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Efficiency enhancement of dye sensitized solar cell by using dyes; A green view from Pakistan

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ABSTRACT :

The global energy landscape is facing a critical challenge due to the rapid exhaustion of fossil fuel resources and their harmful impact on the environment, particularly in accelerating climate change. In response, renewable energy technologies are being pursued vigorously, with dye-sensitized solar cells (DSSCs) emerging as a promising third-generation photovoltaic option. DSSCs are notable for their cost-effective production, ease of assembly, reliable operation under low-light conditions, and compatibility with a variety of synthetic and natural dyes, enabling aesthetic flexibility through multi-color designs.

While DSSCs generally offer lower power conversion efficiencies compared to conventional silicon-based and thin-film solar cells, their performance can be significantly improved through strategic modification of the dye component. Natural dyes, derived from abundant plant and biological sources, present a sustainable and environmentally friendly alternative due to their simple extraction processes and green chemistry benefits.

However, the internal dynamics of these systems, particularly the charge transfer mechanisms in cells utilizing natural dyes, remain inadequately understood. To investigate these processes, electrochemical impedance spectroscopy (EIS) has become an essential analytical technique. EIS provides valuable insights into the electrochemical behavior of DSSCs by evaluating charge movement and resistance at different interfaces within the cell, thereby connecting material properties with overall device performance.

DSSCs hold a distinct position among organic solar technologies due to their affordability and ease of implementation. This review aims to examine their scientific and technological relevance by exploring the fundamental principles behind their operation, material components, key advantages, potential applications, performance metrics, and the ongoing challenges in advancing their efficiency—particularly through innovations in dye chemistry and the application of diagnostic tools like EIS.

Introduction

Dye-sensitized solar cells (DSSCs) are a class of low-cost photovoltaic devices designed to convert sunlight—especially in the visible spectrum—into electrical energy with notable efficiency. In the face of rising global population, industrial growth, and rapid technological development, the demand for reliable and sustainable energy continues to climb. Addressing this growing energy need is essential to support global economic progress, ensure political stability, and protect the environment [1].

Second-generation solar technologies, such as thin-film solar cells, were developed primarily to improve upon the limitations of traditional photovoltaic systems based on p–n junction diodes. These devices often use amorphous silicon and offer flexibility in application and reduced material usage [2]. DSSCs, introduced as an innovative approach, address some of these limitations by enabling light-to-electricity conversion through a more flexible mechanism.

A typical DSSC consists of four key components: a photoanode (working electrode), a dye molecule responsible for light absorption, a liquid electrolyte containing a redox couple, and a counter electrode (cathode). These are assembled between two transparent conductive glass layers, which are commonly coated with materials like fluorine-doped tin oxide (FTO) or indium tin oxide (ITO) to provide electrical conductivity while allowing light to pass through [3, 4].

Climate change, largely driven by human-induced greenhouse gas emissions from fossil fuel consumption, has brought increasing attention to clean energy alternatives [5]. The search for carbon-neutral energy systems has therefore intensified, aiming to meet growing energy needs while minimizing environmental harm [6–8].

Projections from international energy organizations suggest a consistent increase in global energy consumption in the coming decades. According to the International Energy Agency, global demand is expected to grow at an average annual rate of 2.2% between 2020 and 2040. This growth would see overall energy use rise from 24 terawatts (TW) to approximately 37 terawatt-hours (TWh), marking an increase of about 54% over the two-decade span [9].

