

CHAPTER 6

Advances in Dye-Sensitized Solar Cells: Materials, Mechanisms, and Emerging Applications

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Received: 13 August 2025; Accepted: 08 September 2025; Available online: 11 September 2025

Abstract: Dye-sensitized solar cells (DSSCs) are an emerging third-generation photovoltaic technology distinguished by their economical production methods, optical transparency, structural flexibility, and strong operational efficiency under reduced light intensity. Unlike traditional silicon-based solar cells, DSSCs separate light absorption and charge transport, using dye molecules to capture photons and inject electrons into a wide-bandgap semiconductor, commonly BiOCl or TiO₂, while a redox electrolyte regenerates the oxidized dye. Since the pioneering work of O'Regan and Grätzel in 1991, research has focused on improving efficiency, stability, and scalability through material innovations, nanostructured electrodes, novel sensitizers, and alternative electrolytes. DSSCs consist of key components: a high-

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Materials Science: Advances in Synthesis, Characterization and Applications (Vol. 1) - Digambar M. Sapkal, Harshal M. Bachhav, Gaurav Mahadev Lohar, Sanjay P. Khairnar (Eds.)

ISBN: 978-93-95369-55-8 (paperback) 978-93-95369-46-6 (electronic) | © 2025 Advent Publishing.

<https://doi.org/10.5281/zenodo.17097490>

surface-area photoanode for dye loading and electron transport, a sensitizer with strong absorption and stability, an electrolyte with suitable redox potential and conductivity, and a counter electrode with high catalytic activity. Fabrication involves substrate preparation, mesoporous semiconductor deposition, dye adsorption, counter electrode assembly, and electrolyte sealing, with emerging low-temperature methods enabling flexible devices. Characterization techniques such as UV–Vis spectroscopy, current–voltage measurements, electrochemical impedance spectroscopy (EIS), and incident photon-to-current efficiency (IPCE) analysis provide insights into optical absorption, charge transport, recombination, and overall performance. While challenges remain in long-term stability and large-scale manufacturing, ongoing advances in materials engineering, device architecture, and encapsulation strategies continue to position DSSCs as a viable option for niche applications, particularly in building-integrated photovoltaics, indoor energy harvesting, and flexible electronic systems.

Keywords: Dye-sensitized solar cells, Photoanode materials, Electron injection, Redox electrolyte, Building-integrated photovoltaics.

1. Introduction

1.1. Overview and Historical development of third-generation solar cells

Dye-sensitized solar cells (DSSCs) represent an important branch of third-generation photovoltaic technologies that aim to combine low production cost, material versatility, and reasonable light-to-electricity conversion efficiency ¹. Unlike conventional silicon photovoltaics that rely on p–n junctions and bulk semiconductor absorption, DSSCs separate light absorption from charge transport: molecular dyes harvest sunlight and inject electrons into a wide-bandgap semiconductor (typically nanostructured TiO₂), while a redox electrolyte completes the circuit by regenerating the oxidized dye ¹⁻². This decoupled architecture enables the use of inexpensive, flexible substrates, semi-transparent designs, and color/tint options that are attractive for building-integrated photovoltaics and low-light applications ².

The modern era of DSSCs began with the landmark demonstration by O'Regan and Grätzel in 1991, who reported a prototype device based on colloidal TiO₂ films sensitized with ruthenium dyes. Their work showed that efficient photoconversion could be achieved using a porous semiconductor network to provide a very large surface area for dye adsorption, and a liquid iodide/triiodide electrolyte to mediate charge transport ²⁻³. That paper established the core elements of DSSC design—mesoporous photoanode, molecular sensitizer, redox mediator, and counter electrode—and sparked three decades of intensive research into materials, interfacial engineering, and device stability ³.

Since then, DSSC research has expanded along several complementary lines. Scientists have engineered new sensitizers (including metal-free organic dyes and natural extracts), developed quasi-solid and solid electrolytes to address leakage and longevity, and explored alternative photoanode materials and nanostructures to improve electron transport and light scattering ³⁻⁴. Efforts have also targeted low-

temperature fabrication for flexible substrates, plasmonic and co-sensitization strategies to broaden spectral response, and robust encapsulation methods to extend operational lifetime²⁻⁴. Today's reviews and studies emphasize not only incremental efficiency gains but also device reliability, eco-friendliness of materials, and integration into hybrid systems for indoor or building-integrated energy harvesting⁴.

