-based dyes as photosensitizers. These dyes, while effective, are costly, rare, and not universally accessible (Khammee et al., 2022).

Recent innovations have incorporated naturally occurring pigments from leaves, flowers, and fruits to enhance DSSC's efficiency, offering a sustainable and less expensive alternative to synthetic dyes (Ponnambalam et al., 2023). Natural pigments from anthocyanin to carotenoids bring unique spectral characteristics and efficiencies (Agarwal et al., 2021). How these pigments interact with the photoanode in DSSCs is influenced by their unique compositions and the solvents used for extraction ((Li et al., 2023). Despite the immense potential of natural dyes, particularly chlorophyll-based dyes, there must be a gap in understanding the nuances of their light conversion efficiencies.

While solar energy's potential is vast, with global consumption expected to soar to 27 TW/yr. by 2050 from 16 TW/yr. 2009 was an inherent need to diversify and optimize solar energy technologies (International Energy Agency, IEA), 2020). Despite their commendable photoconversion efficiency (PCE) of 20-27%, conventional silicon cells suffer from high manufacturing costs. This is where DSSCs, introduced by O'Regan and Grätzel (1991), present a viable alternative. Despite having a relatively lower PCE, they surpass conventional cells in affordability and adaptability.

DSSCs operate on a simple yet effective mechanism: the dye, upon photoexcitation, injects an electron into the TiO_2's conductive band (Ponnambalam et al. 2020). This electron traverses the external circuit, eventually reaching the counter electrode, regenerating the dye (Mohammed et al. 2015). While DSSCs might not rival the efficiency of traditional solar cells, their advantages - especially when integrated with innovations like graphene nanoribbon-based hybrid photoanode materials – must be considered.

This review pursues three core objectives. We aim to evaluate the enhanced electron mobility potential of low-dimensional TiO_2 nanostructured photoanode materials, assess the capability of a bilayer structure in minimizing optical losses, and investigate the potential efficiency gains in photo-conversion through low-dimensional carbon materials. Our analysis encompasses the viability of organic pigments from leaves as DSSC dyes and the synergy between TiO_2 and low-dimensional carbon nanostructures.

A pivotal aspect is comparing the advanced TiO_2/low-dimensional carbon photoanode and its traditional mesoporous TiO_2 counterpart. Our findings underscore the transformative potential of graphene nanoribbon-based hybrid photoanode materials in DSSCs, potentially guiding the creation of innovative photoanode materials for organic pigment-driven solar cells. This review, thus, serves as a foundational guide for future research into graphene nanoribbon-based materials in DSSC applications.

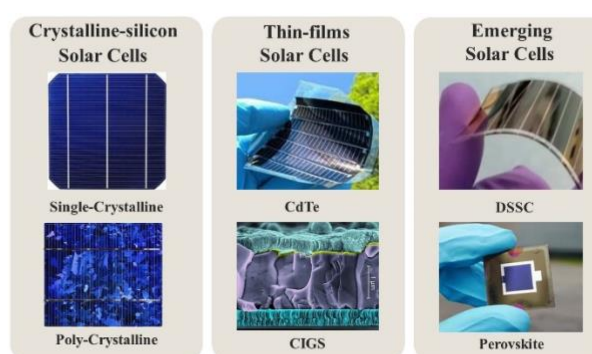

Figure 2. Generations of solar cell

3. Solar cell classifications

Solar cells are broadly categorized into three distinct generations presnted in Figure 2 (Mejica et al., 2023a,b):

- Crystalline solar cell (First generation): These encompass mono-crystalline and poly-crystalline silicon photovoltaic cells, making up the first-generation cells.
- Thin film solar cell (Second generation): The second generation cells comprise thin film varieties like amorphous silicon, copper-indium-gallium-selenide (CIGS), and cadmium telluride (CdTe) cells (Maabong et al., 2015).
- Hybrid thin film solar cell (Third generation): The third generation includes emerging technologies such as dye-sensitized solar cells, quantum dot-sensitized solar cells, and organic photovoltaic perovskite solar cells.

4. Dye-sensitized solar cell (DSSC)

Dye-sensitized solar cells (DSSCs) represent a remarkable class of cost-effective and high-efficiency solar cells that adeptly convert visible light into electricity, even in conditions of low illumination. These cells ingeniously emulate the process of photosynthesis by harnessing natural light (Khammee et al., 2020). With a simple yet ingenious structure and materials, DSSCs offer a promising solution to address imminent energy challenges.

Principle of Operation: DSSCs operate on a principle analogous to photosynthesis. In plants, chlorophyll absorbs sunlight and initiates a chain of reactions, producing energy-rich compounds (Mejica et al., 2020). In DSSCs, the dye molecule plays a similar role to chlorophyll. Electrons are excited to a higher energy state when sunlight strikes the dye molecules. These electrons are then injected into the conduction band of the TiO_2 layer, leaving the dye molecule in an oxidized state. The electrolyte surrounding the dye provides ions to the dye, returning it to its ground state. These ions then migrate to the counter electrode, returning to their original state and sent back to the dye, completing the circuit. Figure 3 displays a diagram of the standard DSSC device structure, adapted and modified (Agarwal et al., 2021).

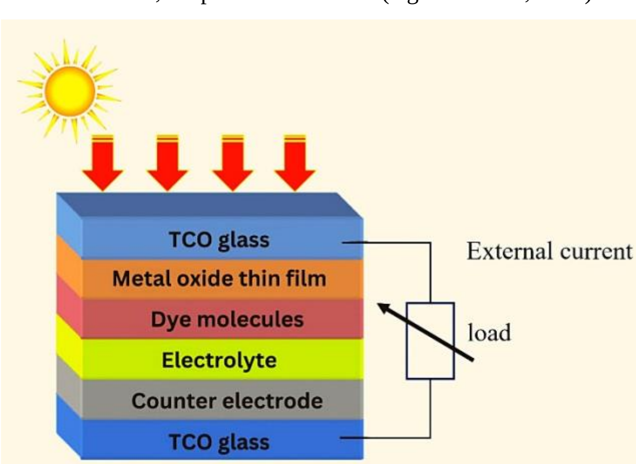

Figure 3. A diagram of the standard DSSC device structure

Figure 3 illustrates a standard configuration of DSSCs, showcasing their fundamental structure. The operational electrode in DSSCs is traditionally composed of a mesoporous network of TiO_2 nanocrystals coated with a monolayer of light-absorbing dye. This electrode is positioned on a conductive glass substrate (Jasim, 2012). As for the counter-electrode, materials like platinum, palladium, or gold are viable options (Mejica et al., 2022). Bridging the electrodes is a gap typically filled with a molten salt containing a redox couple, denoted as A/A-. This salt serves the dual purpose of being an electrolyte and a hole conductor (Li et al., 2023). Due to its commendable stability and reversible behavior, many DSSCs under investigation employ the iodide/tri-iodide (I^-/I_3^-) redox couple as the electrolyte (Boschloo and Hagfeldt, 2009; Supriyanto et al., 2018). Nonetheless, alternative hole conductors, both solid and ionic electrolytes, hold potential for use. Summarily, DSSCs leverage light to generate electrical power while undergoing no permanent chemical alterations. Components of a DSSC given below:

- Electrolyte: Often a liquid but can be in solid-state or gel form. It carries the electric charge between the titanium dioxide and the external circuit. Iodide/triiodide solutions are the most common electrolytes used.
- TiO_2 Layer: This layer is porous, allowing maximum dye absorption. When the dye is excited by sunlight, electrons are released and travel through this layer.
- Dye molecules: They absorb the incoming photons from sunlight. When these molecules are excited by the sunlight, they release an electron into the titanium dioxide layer.
- Counter electrode: Often made of platinum, this component collects electrons before sending them through an external circuit.

DSSCs have become prominent in alternative energy sources due to their low production costs, promising efficiencies, and wide adaptability. One such limitation is the phenomenon known as trap-limited diffusion, which can significantly curtail the device's efficiency.

4.1 Trap-limited diffusion in DSSCs

Trap-limited diffusion can occur when electrons traverse the TiO_2 thin film in a DSSC. This phenomenon results from electron traps in the titanium dioxide layer. When electrons encounter these traps, they get ensnared briefly before continuing their journey, thus slowing the overall electron transport (Boschloo and Hagfeldt, 2009). This decelerated movement results in a sluggish transport mechanism, reducing the cell's efficiency. Furthermore, the sintering process of TiO_2 necessitates a high-temperature heat treatment, often reaching 450 °C. Such intense heat demands substrates that can endure high temperatures without undergoing degradation. A promising approach to enhance DSSC efficiency is employing nanostructured materials instead of sintered nanoparticle photoanodes.

4.2 Conventional DSSC cell architecture & operation

In examining the DSSCs framework, Figure 4 offers an intricate architectural representation distilled from the seminal research by Carella et al. (2018). The architecture of DSSCs is seminal to understanding their operational efficacy. At the core of the DSSC's function is the photosensitizer, which plays a pivotal role in photon absorption and subsequent electron excitation.

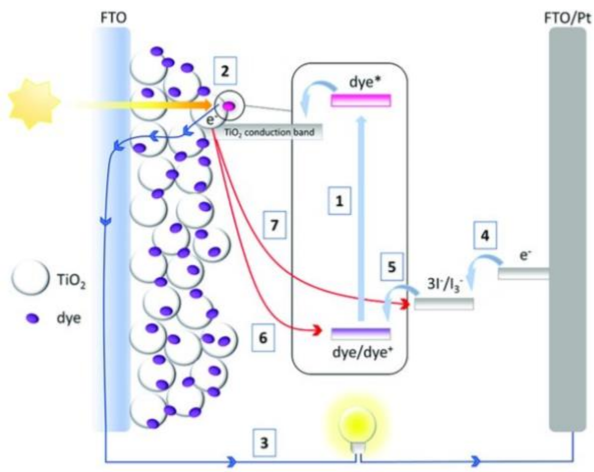

Figure 4. Architecture and operations of DSSC

Photoanode: The foundation of the photoanode is a transparent conducting oxide (TCO), such as indium-doped tin oxide (ITO) or fluorine-doped tin oxide (FTO), which is deposited on a glass substrate (Li et al., 2023). A thin, mesoporous TiO_2 layer is introduced atop this TCO, acting as an electron transport medium. This layer is typically a few micrometers thick and is applied using doctor's blades, screen printing, or inkjet printing methods (Figure 5). Upon exposure to sunlight, the semiconductor metal oxide (SMO) layer captures light energy, and dye molecules anchored onto it are excited. These excited dye molecules release electrons into the SMO, which are then transported to the TCO substrate.

Photosensitizer: The dye or photosensitizer is paramount for DSSC function. There's a plethora of potential photosensitizers available, both natural and synthetic. Organometallic dyes contain transition metals and are often constructed around ruthenium compounds, while organic dyes use a range of organic chromophores. Although ruthenium-based dyes exhibit many benefits, including absorption in the visible spectrum and efficient electron injection, they have the disadvantage of being expensive and challenging to synthesize.

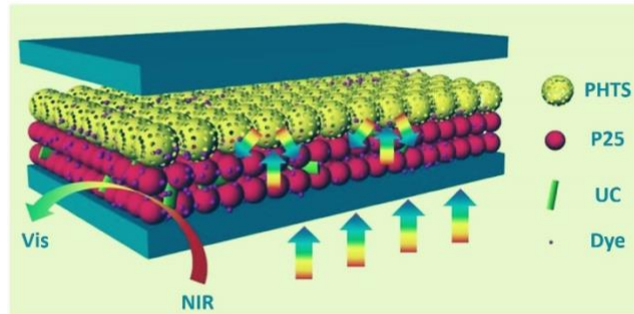

Figure 5. Schematic diagram of the photoanode configuration of DSSCs

Electrolyte: The electrolyte is a pivotal component in DSSCs. Its primary function is to rejuvenate the oxidized dye molecule, restoring it to its initial, unexcited state. Iodide/tri-iodide (I^-/I_3^-) systems are the most commonly used, though their corrosive nature poses certain challenges (Bohnenkamp et al., 2018).

Counter electrode: The counter electrode gathers electrons from the external circuit and facilitates the redox reactions within the electrolyte. To achieve this, thin films of noble metals are employed, though alternative, more affordable materials like graphene and carbon nanotubes have also been explored.