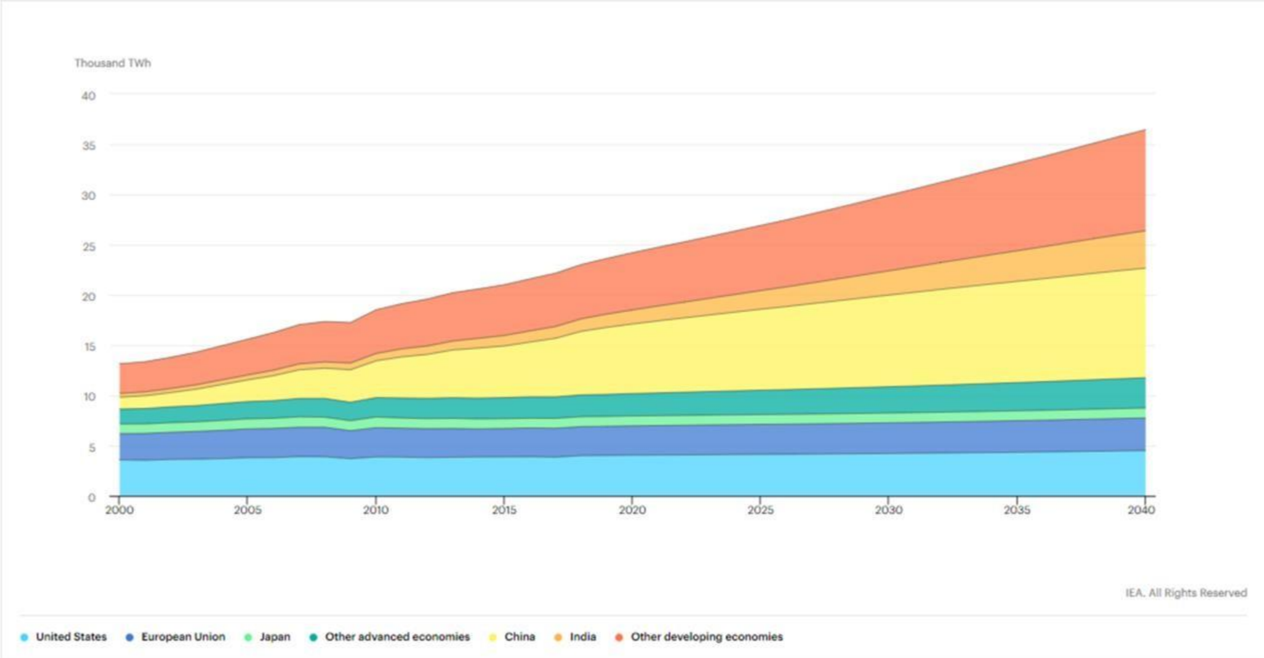


Fig 1: World energy demand projection until 2040

One of the primary limitations in dye-sensitized solar cells (DSSCs) is the comparatively lower efficiency of natural pigments when measured against their synthetic counterparts [10]. This review aims to examine the underlying working mechanisms of DSSCs and explore strategies for enhancing the photovoltaic efficiency of devices that utilize natural dyes. Solar cell efficiency, typically referred to as power conversion efficiency (PCE), represents the percentage of incident solar radiation that a cell can transform into usable electrical energy [11]. The efficiency (η) of a DSSC can be calculated using the following formula [12]:

$$\eta = Isc \times Voc \times ff / P_{in}$$

In this equation, IscI_{sc}Isc denotes the short-circuit current (or current density JscJ_{sc}Jsc), VocV_{oc}Voc is the open-circuit voltage, ffffff represents the fill factor, and PinP_{in}Pin is the incident light power.

While synthetic dyes—especially those based on ruthenium complexes—often outperform organic or natural counterparts in terms of efficiency, they involve multi-step synthesis and use of expensive materials [13, 14]. In contrast, natural dyes, such as chlorophyll, which plays a vital role in the photosynthesis process of plants [15], are drawing increased attention as environmentally friendly and cost-effective alternatives. Their simple extraction process and natural abundance make them appealing for sustainable DSSC fabrication [16].

Countries with rich biodiversity, like Iran, possess an extensive variety of plants that serve both medicinal and industrial purposes, including natural dye production [17, 18]. This botanical diversity has recently sparked interest in developing natural dye-sensitized solar cells (NDSSCs) within Iran, driven by the benefits of low material cost, ecological sustainability, and ease of preparation [19].

Despite these advantages, several technical challenges remain in optimizing the performance of NDSSCs. This review will first explore the operational principles, benefits, and structural elements of DSSCs. It will then delve into the selection and characterization of natural dyes used as sensitizers, discuss fabrication methods, and assess the photoelectric behavior of these devices—particularly those developed using flora native to Pakistan. The paper will conclude with an analysis of the current barriers in this field and offer insights into future directions for improving the efficiency and stability of natural dye-based DSSCs.