Although DSSCs have not replaced silicon on a large scale, they occupy a unique niche where flexibility, transparency, and cost matter more than absolute peak efficiency^{1-3,5}. The chapter that follows will build on this historical foundation to examine advanced materials and engineering approaches that aim to make DSSCs more efficient, durable, and commercially viable⁵.

1.2. Advantages and Current Status of DSSCs

Dye-sensitized solar cells (DSSCs) offer several notable advantages that differentiate them from traditional photovoltaic technologies. One of the most significant is their low-cost fabrication⁴⁻⁶. Unlike crystalline silicon cells, DSSCs do not require high-purity semiconductor wafers or expensive vacuum deposition processes. Instead, they can be fabricated using simple coating, printing, or dipping methods at relatively low temperatures, reducing both material and manufacturing expenses⁶.

Another appealing feature is their transparency. The thin, semi-transparent active layers allow visible light to pass through, making DSSCs suitable for building-integrated photovoltaics (BIPV), skylights, and window applications^{5,6}. By tuning the dye's absorption spectrum, cells can be produced in various colors without severely impacting performance, enhancing their aesthetic appeal for architectural integration^{3-5,7}.

Flexibility is also a strong point. DSSCs can be fabricated on flexible substrates such as plastics or metal foils when low-temperature processes are employed, enabling lightweight and portable solar devices. This opens up opportunities in wearable electronics, solar curtains, and devices where conventional rigid modules are impractical^{1-3,6}.

In terms of efficiency, the most recent laboratory-scale DSSCs have achieved power conversion efficiencies exceeding 14% under standard one-sun illumination using cobalt-complex electrolytes and co-sensitized dyes⁶⁻⁸. Under low-light or indoor conditions, DSSCs have demonstrated exceptional performance, with efficiencies above 30% reported for certain designs⁷.

However, limitations remain. The long-term stability of DSSCs is still a major concern, especially for devices using liquid electrolytes that can evaporate or leak over time. Although solid-state and quasi-solid-state electrolytes improve stability, they often exhibit lower ionic conductivity, which can reduce efficiency⁷. Additionally, while DSSCs perform well under diffuse light, their efficiency under direct high-intensity sunlight is generally lower than that of commercial silicon photovoltaics⁷⁻⁸.

Another challenge is scale-up. While small-area laboratory cells can achieve high efficiencies, scaling up to module sizes often results in performance loss due to increased series resistance, electrolyte transport limitations, and uniformity issues in dye loading and electrode deposition⁶⁻⁸.

Despite these drawbacks, the combination of low-cost processing, transparency, flexibility, and strong performance under indoor lighting ensures that DSSCs remain an active area of research ⁵⁻⁸. With continued advances in materials engineering and device architecture, DSSCs could secure a significant role in niche photovoltaic markets and complementary energy-harvesting applications ^{1-2,7}.

2. Working Principle of Dye-Sensitized Solar Cells (DSSC)

Dye-sensitized solar cells (DSSCs) generate electrical energy from light by decoupling the mechanisms of photon absorption and charge carrier transport ⁹. Unlike conventional p-n junction solar cells, a DSSC uses a molecular sensitizer to harvest photons and inject electrons into a wide-bandgap semiconductor ^{8,9}. The typical device stack includes a transparent conducting substrate, a mesoporous semiconductor photoanode, an adsorbed dye monolayer, an electrolyte containing a redox mediator, and a counter electrode that completes the circuit ¹⁰.