Table 1. Comparison of solar cell performance of different transparent conducting oxides

Cell No.	Anode	Counter Electrode	I_{sc} (mA)	J_{SC} (mA/cm)	P_D (mW/cm)	V_{oc} (mV)	F.F.	η%
1	FTO	AZO	13.6	4.35	1.56	774	0.46	1.30
2		FTO	14.1	4.51	2.46	788	0.69	2.05
3		ITO	7.8	2.50	0.98	785	0.50	0.82
4	AZO	AZO	18	5.76	2.27	789	0.50	1.90
5		FTO	15.5	4.96	2.77	807	0.69	2.41
6		ITO	7.6	2.43	0.89	796	0.46	0.75
7	ITO	AZO	6.6	2.11	0.57	702	0.38	0.48
8		FTO	6	1.92	0.49	669	0.38	0.41
9		ITO	13.4	4.29	1.11	674	0.39	0.93

Transparent conductive substrates: These are essential in DSSC fabrication, sandwiching the ingredients of the cell. They need to be transparent (typically >80% light penetration) to permit optimum sunlight absorption and also need to be conductive, ensuring efficient charge transport (Table 1). For the fabrication of a DSSC, two transparent and conductive substrates are necessary (Bohnenkamp et al., 2018). The ingredients of DSSCs are sandwiched between these substrates. For a substrate to be suitable for DSSCs, it should have the following two features.

- The substrate should have more than 80% transparency to allow an optimum amount of sunlight to pass through to the cell's effective area, i.e., it should let maximum light pass through it.
- The substrate should be high electrically conductive and should efficiently transfer the charge carriers and reduce any optical losses in DSSCs.

- Generally, fluorine-doped tin oxide (FTO), ITO, and aluminum-doped zinc oxide (AZO) were used as conductive substrates for DSSCs. However, FTO-based cells have been shown to have the highest efficiency in all aspects, as compared to others. Comparisons of the performances of ITO, FTO, and AZO-coated glass substrates have been reported by Patni et al. (2018) shown in the below table.

Operating Principles: In a DSSC, the photosensitizer captures light energy, exciting electrons that migrate to the SMO's conduction band. They are subsequently transferred to the working electrode's TCO layer. Connecting the working electrode to the counter electrode via an external circuit, the excited electrons flow to the counter electrode, interacting with the redox electrolyte. This electrolyte then takes the electrons and returns them to the photosensitizer, thus completing the circuit.

In DSSC, dyes function as molecular electron pumps (Ruffieux et al., 2012). When these dyes absorb visible light, they elevate electrons from their ground state in HOMO to an excited state in LUMO (eq 1). Once excited, the electron (D*) is propelled into the TiO_2's conduction band, leaving an oxidized dye (D+) behind. This electron migrates through the TiO_2 film to the ITO glass (eq 2). Simultaneously, the oxidized dye (D+) retrieves an electron from the reduced form of the redox couple (RE) in the electrolyte, leading to the creation of its oxidized version (OX) (eq 3). The OX then moves ionically towards the counter electrode to acquire its absent electron. The RE gets restored through the OX's reduction reaction at the counter electrode, concluding the electrical loop via electron transfer through the external load (eq 4). However, there are two potential interrupting reactions: one where electrons in the TiO_2 film recombine with the oxidized dye (eq 5), and another where the electrons in TiO_2 combine with the OX, causing recombination (eq 6).

$$\mathrm{DTiO_2} + h\nu \xrightarrow{\text{Photon Excitation}} \mathrm{D^*ITiO_2} \qquad (.)$$

$$\mathrm{D^*ITiO_2} \xrightarrow{\text{Electron Injection}} \mathrm{D^+|TiO_2} + \mathrm{e^-|TiO_2} \qquad (.)$$

$$\mathrm{D^+|TiO_2} + \mathrm{RE} \xrightarrow{\text{Dye Regeneration}} \mathrm{D|TiO_2} + \mathrm{OX} \qquad (.)$$

$$\mathrm{OX} + \mathrm{e^-} \mid \mathrm{CE} \xrightarrow{\text{Electrolyte Regeneration}} \mathrm{RE} \qquad (.)$$

$$\mathrm{e^-|TiO_2} + \mathrm{D^+|TiO_2} \xrightarrow{\text{Recombination by } \mathrm{D^+}\text{,Dark Reaction}} \mathrm{D|TiO_2} \qquad (.)$$

$$\mathrm{e^-} \mid \mathrm{TiO_2} + \mathrm{X} \xrightarrow{\text{Recombination by } \mathrm{Ox}\text{,D ark reaction}} \mathrm{RE} \qquad (.)$$

In a standard DSSC, the transformation from light to electrical energy is intricate. Reactions 1−4 play a pivotal role in facilitating this energy conversion. In contrast, Reactions 5 and 6 pertain to electron recombination, commonly termed "dark reactions." While these dark reactions can potentially undermine DSSC efficiency, their impact is minimal due to their slower rate compared to the forward reactions (equ 1−4). The forward reactions are symbolized in green, and the dark reactions in red, based on their respective time constants. Beyond these reactions, electron diffusion within the TiO_2 thin film and the migration of OX and RE ions are crucial factors influencing DSSC performance. The time constants for the forward reactions (green) and the dark reactions (red) are shown in the Figure 6. Apart the above reactions, the diffusion of electrons in TiO_2 thin film and the diffusions of OX and RE ions are also significant for the performance of the DSSCs.

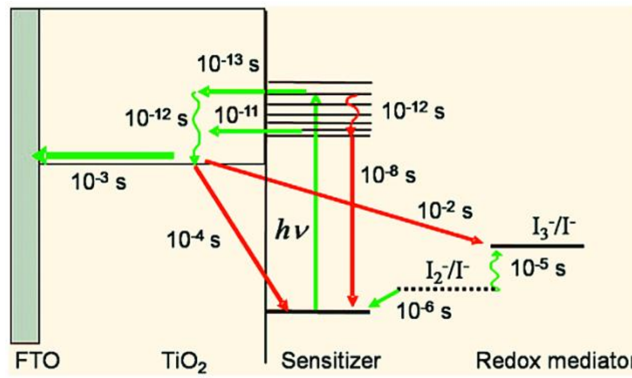

Figure 6. Reaction time of the process in DSSC: Typical time constants for the forward reactions (green) and the dark reactions (red) in a Ru-dye-sensitized solar cell with iodide/triiodide electrolyte under working conditions (1 Sun). Adoped from Boschloo and Hagfeldt, 2009

For a DSSC to operate effectively, the redox electrolyte must regenerate the dye faster than any potential recombination of the dye and the electrolyte's oxidized form (Boschloo and Hagfeldt, 2009). This intricate dance of electrons, which includes their excitation, transportation, and ultimate return to the dye molecule, determines the efficiency of a DSSC. In conclusion, DSSCs offer a promising path for renewable energy. However, understanding the nuances of their operation, from trap-limited diffusion to the intricacies of their construction, is crucial for further advancements and optimizations in this domain.

