



A review on co-sensitization of dyes with semiconductor nanoparticles

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Abstract

The expeditious exhaustion of fossil fuels drives us to look for sustainable energy resources to meet energy demand. Third-generation photovoltaic cells are the most significant scientific contribution to the alternative energy approach. The potential of solar cells as a reliable solution to world energy crises is enormous. Historically, inorganic materials such as silicon were used for traditional solar cells. Now, photoelectrochemical or dye-sensitized and hybrid solar cells have been used instead of conventional solar cells. The titania TiO_2 is most commonly used photoanode in photoelectrochemical cells, but its restricted optical features and interfacial features lead to decrease its performance. A solar cell's photovoltaic performance is highly dependent on its semiconductor material. Organic dye molecules and nanoparticles which are semiconductors have greatly known for their participation in solar energy produced by co-sensitization. The functionalization of organic dye molecule assists by harvesting many photons and hence, increases efficiency. Semiconductor nanomaterials are used because of their amazing structural, chemical, and optical properties. Inorganic semiconductor nanoparticles offer size tunability and high absorption coefficients, by altering their size the bandgap can be tuned therefore absorption rate is changed. Various organic dyes and semiconductor nanomaterials have been used in dye sensitized solar cells to improve their productivity. Out of them, co-sensitization is proved as the most promising approach. In recent years, 14% efficiency of these cells has been increased by co-sensitization. This review talks about methodology, materials, multiple aspects and function of co-sensitization to increase working of dye sensitized photoelectrochemical cells by using semiconductor nanoparticles.

Keywords: Co-sensitization, Organic dyes, Photoelectrochemical cells, semiconductor nanoparticles, dye sensitization, Third generation Solar cell

Introduction



There has been an increase in demand for sustainable energy sources to meet domestic and commercial needs due to the utmost depletion of fossil fuels over the past few years. In the past few decades, the use of reliable energy sources specifically photon harvesting through solar cells have great interest in this field. The conversion of sun energy into electricity is an abundant, clean, and renewable source. In the solar photolytic industry silicon based solar energy technologies were a major breakthrough in this area. The traditional solar cells made up of inorganic materials efficiency of up to 24% [1], using intensive processing techniques and expensive materials of high purity. Photochemical cells must be manufactured in modern ways that are scalable, productive, and cost-effective. Various solar cell technologies are being developed, including polymer bulk heterojunctions, small molecules thin films, dye-sensitized nanocrystalline solar cells, and organic-inorganic hybrids.

Gratzel et al. fabricated the 1st solar cell made by dye, In the year 1991 [2] and thus opened the door for sensitization of mesoporic TiO₂ layer by inorganic and organic nanometallic dyes and has become the main research area because of its ease of fabrication, low cost, and low toxicity. A DSSC consists of three main components: (1) a photoanode (2) a counter electrode and (3) an electrolyte.

As a key component, the photo anode performs the following functions:

- Electrons released after photoexcitation are collected and transported to the current carrying circuit [3].
- Facilitate dye adsorption. A typical anode has porous morphology for dye adsorption and is made of fabricated materials with wide bandgaps, such as TiO₂, ZnO, and Nb₂O₅. The counter electrode performs followings functions: (A) reduction of electrolyte oxidation by regeneration of the dyes (B) attract holes toward AC a wide range of nanomaterials are used for the production of CEs, including platinum, carbon nanotubes and other carbon-based materials[4]–[7].