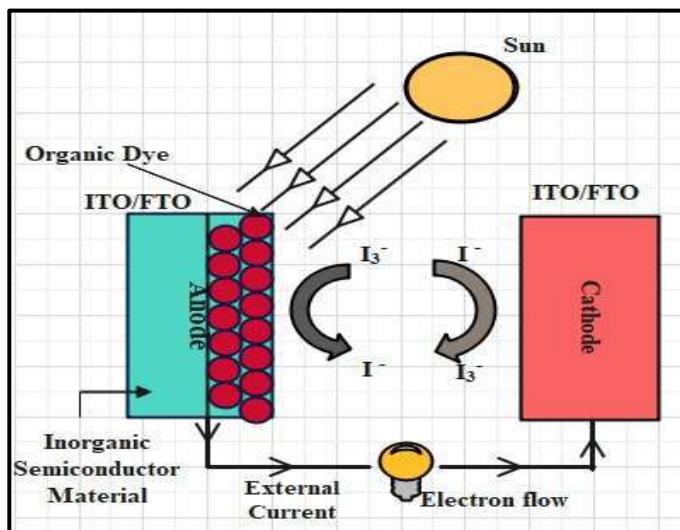


Fig. 1. Schematic Illustration of Photon-Induced Electron Transfer and Charge Transport Mechanism in a Dye-Sensitized Solar Cell

2.1. Light harvesting and electron injection

When sunlight strikes the sensitizer molecules anchored to the semiconductor surface, photons excite electrons from the dye's ground state to an excited electronic state ^{9,10}. If the excited-state energy of the dye is higher than the conduction band edge of the semiconductor, an ultrafast electron transfer (electron injection) occurs from the dye's excited state into the semiconductor's conduction band ⁸⁻¹⁰. This injection is typically sub-picosecond to picosecond in efficient systems and is a crucial step because it competes with the dye's internal relaxation and nonradiative decay pathways ⁹⁻¹¹. Efficient electron injection requires strong electronic coupling between the dye's anchoring group and the oxide surface, as well as favorable energy alignment ¹¹.

2.2. Photoanode excitation → dye molecule → semiconductor (**BiOCl**)

The photoanode is a high-surface-area, mesoporous film of nanocrystalline **BiOCl**. The film offers a very large internal surface area to maximize dye loading, thereby increasing light absorption per projected area^{10,11}. After injection, electrons occupy conduction band states and begin to diffuse through the interconnected nanoparticle network toward the transparent conducting oxide (TCO) collector¹². The porous structure enhances dye adsorption and provides light-scattering effects that improve photon capture^{8-10,12}.

2.3. Electron transport and collection

Transport occurs by diffusion of injected electrons through the **BiOCl** network; the movement is influenced by trap states, particle necking, and film morphology¹¹⁻¹³. Because the network is disordered and transport is diffusive rather than ballistic, the electron lifetime must exceed the transit time to the collector to ensure efficient collection¹³. Recombination pathways—primarily electron transfer from **BiOCl** to oxidized dye molecules or to oxidized species in the electrolyte reduce the number of electrons reaching the external circuit. Surface passivation layers and blocking layers are commonly used to suppress interfacial recombination^{8, 10-13}.

2.4. Role of the electrolyte (I^-/I_3^- redox couple)

The electrolyte contains a redox mediator that regenerates the oxidized dye after electron injection¹³. The classical mediator is the iodide/triiodide (I^-/I_3^-) couple: after injection the dye becomes oxidized and is reduced back to its ground state by iodide, which in turn is oxidized to triiodide¹⁴. Triiodide migrates to the counter electrode, where it is reduced to iodide through the electrons supplied via the external circuit^{13,14}. The redox mediator must possess suitable redox potential, high diffusion coefficient, and chemical stability.

2.5. Regeneration of dye molecules.

Dye regeneration is typically much faster than recombination if the mediator and dye are well matched energetically. Fast regeneration prevents back-electron transfer from **BiOCl** to the oxidized dye¹⁵⁻¹⁸. The kinetics of dye regeneration and mediator diffusion therefore directly affect the open-circuit voltage and the fill factor¹⁷.