STRUCTURAL DESIGN OF DSSCs

A typical dye-sensitized solar cell (DSSC) is engineered to facilitate the conversion of sunlight into usable electrical energy and is composed of four critical components, each playing a distinct and essential role in the energy conversion process [20–24]:

1. **Sensitizing Dye** – Acts as a light absorber that captures photons and initiates electron generation.
2. **Photoanode** – Serves as the substrate for dye attachment and facilitates electron transport.
3. **Electrolyte** – Regenerates the oxidized dye after electron injection and maintains charge balance by mediating redox reactions.
4. **Counter Electrode (CE)** – Collects and returns electrons from the external circuit back into the electrolyte to complete the electrical cycle.

Operating Mechanism of DSSCs

The energy conversion in DSSCs follows a stepwise sequence of physical and electrochemical events, described as follows [25–29]:

1. **Light Absorption and Electron Excitation**: When sunlight hits the cell, the dye molecules anchored to the photoanode absorb photons. This energy excites electrons from the ground state (Highest Occupied Molecular Orbital, HOMO) to an excited state (Lowest Unoccupied Molecular Orbital, LUMO), initiating the generation of charge carriers.
2. **Electron Injection**: The excited electrons are rapidly transferred from the dye's LUMO to the conduction band of the photoanode, typically made from a mesoporous semiconductor like titanium dioxide (TiO_2).
3. **Electron Transport**: Once injected, these electrons travel through the semiconductor network toward the conductive glass substrate and then move through the external circuit, providing electrical power to a load.
4. **Dye Regeneration**: As the dye molecule loses an electron during excitation, it becomes oxidized. The redox electrolyte donates an electron to the dye, thereby restoring it to its ground state and enabling it to absorb light again.
5. **Electron Return via Counter Electrode**: The electrons that have passed through the external circuit eventually return to the cell through the counter electrode. Here, they reduce the oxidized form of the electrolyte, completing the circuit.

This cycle continues as long as the cell is exposed to light, enabling a continuous flow of electrons and consistent energy generation.

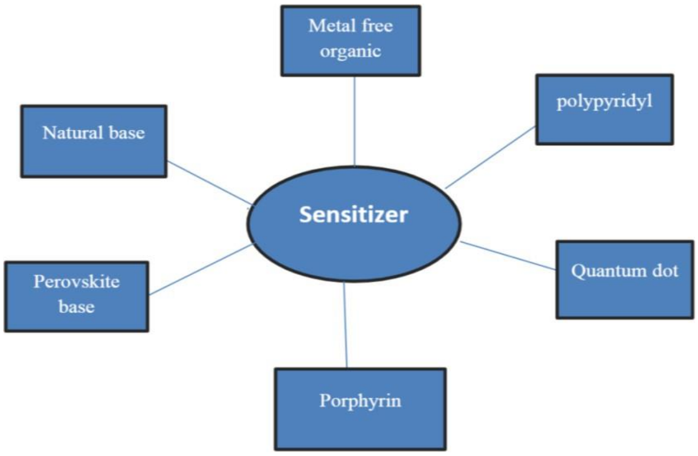


Fig 2: Different Types of Sensitizers Used in DSSCs

When the dye molecule (sensitizer) absorbs sunlight, it enters an excited state and subsequently releases an electron. This excited electron is transferred into the conduction band of the semiconductor, usually titanium dioxide (TiO_2). Once injected, the electrons travel through the interconnected TiO_2 nanoparticles, reaching the transparent conducting oxide (TCO) layer. From there, they are directed through an external circuit toward the counter electrode, creating an electric current and completing part of the electrical loop [30].

Following electron injection, the dye molecule remains in an oxidized state. To ensure continuous operation, the oxidized dye must be returned to its ground state. This regeneration is facilitated by the redox couple in the electrolyte, commonly iodide/triiodide (I^-/I_3^-). The iodide ions donate electrons to the oxidized dye, effectively restoring its original configuration and enabling it to participate in further light absorption cycles [31].

Meanwhile, the oxidized triiodide ions produced during the dye regeneration process must be converted back to iodide ions. This reduction occurs at the counter electrode, often coated with platinum due to its high catalytic activity. The electrons that have passed through the external circuit reduce triiodide (I_3^-) back to iodide (I^-), maintaining the redox balance within the electrolyte and sustaining the continuous flow of charge.

It is important to note that during these processes, two major recombination pathways can diminish cell performance. These include the back-transfer of electrons from the TiO_2 to either the oxidized dye or triiodide ions. These recombination reactions typically occur on a microsecond timescale (10^{-6} seconds) and are a key focus in efforts to enhance DSSC efficiency [30,31,32].