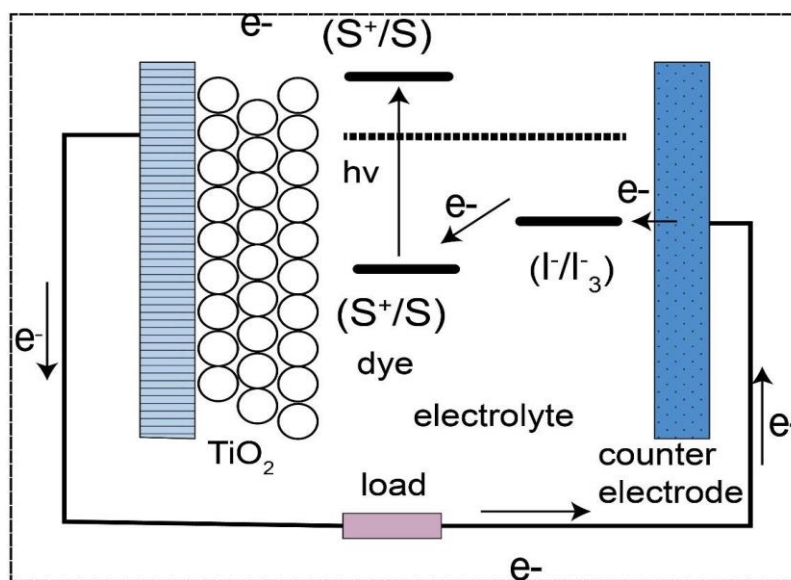
Between the photoanode and the CE, electrolytes play a crucial role in DSSCs. The electrolyte's curative function is the regeneration of photoexcited dye. Key elements of DSSCs include photosensitizers like TiO₂ and ZnO that have been absorbed on semiconducting material. Photosensitizers or dyes control the PEC of solar cells. In DSSC, a dye generates holes and pairs of electrons that move through semiconductor materials. The DSSC technology has made incredible progress in recent years, attaining efficiency of 14%. However, in order for these solar cells to be manufactured at large scale, their efficiency must be improved. In the 400–900 GHz range of electromagnetic spectrum, there is no sensitizer that can absorb energy. The creation of hybrid solar cells involves a variety of techniques, including bulk heterojunction cells using a variety of nanoparticles, including TiO_x [8]–[11], CdSe [12], [13], PbS [14]–[16], and CuInS₂ [16], as well as solid-state dye-sensitization. CdS [17] and ZnO[18], [19].



- The dye-sensitized solar cell consists of several components, including electrodes, organic salts, organic or inorganic dyes, nanoporous TiO₂, and metal catalyst [20]–[22].
- After the photon is absorbed, the ejected electron from the dye is transported to the TiO₂ conduction band and passes to the contact through the porous electrode (TiO_x) network. In DSSCs, the reduction of the oxidised sensitizer molecule to its initial state is carried out using electrons delivered through liquid electrolytes see Figure 1 [22].

Figure 1: Operation principal of a dye sensitized cell

The photoelectric conversion system works by expanding the band gap of semiconductor surface molecules to harvest light. Little light is harvested by a monolayer dye. In this situation, increasing the contact between the electrode and semiconductor oxides is helpful. Utilizing nanoparticle-based electrodes that improve the photoactive interface improves this [22]



By co-sensitizing several dyes with complimentary absorption spectra on TiO₂ layer, the light harvesting capacity of DSSC can be further improved. The inside surfaces of the TiO₂ electrode are covered with dye molecules that absorb the photons of light from the sun in order to dye-sensitize semiconductor electrodes[23]. In Figure 2[22], the co-sensitization of the dye with the semiconductor has the effect of shifting the incoming photon to current efficiency (IPCE) to higher wavelengths [23].

A perfect dye would be affixed to the surface of a semiconductor oxide, absorb light below the threshold wavelength, and aid in the migration of light-exiting electrons into the conduction



band of oxides[21]–[23]. Numerous substances, including transition metal complexes[24], [25] porphyrins [26]–[29], phthalocyanines [30]–[32], and coumarin [25], have been studied for semiconductor sensitization of dyes. The most desirable characteristics of these nanomaterials include their intense emission spectra, processability, high photobleaching and chemical stability, surface functioning, and continuous absorption band.

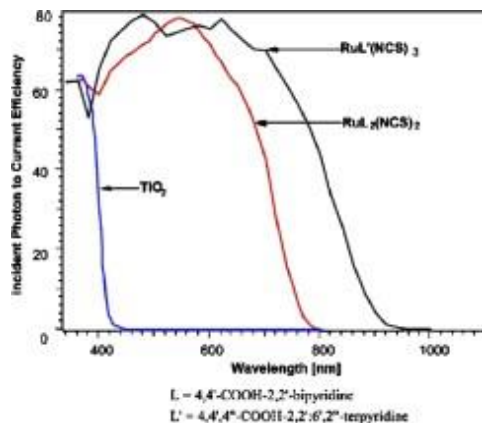


Figure 2: When dye is applied on TiO_2 , as opposed to when TiO_2 is exposed to the air, the incident photon to current efficiency curves shift to higher wavelengths, exhibiting the sensitization effect.