5. Graphene nanoribbon (GNR)

Graphene nanoribbons (GNRs), which are elongated sheets of graphene possessing a width typically less than 100 nm, offer a fascinating glimpse into the nanoscale world of materials. The foundational theoretical framework for GNRs was pioneered by Mitsutaka Fujita. A hallmark of GNRs is the presence of unique edge-localized states, which are instrumental in bestowing upon them their distinctive optical and electrical behaviors (Tiwari and Snure, 2008). Diving deeper into their structural composition, the electronic band framework of GNRs is intricately tied to the configuration of their edges. These configurations predominantly manifest in two forms: armchair and zigzag, as illustrated in Figure 7.

In the zigzag form, the succeeding edge segments orient themselves in antithetical angles, providing a sense of alternating directions. Contrarily, the armchair formation showcases a configuration wherein every consecutive pair of segments undergoes a rotational shift of 120 degrees compared to its preceding counterpart. It's imperative to note that among these configurations, only the zigzag-edged GNRs displayed edge localized states possessing non-bonding molecular orbitals in close proximity to the Fermi energy. This characteristic further accentuates the intriguing interplay between structure and properties at the nanoscale.

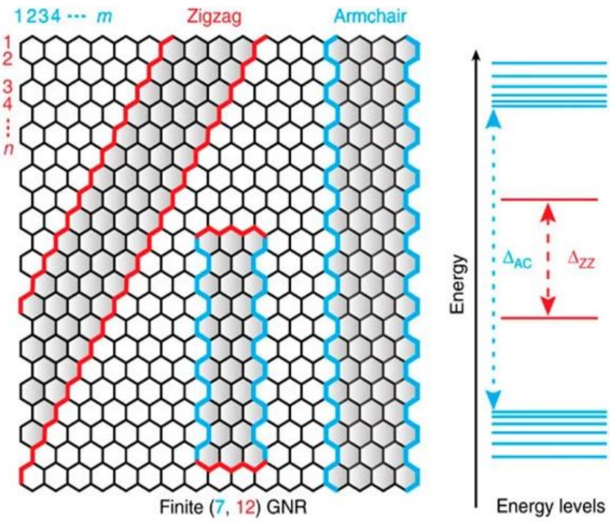

Figure 7. Schematic of graphene nanoribbon zigzag (blue) and armchair (Red), adopted (Tiwari and Snure, 2008)

5.1 Electronic Structure of GNR

Using tight-binding theory, it's theorized that zigzag GNRs are metallic, whereas armchair GNRs can be semiconducting or metallic based on their width. Notably, the band gap in armchair GNRs shrinks as the width increases. STM lithography has enabled the fabrication of GNRs with controlled edge orientation. GNRs can be described as slender slices of graphene. Their distinctive electronic attributes differ from broader graphene sheets and garnered considerable interest. Factors such as the ribbon's width, the configuration of its edges, and imperfections profoundly influence its electronic nature. For a detailed illustration, refer to Figure 8 from Ruffieux et al. (2012) which delves into the electronic structure of graphene nanoribbons.

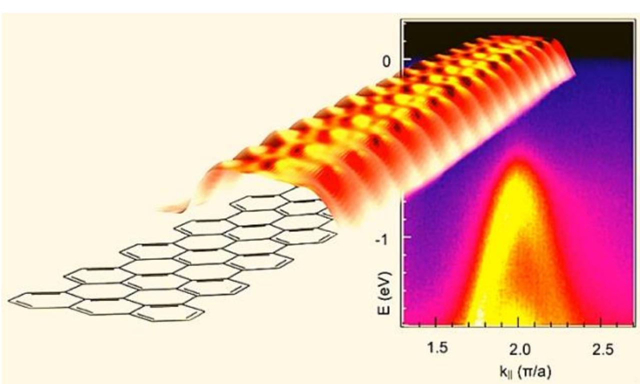

Figure 8. Electronic structure of graphene nanoribbons

5.2 Carbon nanotube

Recent studies highlight the potential of carbon nanotubes (CNTs) as solutions to various challenges, given their exceptional electrical, optical, chemical, physical, and catalytic characteristics. There's a growing body of research exploring the use of CNTs and their composite materials in transparent conducting electrodes (TCEs), semiconductor layers, and counter electrodes within DSSCs (Batmunkh et al. 2015). Carbon nanotubes (CNTs) are cylindrical carbon structures less than 100 nm in diameter. While single-wall carbon nanotubes (SWCNTs) are a few nanometres in diameter, multi-wall carbon nanotubes (MWCNTs) have several nested cylindrical layers. Their unique structure can be imagined as a hexagonal carbon lattice rolled into a cylinder. Electrical Properties: CNTs differ from two-dimensional graphene in electrical behavior. Depending on the chirality, CNTs can be metallic or semiconducting. Their impressive conductivity has driven research into their use in various electrical applications.

6. Photosynthetic pigments and their role in DSSCs

Photosynthetic pigments hold a paramount position in the realm of biology (Pimpimol et al., 2020). Found in plants, algae, and certain bacteria, these pigments are essential (Ramaraj and Dussadee, 2015; Ramaraj et al., 2013), not only for these organisms but also as a linchpin that supports life across multiple kingdoms in nature (Ramaraj et al., 2015). Such pigments facilitate the crucial process of photosynthesis, where light energy is absorbed and converted into chemical energy, providing sustenance for the vast majority of life on Earth. The diverse color palette of nature – be it in flowers, leaves, or fruits – is not just a visual spectacle. Each hue is indicative of different pigments present within these structures. Beyond their biological role, these pigments have been identified as potential candidates for renewable energy technologies, specifically in the context of DSSCs.

DSSCs stand out in the solar technology landscape due to their unique operational mechanism. Instead of relying on the p-n junction typical of traditional solar cells, DSSCs utilize dye molecules that absorb sunlight and release electrons (El-Agez et al. 2022). When harnessed as dye sensitizers, these photosynthetic pigments perform a pivotal role in this mechanism. Upon absorbing photons from sunlight, the dye molecules in DSSCs become excited and release electrons. These electrons are then transferred to semiconductor materials present in the cell, initiating an electric current. In essence, the dye sensitizers in DSSCs act as intermediaries, capturing solar energy and setting the stage for its conversion to electricity.