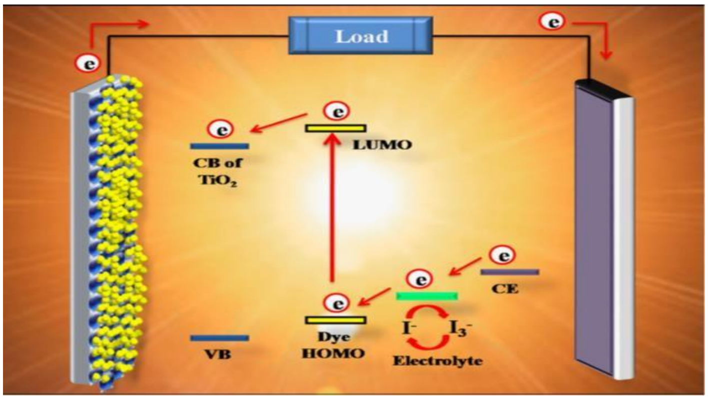


Fig 3: Working Principle of DSSC

Natural Dyes

The exploration of natural dyes as photosensitizers in dye-sensitized solar cells (DSSCs) has gained significant attention due to their cost-effectiveness and environmental benefits. Unlike synthetic dyes, natural dyes such as anthocyanins, chlorophyll, flavonoids, and carotenoids offer a sustainable alternative. These pigments, derived from various plant sources, have been utilized in DSSCs to enhance light absorption and electron injection processes .

1. Anthocyanins: Found abundantly in fruits like blueberries and mulberries, anthocyanins are water-soluble pigments that exhibit strong absorption in the visible spectrum. Their presence in DSSCs has been shown to improve power conversion efficiency, with mulberry-based DSSCs demonstrating a significant increase in power output under natural sunlight conditions .

2. Chlorophyll: As the primary pigment in plants responsible for photosynthesis, chlorophyll has been investigated for its potential in DSSCs. Studies have indicated that chlorophyll extracted from sources like Peltophorum pterocarpum leaves can achieve power conversion efficiencies up to 6.07%, highlighting its effectiveness as a natural sensitizer .

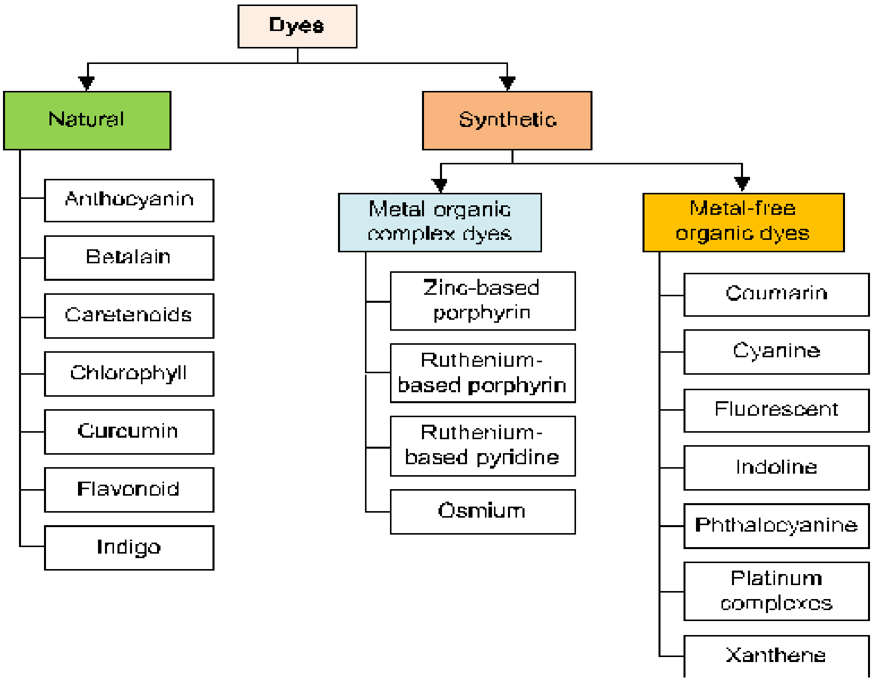
3. Flavonoids: Present in various plant parts, flavonoids contribute to the coloration and UV absorption properties of plants. Their incorporation into DSSCs has been explored, with research focusing on optimizing extraction methods and understanding their role in enhancing cell performance .