There are two methods to make a co sensitization:

- The cocktail approaches

The molar ratios of the two dyes are co sensitized in a mixed dye solution.

- The stepwise approach

Adsorption of the two dyes in consecutive approach.

Conditions like [a] a dye sensitizer with broad absorption and adequate energetic positions are needed to improve the performance of DSSCs. [b] an effective electron transporting firmly bound sensitizer [33], [34]. Co-sensitization, often known as the "dye-cocktail" method in dye sensitized solar cells, is a regularly used tactic in these organisations. Co-sensitization enables a rise in the resultant spectrum's absorption edge as well as a rise in the dye-sensitive solar cell's internal photon conversion efficiency (IPCE). By combining two separate solvents that can dissolve the dyes, co sensitization can be produced. These are the main traits of the prospective co-sensitizer.

- A semiconductor conduction band energy level that lies above the lowest unoccupied molecular orbital (LUMO).



- An energy level beneath the electrolyte's redox potential constitutes the highest occupied molecular orbital (HOMO).
- The presence of a group that couples semiconductors to dyes
- Photoexcitation of a semiconductor by a donor induces intramolecular charge transfer.
- dye sensitizers and high chemical compatibility
- A high molecular extinction coefficient is required.
- It ought to lessen the charge recombination.

The photoanode (metal oxide) surface must be suitable for effective adsorption[35], [36]. In co sensitization, several dyes are employed to absorb various sun spectrum ranges, resulting in a panchromatic absorption spectrum. By doing so, the rise in light harvesting improves the current density of manufactured photovoltaic cells, which raises the device's voltage [37]. It is therefore crucial that the absorption spectra of two or more dyes with comparable energy levels complement each other in the co sensitization process[38].

Methodologies and Methods for Co-sensitization

The co-sensitization process involves two steps. The mesoporous TiO₂ electrode is first sensitised by dye 1 in a suitable solvent system in order to anchor the functional group of the organic dye on the carboxylate end of the TiO₂ surface. Then dye 2 was sensitised using an appropriate solvent system, which is not meant to have an impact on the dye.

Continuity of Deposition

This approach to co-sensitization is most frequently used. Three crucial characteristics that depend on the anchoring group moieties These include: (1) packing and orientation of dye molecules that have been absorbed; (2) electrical interaction between dye and metal oxide photoanode; and (3) long-term device stability[39], [40].

Method of co-sensitization with dipping

In the dipping approach, a mesoporous TiO₂ layer that has been applied to a conducting substrate is dipped in the first dye for a set amount of time before being exposed to the second dye. The main issue with the co-sensitization procedure is the buildup of dyes on the mesoporous layer. The performance of solar cells created via a self-deleting technique is significantly decreased as a result. Therefore, for effective co-sensitization, careful observation, sensitization period, selection of appropriate solvent, and appropriate deposition procedure must be used.



Recordings from dyes are impacted by the anchor groups present, and the type of dye loading via parallel or complimentary adsorption has also been discovered to be a significant influence on symbiosis [41]. The kind of function group affects this. For instance, we can infer by experimentation The anchor groups that are present have an impact on recording from dyes. The kind of function group affects this. As an illustration, we can infer from experiments that the bond of benzoic acid is in the bidentate mode and that of cyanoacrylic acid is in the tridentate mode

[42] different types of dyes being deposited. Their geometrical parameters have an impact as well [43], [44]. Each dye has a few unique adsorption sites on its surface, which gives it some benefits. places where a second dye could be absorbed. Simply in case the first dye adsorbed in the sequential deposition process is present. The second contains more dye than can be absorbed. A functional group's binding energies vary depending on what it does. The surface of the dye nanoparticles is eventually a value that suggests inappropriate dye loading Device Final Photon Conversion Efficiency (IPCE) This idea is covered in a recent study by Zhao et al., colour impact of adsorption time using porphyrin dye LP-2 (in ethanol/Tetrahydrofuran) and N719 dyes [45]. The authors used LP-2 sensitization for five hours and N719 sensitization for twenty-one hours. A maximum efficiency of 7.7% was provided. In order to improve the effectiveness of the co-sensitization technique, a number of parameters are handled due to the type of the dye. synergistic absorption of two distinct pigments in stages (sequential deposition) A promising strategy as well [46] Experiment: When depositing two sensitizers, stepwise co-sensitization of organic dyes improves performance efficiency in comparison to the dye cocktail approach [47], [48]. The mesoporous photoanode's dye is a dye whose synergy in the adsorbed state reduces the first dye's harmful interactions. For sensitization of two distinct dyes, there are many different techniques, and they all have their own advantages and disadvantages. However, it has a significant impact on the effectiveness of the gadget. Ionic liquid or the conventional iodine/triiodide redox pair are the major electrolytes [49].