The efficacy of DSSCs, therefore, hinges significantly on the efficiency of these dye sensitizers (Mejica et al., 2023). Their ability to absorb light across different wavelengths, their stability, and their compatibility with the other materials in the cell all play a critical role. Given that the essence of a DSSC is to absorb sunlight and convert it to electricity, the choice and performance of dye sensitizers have a direct bearing on the cell's light-harvesting efficiency and overall photoelectric conversion capability.

In recent years, with the pressing need for sustainable and green energy solutions, the exploration of naturally derived photosynthetic pigments for DSSCs offers an intriguing blend of biology and technology. Harnessing the time-tested efficiency of nature and integrating it with cutting-edge technology might pave the way for more sustainable and efficient renewable energy solutions in the future.

6.1 Chlorophylls

Chlorophylls are the primary pigments responsible for the green coloration in plants and play a central role in photosynthesis, the process through which plants convert sunlight into chemical energy (Unpaprom et al., 2017). Their molecular structure is well-suited for capturing and transferring energy from sunlight (Mejica et al., 2023a). When we discuss chlorophylls, it's important to note that there are different types, including chlorophyll-a, chlorophyll-b, and others, each with a slightly different structure and absorption spectrum. These distinctions allow them to absorb light most efficiently across different wavelengths.

In the context of DSSCs, chlorophylls are of significant interest due to their intrinsic ability to harness solar energy. The molecule's structure, particularly its central magnesium ion, facilitates the transfer of electrons, a principle that's leveraged in DSSCs. Extracted chlorophyll, when used as a sensitizer in these solar cells, absorbs sunlight and releases electrons, analogous to their function in natural photosynthesis, which can then be harvested for electricity.

6.2 Carotenoids

Carotenoids are organic pigments responsible for imparting vibrant colors (ranging from yellow to red) to many fruits and vegetables. Functionally, they protect plants from excess light and act as a secondary light-absorbing pigment, assisting chlorophyll in capturing energy from light (Tipnee et al., 2015).

There are two main categories:

(1) Carotenes: Purely hydrocarbon-based, examples include alpha-carotene and beta-carotene, the latter being a precursor to vitamin A. And (2) Xanthophylls: Oxygenated derivatives of carotenes like lutein and zeaxanthin. For DSSCs, carotenoids' ability to capture and transfer energy can be exploited, much like chlorophyll, to produce electrical energy from sunlight.

6.3 Lycopene

Lycopene is a bright red carotenoid found predominantly in tomatoes, watermelons, and other red fruits. Structurally, it is a tetraterpene assembled from eight isoprene units devoid of oxygen, distinguishing it from other carotenoids. While many carotenoids can be converted into vitamin A within the human body, lycopene lacks this capability (Septiani et al., 2022). In DSSCs, lycopene could serve as an efficient photon absorber. Its vibrant color indicates a strong absorption in a specific region of the visible light spectrum, which can be useful for enhancing the light-harvesting efficiency of the solar cell.

6.4 Anthocyanin

Anthocyanins are water-soluble pigments responsible for the red, blue, and purple colors in a variety of plants, including berries, grapes, and flowers. Beyond their role in plant coloration, anthocyanins have potent antioxidant properties and protect plants from UV radiation.

In the DSSC framework, anthocyanins can serve dual purposes. First, their strong light-absorption capacities make them suitable as sensitizers. Second, their antioxidant properties can potentially enhance the longevity and stability of DSSCs by preventing or reducing oxidative degradation of the cell components. In conclusion, the intersection of biology and technology as seen in DSSCs is a testament to nature's potential in advancing renewable energy solutions. By leveraging the inherent light-harvesting properties of these pigments, researchers can develop more efficient and sustainable solar energy devices.

7. Demo of plant-based materials and dye extraction

A demo of plant-based materials and dye extraction suggests a demonstration or practical showcase of how materials derived from plants, specifically their leaves, can be used for extracting dyes (Ponnambalam et al., 2020; 2023a,b).

- *Ficus Benjamina* (Weeping fig): This is a common indoor plant, often recognized for its drooping limbs, which is why it's named the "Weeping" fig. Its leaves, like many plants, contain natural pigments.
- *Syzygium Samarangense* (Thai Wax Apple): This is a tree that produces a fruit commonly referred to as the "wax apple" or "rose apple." The fruit has a shiny appearance, somewhat resembling an apple, but is typically more bell-shaped. The tree's leaves, just like the fruit, might contain distinct pigments.
- *Sandoricum Koetjape* (Santol): This is a tropical tree known for its round, yellowish fruit called Santol or Cottonfruit. The tree's leaves, similar to its fruit, have distinct properties and can be a source of specific pigments.

The reference to these leaves being "sourced from Maejo University, Chiang Mai, Thailand" indicates that the leaves used for this demonstration were collected or procured from trees located within the Maejo University campus or its associated botanical facilities. The university might have been chosen due to its botanical resources, research facilities, or the specific species of trees available there. The extraction of dyes from such leaves suggests a study or experiment to harness these natural pigments for various applications, possibly in sustainable or eco-friendly technologies (Ponnambalam et al., 2023a).

Leaves from *F. benjamina, S. samarangense*, and *S. koetjape* (Santol) were sourced from Maejo University. The extraction of chlorophyll was performed using ethanol. For preparing the FTO glass (with a resistance of 20 ohm/sq.cm), acetic acid and a soap solution were utilized as pre-treatment agents (Ponnambalam et al., 2023b). Essential components for synthesizing graphene nanoribbon by unzipping the CNT include sodium nitrate, potassium permanganate, hydrogen peroxide, nitric acid, and deionized water. TiO_2 nanoparticles, with a size range of 15-20 nm, and either platinum or activated carbon were chosen for the counter electrode. To obtain chlorophyll dye for the solar cell, the Doctor blading is another technique to create working electrodes and was trailed in the initial phase method was employed.