4. Carotenoids: These pigments are responsible for the red, orange, and yellow colors in many fruits and vegetables. Carotenoids have been studied for their potential in DSSCs, with research examining their light absorption capabilities and stability under operational conditions .

Dual-Layer Photoanode in DSSCs

To further enhance the performance of DSSCs, the implementation of a dual-layer photoanode has been proposed. This configuration typically involves a thin blocking layer beneath a mesoporous TiO_2 film, which serves to improve electron transport and reduce recombination losses. Notably, this approach can be effective without the need for treatment with a $TiCl_4$ solution, simplifying the fabrication process while maintaining or even improving cell efficiency .[33,34,35]

Approximately 90% of the world's saffron is produced in Iran [36]. Saffron (Crocus sativus) is primarily cultivated in arid and semi-arid regions and is



widely used as a natural ingredient in food. Each year, around 12,000 tons of saffron petals are produced, which are typically discarded as agricultural waste since only the stamen of the saffron crocus is utilized as the spice [37]. However, these saffron petals are rich in valuable compounds such as flavonoids, anthocyanins, and flavonols [38], which make them an excellent source of natural pigments for dye-sensitized solar cells (DSSCs). One notable compound, delphinidin, an anthocyanin with six hydroxyl groups, can be efficiently extracted from the petals using an acidic ethanol solution (pH ≈ 2) at 25.8°C [38]. Recent research by Hosseinpanahi and colleagues explored the potential of saffron petal extract as a photosensitizer in natural dye-sensitized solar cells (NDSSCs) [39]. Their study revealed that the extract has a maximum absorption wavelength of 510 nm.

S no	parameters	Natural dyes	Synthetic dyes
1	cost	Locally available resource, extracted from plants, flowers, fruits and roots. This results low cost [40].	Complex material formed by different chemical reaction therefore results in high cost [45, 46].
2	Environment effect	Less effects on the environmental due being its natural occurrence [41].	Bad effects on the environmental due to its chemical nature [41].
3	stability	Degradation of natural dye in the presence of sunlight radiation results stability[42]	Slowly degrade in the presence of sunlight therefore long life of DSSC [43].
4	Adsorption spectrum	The dyes have shown absorption in broad range of the visible region (400–700 nm) of the solar spectrum.[40]	N3 dye has absorption upto 800 nm [46,43]
5	efficiency	The efficiency of NDSSC is low due to degradation of natural dye [42].	DSSC based on synthetic dyes have shown higher efficiency as compared to NDSSC.
6	Availability	Natural thus 100% availability [43].	Noble material thus no long term availability [47,48]
7	Fabrication process	Requires simple and direct chemical procedures, making natural dye production less expensive [44]	Requires multi procedures, which involves a variety of solvents and time consuming purification processes, making synthetic dye production very expensive [49]

Table 1: Differentiation Between Natural and Synthetic Dyes

The problem of stability results less efficiency still we know that natural dyes are environmental friendly. Absorbance of Ruthenium complexes have shown maximum value in visible region. Therefore, these sensitizers gives considerable electrical output than natural dyes. Contrary, the benefits of natural dyes are non-toxic effect and its natural occurrence [50–60]

Plant source	Photo	JSC (mA.cm^{-2})	VOC (mV)	FF	h (%)	ref
saffron petal		2.31	0.397	0.71	0.66	[61]
Radish		5.1	0.49	0.59	1.47	[63]
Red grape		4.3	0.55	0.55	1.3	

Sambucusebul us Sour		3.25	0.58	0.54	1.01	
bitter orange peel		1.53	0.59	0.60	0.54	
Red onion peel		0.31	0.61	0.60	0.11	
Adonis Flammea		0.40	0.59		0.16	
Pastinaca sativa		7	0.42		0.95	[64]
sour pomegranate		0.5	2.97		0.73	[65]
sweet pomegranate		0.62	4.60		1.57	
Red onion		1.5e4.33	0.38e0.66	0.85e0.98	n.a	[66]
Red cabbage		1.81e6.14	0.39e0.54	0.77e0.94	n.a	
Egg plant		1.41e3.81	0.22e0.54	0.39e0.89	n.a.	
Saffaron		0.17	0.51	0.71	0.06	[67]