For QDSSC sequential sensitization, when a first layer of QDs is being deposited, a photoanode is typically immersed in an aqueous solution of their ionic precursors at regular intervals. Then, the process is repeated for the second layer of QDs. This approach is a widely used technique known as continuous approach adsorption and response (SILAR). For the purpose of making high-efficiency QDSSC. Precursor concentration, immersion period, immersion cycle, medium pH, and test conditions' efficacy in the SILAR process following a period of time spent soaking the photoanode safe annealing in the precursor solution at a particular temperature. Before deposition, the solvent must be evaporated. Create a new semiconductor QD layer that glows carefully controlling the procedure to avoid damaging the previously placed QD layer. Chemical bath deposition (CBD) is a crucial co-sensitization technique for quantum dots. This method is fairly straightforward and frequently produces thin films of cadmium chalcogenide in solution.



The necessary Scale is created and deposited chemically in this process. The identical bathing solution [50] In this instance, chalcogenide sources and solvation metal complexes interact to generate a solid layer on a substrate. For layer deposition, chemically stable substrates like glass are employed. There are numerous factors, including crystallinity, that affect CBD. solvent, medium pH, temperature, and formed layer Timing, post-processing, and layer thickness. Synergistic effects, such as those of CBD QDs using SILAR and CBD techniques, are shown

schematically. Amazing improvement in power conversion efficiency thanks to different co-sensitization techniques.

Effect of co-sensitization on solar cell efficiency

For improvement, the co-creation process is essential. efficiency of solar cells using dye and QD sensitization. Quantum dots and dye bind. Additionally, it is presented through technological interactions in a superb way. a result of effective charge transfer (also known as FRET, or Forster resonance energy transfer). These ideas and specifics will be explained later.

Co-sensitization of a TiO₂ photoelectrode with molecular dyes

One of the key requirements for producing effective DSSC is the effective sensitization of TiO₂ electrodes by suitable organic dyes that have broadened the absorption spectra. An essential organometallic dye with ruthenium as its base is employed in DSSC as a sensitising dye. Excellent photoelectrochemical and physical properties make these dyes ideal for DSSC applications[51]. With the exception of a few limited dyes covering the NIR, the chemical structures of routinely used ruthenium dye are known to sensitise organometallic dyes mostly in the visible spectrum [52]. The fundamental issue with ruthenium base organometallic dyes is also their poor molar extinction coefficient. using two distinct dyes in this circumstance. It has been discovered to greatly improve the photocurrent. Applications for DSSC [53], [54] A separate dye is applied to achieve this. For charge transfer to occur, the energy levels (LUMO and HOMO positions) of the other dye must be appropriate. With regard to cyanine, squaraine, hemicyanine, and phthalocyanine dye to the pigments they contain, dyes are used. The same level of energy as ruthenium dyes. For instance, the output of solar cells co-sensitized with squaraine dyes was approximately 6.36%, which was superior to their individual outputs[55]. Cyanine At 662 nm, the squaraine dye had an extinction coefficient of effectiveness of 319,000 M⁻¹ cm⁻¹. By pyrenimidazole co-sensitization, up to 6.7% can be achieved. Organic dyes with bases [56] In DSSC, these dyes are hardly ever utilised. The quantity of these dyes enables effective charge transfer to one another and raises efficiency. Additionally, the acceptor molecule's molar extinction coefficient, the position of the chromophore, and the transit of electrons from non- recombinant dye. Additionally, symbiosis is significantly impacted [57],