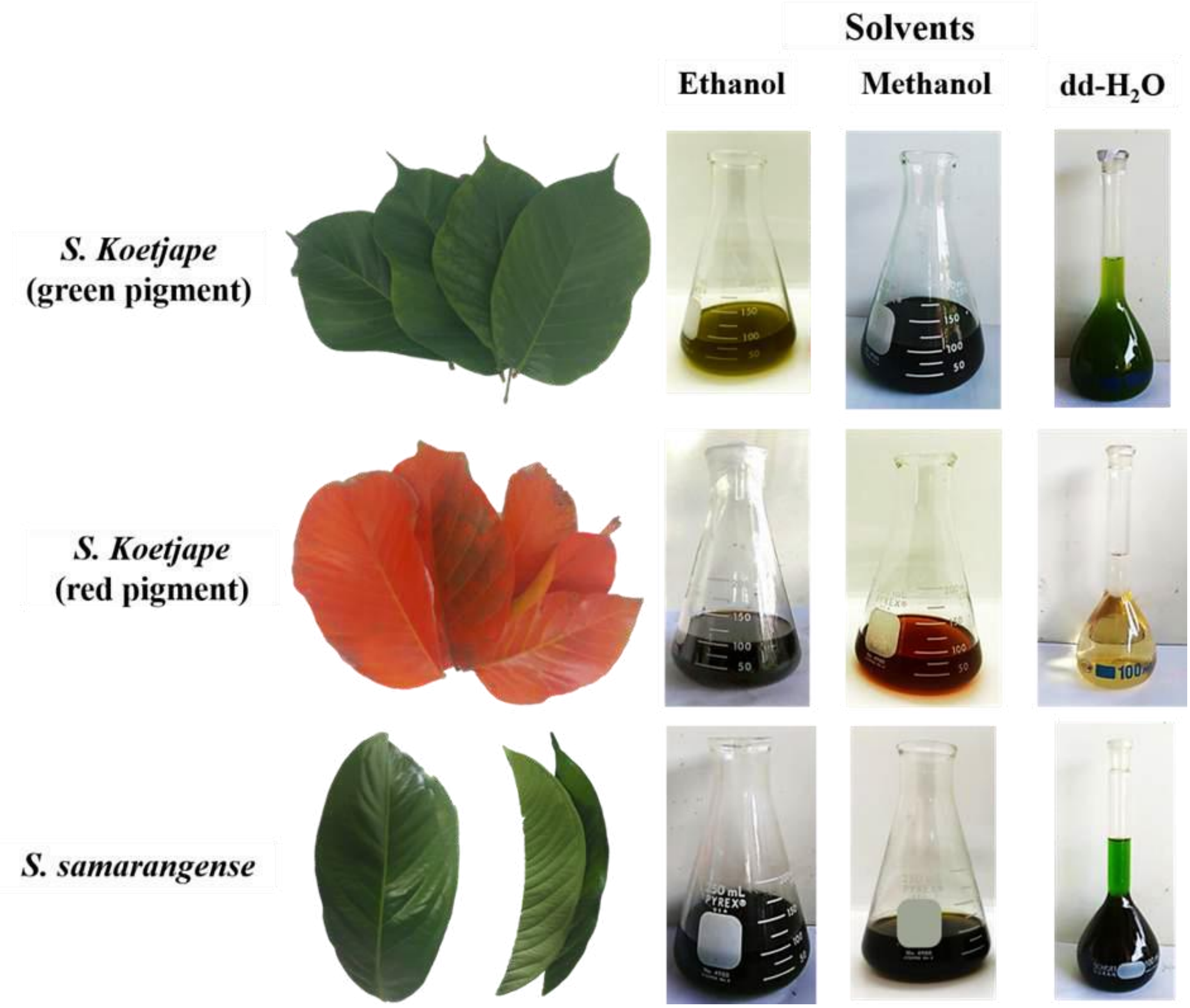

Figure 9. Plant-based materials and dye extraction

Leaves were initially blended with 100 ml of ethanol. After blending, the mixture was placed in a dry area for 10 minutes, allowing the ethanol to interact with the leaf components. The resulting mixture was then subjected to vacuum filtration using filter paper. The resulting extracts were gathered and sealed with aluminum foil to shield the chlorophyll from potential degradation. The physicochemical properties of the solvent used in the reaction of pigment extraction from leaves also have an important role to play (Figure 9). Several studies have indicated that chlorophyll-a can be degraded into chlorophyllide by catalyzing the hydrolase enzyme, chlorophyllase (CLH), during pigment extraction. This degradation pathway is reported to be the dominant natural degradation pathway (magnesium de-chelating) when the polar solvent-to-water ratio is lower than 1.0.

Natural dyes based on chlorophyll have many advantages compared to synthetic dyes, including a high absorption coefficient, a simple extraction process, and complete biodegradability. Chlorophyll is also known to have the highest light-harvesting ability among other naturally occurring pigments. However, despite this fact, it cannot be considered the perfect photosensitizer for DSSC on its own. This is because the light-harvesting ability of natural dyes in DSSC depends on several factors, such as the molecular interaction between the dye and the photoanode surface and the efficiencies.

Researchers have improved the energy conversion efficiency of natural photosensitizers by blending different dyes, pigmentation, and acidification. These strategies categorize photosensitizers based on natural molecules like carotenoids, betalains, flavonoids, and chlorophyll. Sensitizers are designed with functional groups like -COOH, -PO_3H_2, and -$B(OH)_2$ for stable adsorption onto semiconductor substrates, such as nanostructured TiO_2. Extracting dyes from fresh purple cabbage, spinach leaves, and turmeric stems, and combining them as photosensitizers with nanostructured ZnO-coated FTO substrates