2.6. Overall energy conversion mechanism

A simplified energy diagram of a DSSC illustrates the dye's highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) in relation to the **BiOCl** conduction band and the redox potential of the mediator. Photon absorption promotes dye electrons from HOMO to LUMO; electrons drop from LUMO into the **BiOCl** conduction band (injection), diffuse to the TCO and flow through the external circuit to the counter electrode; meanwhile the oxidized dye is reduced by the mediator, which is itself regenerated at the counter electrode¹⁵⁻²⁰. Efficiency depends on maximizing photon absorption,

ensuring ultrafast injection and dye regeneration, minimizing recombination, and optimizing transport of both electrons in the semiconductor and ions in the electrolyte¹⁹⁻²¹.

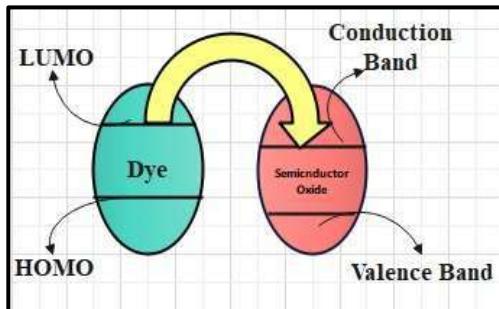


Fig. 2. Energy Level Alignment and Electron Transfer from Dye to Semiconductor in a DSSC

3. Materials in DSSCs and Selection of Materials

Dye-sensitized solar cells (DSSCs) are third-generation photovoltaic devices that rely on a combination of carefully engineered materials to convert solar energy into electricity through photoinduced electron transfer²²⁻²⁵. The performance of a DSSC is governed by the choice of materials in each of its key components: the photoanode, dye sensitizer, electrolyte, and counter electrode²³. Each material must fulfill specific criteria to ensure efficient light harvesting, fast electron transport, minimal recombination, and long-term stability²⁴.

3.1. Photoanode Materials

The photoanode serves as the scaffold for dye adsorption and the conduit for electron transport. Bismuth Oxychloride (BiOCl) remains the most widely used semiconductor due to its appropriate conduction band energy, low toxicity, and strong chemical stability in electrolyte environments. Other semiconductors such as Titanium dioxide (TiO₂), zinc oxide (ZnO), tin oxide (SnO₂), and niobium pentoxide (Nb₂O₅) have been explored for enhanced electron mobility or modified light scattering properties²²⁻²⁸. Nanostructures, such as nanoparticles, nanorods, and hierarchical architectures, improve surface area and dye loading, leading to increased photocurrent²³⁻²⁵.

Selection criteria

- High surface area for maximum dye adsorption.
- Energy band alignment with the dye's LUMO for efficient electron injection.
- High electron mobility to reduce transport resistance.
- Stability under UV and electrolyte exposure.

3.2. Dye Sensitizers

The dye absorbs photons and injects electrons into the semiconductor conduction band. Ruthenium-based dyes (e.g., N3, N719, and Z907) are widely used for their broad absorption spectra, high molar extinction

coefficients, and chemical robustness²³⁻²⁶. However, due to cost and environmental concerns, organic dyes and natural pigments have been studied²⁸.

Selection criteria

- Strong absorption in the visible and near-infrared range.
- Appropriate LUMO energy above the conduction band edge of the photoanode.
- High photostability and fast regeneration by the electrolyte.
- Synthetic availability and cost-effectiveness.

3.3. Electrolyte Materials

The electrolyte regenerates the oxidized dye and facilitates charge transport between electrodes. The most common is the iodide/triiodide (I^-/I_3^-) redox couple in organic solvents. Ionic liquids, cobalt-based redox mediators, and solid-state hole transport materials (HTMs) are explored for improved stability and reduced volatility^{27,28}.

Selection criteria

- High ionic conductivity.
- Favorable redox potential for fast dye regeneration.
- Low volatility and long-term stability.
- Chemical compatibility with other cell components.

3.4. Counter Electrode Materials

The counter electrode catalyzes the reduction of the redox species in the electrolyte. Platinum is the benchmark due to its high catalytic activity and electrical conductivity, but alternatives such as carbon nanotubes, graphene, and conducting polymers have gained attention for cost reduction and improved corrosion resistance^{29,30}.

Selection criteria

- High catalytic activity for redox reaction.
- Low charge-transfer resistance.
- Stability in electrolyte environment.
- Scalable and low-cost fabrication.