[58]. Recent Analysis Predicting Extinction Coefficients in one instance after sensitization, the organic dye T191 has a higher value due to the emergence of novel electronic transitions, than value in the in solution [59] Such initiatives incorporate novel functional groups, and the results of their investigation. Metal-free organic dyes, such coumarin dyes, have a particular sensitising effect when used in DSSC fabrication. Improved [60] When coumarin units are linked to low bandgap chromophores like 3,4-ethylenedioxythiophene (EDOT), benzothiadiazole, etc. Another type of luminous substance exists. dyes that can increase the DSSC's spectrum sensitivity without lowering the absorption coefficient. "Energy" is the name of a FRET-operating dye. Co-Sensitization methods include Relay

Dyes (ERD) [61]–[64] Of course, dyes are also showing up as a potential use for his DSSC in addition to the aforementioned artificial colouring compounds [65], [66]. Some research groups have successfully explored the co-competition process for natural dyes in this setting [67]–[71].

Summary and Discussion

It has been investigated how well dye-sensitized solar cells function photovoltaically. As photosensitizers, these cells employ a variety of dyes, and the electrodes are composed of nanoporous oxide semiconductor thin films made of TiO₂, Nb₂O₅, ZnO, SnO, and other oxides produced using a range of techniques. Semiconductor surfaces coated with various dyes have the ability to absorb visible light at a range of wavelengths. Good cell performance was reached, particularly for solar cells constructed of TiO₂, ZnO, SnO₂, and In₂O₃. The incident photon-to-current efficiency (IPCE) of a mercurochrome-sensitized ZnO solar cell with an I-/I₃-redox electrolyte was 69%, which is quite high. The solar energy conversion efficiency, measured under AM1.5 (99 mW cm⁻²), reached 2.5% with a value of 7.44 mA cm⁻², a Voc value of 0.52 V, and a ffvalue of 0.64. A considerable number of dyes adsorbed on semiconductor nanoparticles results in very efficient photo-to-electron conversion, which leads to high light harvesting efficiency. Additionally, we investigated the connection between semiconductor thin film thickness, semiconductor particle size, light intensity, irradiation time, and photovoltaic performance of dye-sensitized solar cells. As the semiconductor thin-thickness film thickness increased, the cell's Jsc increased, but the Voc decreased due to a considerable loss of injected electrons and the reaction's rate constant. Jsc and Voc exhibited stability for more than 24 hours, even when using an open cell. The system was sufficiently stable during irradiation as evidenced by the molecule's turnover rate, which was over 18000. These results showed the possibility of good performance of organic dye-sensitized solar cells.



Outlook for the future

Over the past 20 years, dye advancements have received a lot of attention in order to create panchromatic dye sensitizers and increase the effectiveness of synthetic ruthenium-based dyes in photovoltaic cells[72]. Due to the electrolytes' rapid breakdown, overall efficiency is around (4%). Finally, Etgar et al. [73], [74] described a heterojunction device based on a $\text{CH}_3\text{NH}_3\text{PbI}_3/\text{TiO}_2$ nanocomposite, where $\text{CH}_3\text{NH}_3\text{PbI}_3$ can function as both a hole transport medium and a light harvester[75]. In recent years, the efficiency of solar cells has increased from 3% to 22% [76]. Stability for optimal usage duration in future work is one of the most crucial improvements to the cell. The Pt catalyst in the DSSC has also failed due to the repeated leaks of liquid electrolyte. Therefore, a solid-state hole transport medium is required in photoelectric cells[77]. According to Gratzel's estimation, after these issues are fixed, the lifespan of the DSSC can be extended by up to 20 years. One of the major causes of the degradation of solar cell perovskite crystals under sunlight is the interaction with moisture. Additionally, suitable sealing media for photocells is required while they are operating at their highest temperature settings in order to prevent environmental effects[78]. As efficiency increases, it is crucial to keep costs low and cut back on medium usage[79]. The dye is another substantial component that employs harmful materials and requires additional processing methods to make it less poisonous. Therefore, it is necessary to employ natural sensitizers in DSSC, which is taken from leaves and flowers. The performance of the DSSCs is maximised by using vegetable dyes up to a significant limit. Because PDSSCs are less durable and have shorter lives than polycrystalline Si-based solar cells, commercialising them will be difficult. Until the solid-state electrolyte is adjusted with good efficiency, durability, and use of eco- friendly chemicals, the sustainability of DSSC cells is still in doubt[77]–[79].

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