Table 2: Photochemical properties of natural dyes based on DSSC

Natural dyes, typically derived from plant materials, fruits, and flowers, exhibit unique photochemical properties that make them effective sensitizers for dye-sensitized solar cells (DSSCs). These characteristics determine how efficiently the dye can absorb sunlight and convert it into electrical energy. The primary photochemical characteristics that influence the performance of natural dyes in DSSCs include: For natural dyes to be effective in DSSCs, they must absorb light efficiently, especially in the visible spectrum (400–700 nm), allowing them to trap solar energy effectively. Common natural dyes such as anthocyanins, carotenoids, and betalains absorb light strongly in this range:

- *Anthocyanins* (found in berries, hibiscus, etc.) absorb blue-green light.
- *Carotenoids* (from carrots, marigold, etc.) absorb blue-violet light.
- *Betalains* (from beets) absorb green light.

Molar efficiency coefficient: This property refers to the dye's ability to absorb light at a particular wavelength. A higher molar extinction coefficient means the dye can absorb more light, even at lower concentrations. While natural dyes typically have moderate extinction coefficients, they can still be effective if optimized for DSSC applications.

Electron Efficiency Engine: Upon photon absorption, a natural dye becomes excited and must inject an electron into the conduction band of the TiO_2 semiconductor in the DSSC. Efficient electron injection is essential for generating a flow of electrical current, making this property vital for the overall performance of the solar cell.

Regeneration by Electrolyte: After electron injection, the oxidized dye needs to be rapidly regenerated by receiving an electron from the redox couple in the electrolyte, typically iodide/triiodide. This regeneration process helps to prevent recombination and ensures a continuous cycle, keeping the solar cell functioning efficiently. The redox potential of the dye must align with that of the electrolyte to enable this regeneration.

Photostability: Photostability is crucial for natural dyes, as they must withstand prolonged exposure to sunlight without degradation. However, many natural dyes tend to break down due to factors such as heat, pH changes, or oxidation. To enhance their stability, natural dyes can be stabilized through:

- pH modification
- Chemical modification
- Co-pigmentation
- Encapsulation

Binding affinity for TiO2: Natural dyes must bind effectively to the surface of TiO_2 to facilitate electron transfer and optimize dye loading. Dyes with hydroxyl or carboxylic groups tend to bind well to TiO_2. For instance, anthocyanins, which contain multiple hydroxyl groups, have a strong binding affinity to TiO_2, aiding in efficient electron transfer.

By understanding and optimizing these key properties, natural dyes can be effectively used in DSSCs, offering a sustainable and cost-effective alternative to synthetic dyes.

Property	Importance in DSSC	Role in Natural Dyes
Absorption Spectrum	Harvests solar energy	Visible range, depends on pigment
Molar Extinction Coefficient	Determines the efficiency of light absorption	Moderate, usually adequate
Electron Injection	Induces current generation	Dependent on energy level of the excited state
Dye Regeneration	Sustains photocurrent	Must match electrolyte redox potential
Photostability	Impacts long-term device performance	Requires improvement
TiO_2 Binding	Facilitates effective charge transfer	Attained through functional groups

Conclusion

1. *Dye-sensitized solar cells (DSSCs)* offer a promising alternative to conventional photovoltaic technologies due to their low manufacturing costs, ease of production, and use of environmentally friendly materials. Among the key components of DSSCs, the dye plays a crucial role in light absorption, electron injection, and overall device efficiency. Natural dyes, particularly those derived from native plants in Pakistan, present sustainable and cost-effective options as sensitizers. These dyes, which are rich in anthocyanins, carotenoids, and betalains, exhibit good light-harvesting properties and can be optimized through functionalization to enhance their binding with TiO_2 and improve charge transfer.
2. While natural dyes offer environmental benefits, they face challenges such as limited photostability, lower molar extinction coefficients, and less efficient regeneration compared to synthetic dyes. However, advancements in co-sensitization, molecular engineering, and hybridization with metal complexes or organic dyes are helping to overcome these limitations and improve the performance of natural dye-based DSSCs.
3. This review highlights the untapped potential of Pakistan's rich biodiversity for developing sustainable green energy solutions. Future research should focus on discovering new plant sources, enhancing dye stability, and developing cost-effective fabrication methods. These efforts will be key to advancing DSSC technology as a viable solution for sustainable energy production, not only in Pakistan but also globally.

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