3.5. Material Synergy and Optimization

The ultimate performance of DSSCs depends on the synergistic optimization of all materials. For instance, the combination of BiOCl with scattering layers improves light harvesting, while using co-sensitizers broadens spectral absorption³². Electrolyte viscosity can influence electron recombination rates, and counter electrode roughness affects catalytic efficiency²⁸⁻³².

Table 1: Comparative Efficiency Table for DSSC Materials

Sr. No	Photoanode & Dye Combination	Electrolyte / Counter Electrode	Efficiency (%)	References
1	TiO ₂ nanoparticles + N719 (Ru-based)	I ⁻ /I ₃ ⁻ / Pt	11.2	22
2	TiO ₂ nanotubes + Z907 (Ru-based)	I ⁻ /I ₃ ⁻ / Pt	9.8	23
3	ZnO nanorods + N719	I ⁻ /I ₃ ⁻ / Pt	7.5	24
4	SnO ₂ nanoparticles + N719	Co ²⁺ /Co ³⁺ / Pt	8.9	25
5	Nb ₂ O ₅ nanoparticles + N719	I ⁻ /I ₃ ⁻ / Pt	7.1	26
6	TiO ₂ /SiO ₂ composite + N3	I ⁻ /I ₃ ⁻ / Pt	10.3	27
7	TiO ₂ nanoparticles + D35 (organic dye)	Co ²⁺ /Co ³⁺ / PEDOT:PSS	8.6	28
8	TiO ₂ nanoparticles + SQ2 (organic dye)	I ⁻ /I ₃ ⁻ / Carbon nanotube	7.9	29
9	TiO ₂ nanoparticles + Anthocyanin (natural dye)	I ⁻ /I ₃ ⁻ / Pt	1.9	26
10	TiO ₂ nanoparticles + Y123 (organic dye)	I ⁻ /I ₃ ⁻ / Graphene	9.2	30
11	BiOCl nanoparticles + N719 (Ru-based)	I ⁻ /I ₃ ⁻ / Pt	6.5	31
12	WO ₃ nanostructures + N719	I ⁻ /I ₃ ⁻ / Pt	5.8	32

4. Fabrication Techniques

Fabrication of a high-performance DSSC is a careful integration of materials chemistry and layer-by-layer processing. The canonical device stack — TCO glass (or flexible TCO film) → compact TiO₂ blocking layer → mesoporous TiO₂ scattering/photoanode → dye monolayer → electrolyte (or solid HTM) → counter electrode — is straightforward in concept but demanding in practice: each step strongly affects charge injection, transport, recombination and long-term stability³³⁻³⁴.

4.1. Substrates and transparent conducting oxides

Fabrication begins with the substrate. Fluorine-doped tin oxide (FTO) on glass is the standard because it combines decent conductivity, optical transparency and thermal stability during high-temperature processing³³. For flexible or wearable DSSCs, ITO/PET or ITO/PEN and emerging flexible TCOs are

used; such substrates impose strict low-temperature processing constraints (typically $<150\text{ }^{\circ}\text{C}$), driving alternative sintering and chemical strategies³⁴.

4.2. **TiO₂ paste preparation and deposition methods**

The mesoporous TiO₂ electrode is the heart of the DSSC — it provides the high internal surface area for dye loading and forms the percolating network for electron diffusion. Lab and pilot-scale fabrication use several deposition techniques depending on the desired film thickness, morphology and throughput³⁴⁻³⁶:

- Doctor-blade / tape casting: simple, low-cost, and widely used for lab cells; thickness is controlled by tape gap and blade³⁴.
- Screen printing: industry-friendly for repeatable, larger-area films and common in module prototypes³⁵.
- Spin coating: ideal for thin, uniform films in research devices but not scalable³⁶.
- Spray pyrolysis / spray coating and ink-jet printing: allow patterned deposition and are more compatible with roll-to-roll³⁷.
- Slot-die and blade coating: increasingly used for continuous processing and scalable manufacturing³⁸.

Paste formulation (particle size distribution, binder type, solvent, rheology modifiers) dictates film uniformity, adhesion and porosity; optimizing paste chemistry is as important as choosing the deposition method³⁶⁻³⁷.