Table 2. DSSC Performance Comparison

Dye	J_{sc} (mA/cm^2)	Voc (V)	ff	η (%)	Reference
Ocimum Gratissimum	0.044	0.466	0.400	0.021	Eli et al. (2016)
Green spinach leaves	0.052	0.590	0.530	0.016	Hasoon et al. (2015)
Morula leaves	0.059	0.472	0.050	0.001	Maabong et al. (2015)
Lemon leaves	1.080	0.592	0.100	0.036	
Black tea leaves	0.390	0.550	0.400	0.080	Abdel-Latif et al. (2015)
Green algae (fresh)	0.134	0.416	0.210	0.010	Taya et al. (2013)
Green algae (dried)	0.397	0.559	0.440	0.100	
Strobilanthes cusia	0.0003267	0.193	0.203	0.00067	
Strobilanthes cusia	0.0051833	0.306	0.462	0.0385	Ponnambalam et al. (2023a)
Strobilanthes cusia	0.0031438	0.283394	0.252	0.0118	
	0.2511	0.0089	14.98	0.016	
Ficus benjamina	0.0616	0.0447	31.72	0.198	Mejica et al. (2023)
	0.6026	0.0060	12.88	0.012	
Verdant turmeric	0.540	1.02	60	0.33	Hossain et al. (2017)
	0.555	0.970	65	0.31	
Acanthus sennii chiov.	0.507	0.491	60.4	0.150	Ayalew and Ayele (2016)
	0.475	0.351	60.6	0.101	
Lyceum Shawii	0.580	0.420	42	0.100	Abdel-Latif et al. (2015)
Doum pericarp	0.37	0.005	63	0.012	Mohammed et al. (2015)
	0.50	0.010	66	0.033	
Turmeric	0.288	0.529	0.48	0.03	Maurya et al. (2019)
Tomato	0.51	0.14	0.37	0.03	
Orange fruit	0.37	0.06	0.58	0.02	Supriyanto et al. (2018)
Carrot	0.36	0.04	0.64	0.009	
Bahraini henna	0.368	0.426	24.6	0.128	Jasim (2012).
Walnuts	0.73	0.304	0.39	0.0104	El-Agez et al. (2022)
Brassica olercea	0.50	0.37	0.54	0.13	Dumbravă et al. (2008)
Black carrot	1.3	0.4	0.47	0.25	Tekerek et al. (2011)
Dragon fruit	0.20	0.22	0.30	0.22	Ali and Nayan (2010)
Rosella	1.63	0.40	0.57	0.37	Grünwald and Tributsch (1997)
Pomegranate	0.50	2.97	0.49	0.73	Hosseinnezhad et al. (2015)
Begonia	0.63	0.537	0.72	0.24	Zhou et al. (2011)
Malabar spinach	0.0227	0.4877	0.32252	0.1021	Mejica et al. (2022)

in DSSCs enhances conversion efficiency. Mixed dyes show remarkable stability and the highest efficiency due to broad solar spectrum absorption, favorable electrochemical responses with fast electron transport, reduced recombination losses, and prolonged electron lifetime. Flowers: Red and purple pigments from flowers and leaves serve as DSSC sensitizers (Maurya et al. 2019). Anthocyanin-rich natural dyes extracted from plants like *Hibiscus rosa-sinensis*, have been used—potential lies in exploring similar dyes from plants like *Malvaviscus penduliflorus*. Enhancing dye absorption within 400-500 nm can be achieved by concentrated solutions or elevated temperatures.

Leaves: Mesoporous TiO_2 benefits DSSCs by providing ample surface for dye adsorption and electrolyte penetration. Natural dyes from Dimocarpus longan leaves, containing chlorophyll-a, chlorophyll-b, and carotenes, show promise. Chlorophyll's absorption peaks at 420 and 660 nm, aligning with dyes' absorption range in the visible region (400-420 nm and 650-700 nm).

Fruits: Natural plant-derived dyes are eco-friendly and cost-effective for DSSCs. Betel nut, rich in gallotannic acid, proves effective due to visible light absorption. Improving efficiency up to 11.9% has been achieved by substituting natural sensitizers, meeting requirements like absorption across solar spectrum and strong binding to semiconductor surfaces.

Other sources: Natural plant pigment dyes address DSSC limitations, enhancing spectral absorption responses. Mondo-grass berries and blackberries have been investigated as photosensitizers. Mondo-grass berry shows better stability and efficiency due to its diverse chemical compounds from anthocyanin and carotenoid families—Table 2. DSSC Performance Comparison, gives a detailed comparison of the performance of different DSSC based on various dye sources. Here are some key insights and discussion points based on the table:

- Dye sources: Various plant and fruit-based dyes have been studied for use in DSSCs. This highlights the efforts to find alternative, potentially sustainable, and eco-friendly materials for solar cell applications.

- Current density (Jsc): The current density values vary greatly across the dyes. Rosella, for example, has one of the highest recorded Jsc at 1.63 mA/cm^2, while *Strobilanthes cusia* has one of the lowest with 0.0003267 mA/cm^2.
- Open-circuit voltage (Voc): The Voc also varies with Pomegranate showing an exceptionally high Voc of 2.97 V, suggesting a higher potential energy difference between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of the dye.
- Fill factor (ff): Verdant-turmeric, Doum pericarp, and Ficus benjamina exhibit unusually high fill factors, reaching 60-65. It's worth noting that typical fill factors are usually below 1. Such values might indicate an anomaly or require further context.
- Efficiency (η): Efficiency is a key performance metric for solar cells. The Pomegranate dye seems to have the highest efficiency at 0.73%, followed by Rosella at 0.37%. This indicates that these dyes might be more suitable for harnessing solar energy.
- Recent research: It's interesting to note that *Strobilanthes cusia* and *Ficus benjamina* have recent studies from 2023 by Ponnambalam et al. (2023a) and Mejica et al. (2023), respectively, suggesting continued research interest in DSSCs.
- Variability within the same dye: Some dyes like *Strobilanthes cusia*, Verdant-turmeric, *Acanthus sennii* chiov., and Doum pericarp have multiple entries with different performance metrics, emphasizing that the processing, purity, and other factors of the dye source can greatly affect the DSSC's performance.
- Historical progress: The dates associated with each reference can offer insights into the progression of DSSC research over time. It would be interesting to plot these efficiencies over time to understand advancements in the field.

Therefore, DSSCs using natural dyes present a fascinating realm of study, offering a bridge between biology and materials science. The results vary based on the dye source, preparation method, and other factors. Continued research in this area promises potential breakthroughs in sustainable and eco-friendly solar technology.

8. Evaluating DSSC performance metrics

DSSCs undergo performance assessment through several key metrics: VOC, ISC, FF, and PCE. Their determinants can be located on the I-V curve, customary for photovoltaic devices (Abdel-Latif et al., 2013; 2015).

VOC: VOC reflects the cell's voltage without any current flow. The highest voltage a solar cell can provide when the electrodes are infinitely resistant. VOC emerges from the disparity between the electrolyte's redox potential and the semiconducting oxide's Fermi level.

ISC: ISC indicates the cell's output current when its voltage is zero. It’s the current acquired from the cell with zero load resistance. More commonly, it's given as the short-circuit current density (JSC), which is ISC measured against the cell's active area.

FF: FF can be defined as the maximum power output's ratio (Pm) against the multiplication of ISC and VOC. In essence, it gauges the electrical and electrochemical losses in DSSCs.

$$\mathrm{FF} = \frac{P_{\mathrm{m}}}{(I_{SC} \times V_{OC})} = \frac{I_{\mathrm{m}} \times V_{\mathrm{m}}}{(I_{SC} \times V_{OC})} \qquad [.]$$

Power-Conversion Efficiency (PCE): PCE is an efficiency metric that gauges the conversion from incident light to electrical power using the following equation:

$$\eta = \frac{J_{\mathrm{SC}} \times V_{\mathrm{OC}} \times \mathrm{FF}}{P_{\mathrm{in}}} \qquad [.]$$

Here, JSC, VOC, FF, and Pin denote the short-circuit current density, open-circuit voltage, fill factor, and incident power.