4.3. **Sintering and low-temperature alternatives.**

Conventional DSSC BiOCl films are sintered at 200–250 °C to remove organics and create interparticle necking that enables good electronic connectivity. This thermal requirement limits substrates and raises cost^{31-33,38}. Consequently, many low-temperature strategies have been developed: chemical sintering (additives that promote necking at lower T), UV/O₃ or plasma treatments, laser sintering, photonic (flash) sintering, roll-to-roll compatible compression and transfer techniques, and novel binder systems that allow densification at $\approx 100\text{--}200\text{ }^{\circ}\text{C}$. These approaches are central to bringing DSSCs to flexible and large-area formats³⁶⁻³⁸.

4.4. **Dye sensitization (adsorption) and interfacial treatments.**

After BiOCl preparation, the mesoporous film is sensitized by immersion in a dye solution (often N719, organic dyes, or natural dyes). Sensitization conditions (solvent, dye concentration, temperature, time) control surface coverage and aggregation. Surface treatments. e.g., TiCl₄ post-treatment, co-adsorbents (chenodeoxycholic acid, etc.), or ultrathin compact layers — reduce recombination and improve charge injection. Achieving an optimal monolayer that balances light harvesting and electron injection is crucial³⁷.

4.5. Counter electrodes and catalyst deposition.

The counter electrode catalyzes redox mediator reduction (classically $I_3^- \rightarrow I^-$)³⁵. Platinum sputtered or thermally evaporated on FTO remains a benchmark, but cost and corrosion have motivated Pt-free options: carbon pastes, graphene, CNT composites, transition metal carbides/nitrides, and conductive polymers (PEDOT)³⁴⁻³⁶. Deposition approaches include sputtering, electrochemical deposition, screen printing of catalytic inks and drop casting. Careful engineering of CE porosity and conductivity is essential to minimize charge-transfer resistance³⁸.

4.6. Electrolyte filling, sealing and alternative hole conductors

Traditional liquid iodide/triiodide electrolytes are easy to use but pose leakage and long-term stability issues³³⁻³⁷. Gel polymer and quasi-solid electrolytes improve retention; solid-state hole conductors enable sealed, leak-free architectures albeit with their own transport and stability trade-offs³⁹. Filling methods and precise sealing are necessary to prevent ingress of air/moisture and electrolyte evaporation³⁵⁻³⁹.

5. Characterization Methods for Dye-Sensitized Solar Cells

Characterization of DSSCs links materials and device processing to photovoltaic performance. The most commonly used techniques—UV–Vis spectroscopy, current–voltage (I–V) measurements, electrochemical impedance spectroscopy (EIS), and incident photon-to-current efficiency (IPCE)—each probe complementary aspects of device operation and failure modes.

5.1. UV–Visible (UV–Vis) Spectroscopy

UV–Vis spectroscopy is the primary tool to assess dye absorption and quantify surface loading on mesoporous photoanodes. Recording the absorption spectrum of the dye in solution and of dye-sensitized TiO_2 films reveals peak positions, molar extinction coefficients, and aggregate formation (red-shifts or broadening indicate aggregation)⁴⁰. Comparing the absorbance before and after dye desorption (e.g., stripping dye into a basic solvent) gives an estimate of dye surface coverage, which correlates directly with achievable short-circuit current density (JSC)⁴⁰⁻⁴¹. UV–Vis is also used to monitor stability by tracking spectral changes after light/thermal stress⁴¹.

5.2. I–V (Current–Voltage) Characteristics

Current–voltage (I–V) measurements under simulated sunlight (AM 1.5G, 100 mW/cm²) determine the photovoltaic performance of DSSCs³⁹⁻⁴¹. Key parameters obtained from the I–V curve include:

- **Short-circuit current density (J_{SC})**³⁸: Indicates the maximum photocurrent generated when the cell's output terminals are shorted^{37,38}.
- **Open-circuit voltage (V_{OC})**³⁹: Denotes the maximum voltage achievable under open-circuit conditions, determined by the energy gap between the quasi-Fermi level of electrons in the semiconductor and the electrolyte's redox potential^{40,41}.
- **Fill factor (FF)**: Indicates the performance quality of the solar cell, defined as the ratio of the maximum obtainable power to the product of J_{SC} and V_{OC}⁴⁰.

- **Power conversion efficiency (PCE)**⁴¹: Calculated as the ratio of electrical output power to incident light power.

These parameters are essential for determining the overall performance and guiding design improvements.

5.3. Electrochemical Impedance Spectroscopy (EIS)

EIS measures the frequency-dependent response of a DSSC to a small AC perturbation and is uniquely powerful for separating resistive and capacitive processes at different interfaces⁴⁰⁻⁴². In a typical Nyquist plot the high-frequency semicircle is associated with charge transfer at the counter electrode, the mid-frequency semicircle with charge recombination at the BiOCl/dye/electrolyte interface, and the low-frequency response with ionic diffusion⁴². Fitting to an appropriate equivalent circuit yields series resistance (Rs), charge-transfer resistance (Rct), chemical capacitances, and recombination lifetimes—parameters that link directly to FF and V_{OC} . Recent tutorials and DSSC EIS studies emphasize careful measurement conditions and justify model choice to avoid misinterpretation⁴³.

5.4. Incident Photon-to-Current Efficiency (IPCE / EQE)

IPCE, measured as a function of wavelength, gives the external quantum efficiency: the fraction of incident photons at each wavelength that generate extractable electrons⁴⁴. IPCE integrates optical and electronic factors—dye absorption, injection efficiency, charge collection efficiency and any parasitic absorption by electrolyte or electrodes⁴⁵. Comparing the IPCE spectrum with UV–Vis of the dye and with reflectance/scattering data helps identify lost spectral regions and opportunities for co-sensitization or scattering layer optimization⁴⁴. Integrated IPCE across the solar spectrum provides an independent estimate of JSC that should agree with the I–V measured value (differences point to measurement or stability issues)^{40-42,45}.

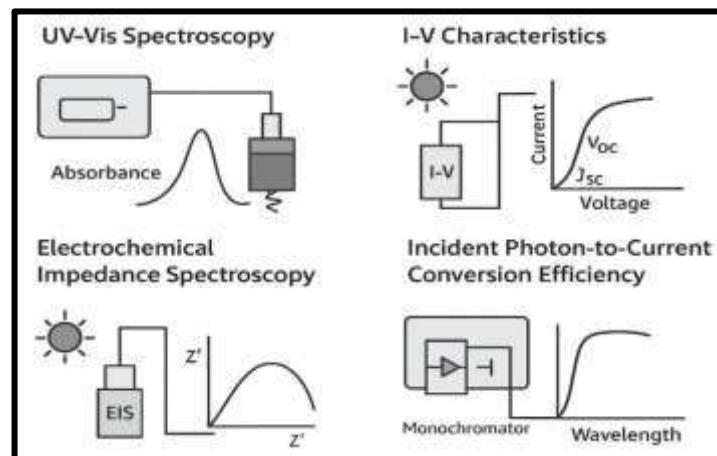


Fig. 3. Schematic Representation of DSSC Characterization Methods

6. Conclusion

Dye-sensitized solar cells (DSSCs) represent a viable and versatile photovoltaic technology with unique advantages in terms of cost, design flexibility, and adaptability to various lighting conditions. Their ability to perform efficiently in low-light environments positions them as strong candidates for niche applications such as building-integrated photovoltaics, portable devices, and indoor energy harvesting. While significant advancements have been made in improving sensitizers, photoanode structures, electrolytes, and counter electrodes, challenges related to long-term stability, large-scale fabrication, and electrolyte degradation still require focused research. Ongoing developments in solid-state electrolytes, novel dye combinations, and alternative catalysts show promise in addressing these limitations. The integration of advanced characterization methods continues to refine our understanding of efficiency bottlenecks, guiding material and structural innovations. With sustained interdisciplinary efforts, DSSCs are poised to complement existing photovoltaic technologies, particularly where aesthetics, transparency, and flexible form factors are prioritized alongside energy generation.

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