9. Methods for scientific analysis in photovoltaic research

Overview: The primary identifier for a Dye-Sensitized Solar Cell (DSSC) is its efficiency in transforming photons into electrons, denoted as photon-to-power conversion efficiency (PCE).

Procedure: A DSSC is exposed to simulated sunlight at an intensity equivalent to 1 sun (1 sun is equivalent to 100 mW.cm–2) in line with standard AM 1.5 conditions. The DSSC's particular region is irradiated, and simultaneously, it's linked to a potentiostat. The potentiostat sweeps through a pre-set voltage range at a determined rate while monitoring the current (I). The DSSC's efficiency is derived from the ratio between the generated power (Pout) and the input power (Pin).

Key Metrics: The theoretical maximum power (Ptheory) that a DSSC can produce, considering zero losses, is based on its short-circuit current density (JSC, at V=0) and the open circuit voltage (VOC, where J=0). The peak power point (Pmax) is where the current density (JMPP) and voltage (VMPP) of the cell are optimized. The fill factor (FF) represents the efficiency of the DSSC. For instance, p-type DSSCs typically exhibit a lower FF (30-40%) than n-type DSSCs (60-80%), which is noticeable from the JV curve shapes.

10. Comprehensive examination and synthesis

The focus of the present study was a meticulous exploration into the interplay between varying solvents - specifically, ethanol, methanol, and deionized water (dd-H_2O) - and the potency of dye-sensitized solar cells (DSSCs) which have been constructed using naturally derived dyes. Extracted from the foliage of *S. koetjape* and *S. samarangense*, these dyes reveal profound nuances in their behavior under the parameters of our analysis.

Upon assessing the salient metrics that determine the performance of DSSCs, including the Is), fill F), and VOC, a noteworthy observation was that DSSCs incorporated with dyes from *S. koetjape*, which were extracted via methanol, achieved an unparalleled peak efficiency of 0.081%. A systematic ranking, influenced by the choice of solvent for extraction, subsequently emerged as: SR-Methanol > SG-Methanol > TWA-Methanol > SR-ethanol > SR-dd-H_2O > SG-Ethanol > SG-dd-H_2O > TWA-Ethanol > TWA-dd-H_2O.

Probing deeper into these results, it becomes clear that methanol reigns superior as the solvent of choice for extracting dyes from these particular botanical sources (Hossain et al., 2017). Due to methanol's inherent electronegativity and pronounced hyperpolarizability, there is heightened dye adsorption onto the TiO_2 photoanode. This surge in dye attachment significantly augments the photo-harvesting capacities intrinsic to the DSSC mechanism. Adding another layer to this understanding, *S. koetjape*, particularly its red pigment, exhibited an edge over its counterpart, *S. samarangense*. A plausible rationale for this lies in its higher chlorophyll-a to the chlorophyll-b ratio in the resultant dye concoction.

Decomposing the findings further: The leaves of *S. koetjape* and *S. samarangense* emerge as viable and potent reservoirs for extracting natural dyes, which have shown to be efficacious in constructing DSSCs. The overarching performance of DSSCs, with these naturally sourced dyes, is contingent upon multiple facets. This includes the intrinsic properties of the dyes, the extraction solvent deployed, and the nuanced concentration gradient of the resultant dye.

An indomitable trend solidified within the data: DSSCs instilled with methanol-derived dyes manifest superior efficiency outcomes. Beyond mere efficiency, when extracted with methanol, these dyes also exhibited stellar durability, remaining undeterred in light-soaked environments and withstanding thermally challenging conditions. The ramifications of this meticulous study are profound, potentially heralding a paradigm shift in DSSC construction. The insights gained intimate the prospective dominance of botanically derived natural dyes over their synthetic counterparts, paving the way for a new epoch in DSSC technology - one marked by ecological responsibility and unparalleled efficiency.

10.1 Advantages of DSSCs

- Cost: DSSCs are cheaper than conventional silicon-based solar cells, as they can be made with abundant, low-cost materials.
- Flexibility: DSSCs can be fabricated on flexible substrates, opening up many applications, from wearable tech to portable chargers.
- Versatility: They can function efficiently in varying lighting conditions, from low-light indoor environments to cloudy days outdoors.
- Aesthetic appeal: DSSCs can be produced in various colors, making them suitable for building-integrated photovoltaics where appearance matters.

10.2 Challenges and limitations

- Stability issues: The liquid electrolyte in DSSCs can cause sealing problems, leading to potential leaks and reduced cell lifespan.
- Efficiency: DSSCs are efficient under low light conditions, but their conversion efficiency is lower than the best silicon-based cells.
- Scaling: Translating the success of small-scale DSSC devices to large-scale production and application has its challenges. In conclusion, while DSSCs may not yet replace the dominant silicon solar cells in the market, they hold promise for niche applications where flexibility, aesthetics, and performance under diffused light are crucial. Continuous research aims to enhance their stability and efficiency, pushing them closer to broader commercial viability.

11. Conclusion

In the rapidly evolving landscape of renewable energy, the shift towards advanced solar cell architectures aims at maximizing photo conversion efficiency. This review delves deep into the marked improvements in DSSC performance by adopting natural photosensitizers, such as chlorophyll and anthocyanin, sourced from fruits, vegetables, and flowers. Due to their cost-effectiveness and ease of synthesis, these natural dyes stand out as formidable alternatives to synthetic counterparts. We have dissected the intricate dynamics between TiO_2 and light-harvesting pigments, the role of solvents in pigment extraction, and various factors influencing the efficiency of DSSCs. Additionally, insights into the modifications in electrolytes, advancements in counter electrodes, and the nuances of interfaces between components of DSSCs have been highlighted. Notably, innovations like nanoporous TiO_2 photoanodes and the prospects of self-charging supercapacitors are emerging as game-changers in this domain. Though challenges, such as compatibility issues and system lifespan disparities, exist, the direction is clear: DSSCs, with their state-of-the-art enhancements, are poised to play a significant role in the future of renewable energy.

Conflict of Interest Declaration

The authors assert that no conflicts or personal affiliations might be construed as impacting the outcomes shared in this research.

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