

Efficiency of Natural Photosensitizer for Renewable Energy Conversion and Storage through Photogalvanic Cells

¹Shachi Tiwari, ²Chandrakanta Mall, ³Jitendra Kumar Chaurasiya, ⁴Rohit Kumar, ⁵Prem Prakash Solanki

^{1/2/3/4/5}Ashoka Institute of Technology and Management, Varanasi

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Abstract

The enhanced global energy need of clean, cheap and sustainable energy has introduced research into solar energy conversion and storage technologies. Photogalvanic cells offer a promising route for sustainable energy conversion directly into electrical energy with inherent storage capacity. The significant component of these cells is photosensitizer which absorb the sunlight and start the cell reaction. Natural photosensitizers are eco-friendly, low cost, high abundance, non-toxic and biodegradable that's why in recent years growing attention has been focused toward the application of it in photogalvanic cell. Hence, this study represents a comprehensive work of use of natural photosensitizer in photogalvanic cells. The basics of photogalvanic cells are also discussed followed by an investigation of the overall performance of the cell. Factor affecting all parameters of the cell, limitations, advantages and recent development to enhance the shortcoming of use of natural photosensitizer in the cell are crucially overview. Lastly upcoming prospects and challenges related to natural photosensitizer in photogalvanic cells are emphasized with their potential character in sustainable solar energy conversion and storage.

Keywords: Natural photosensitizer, solar energy, chlorophyll, reductant, photogalvanic cell, solar energy.

Introduction

The continuous exhaustion of fossil fuels resources and their harmful environment impact have initiated extensive research in the direction of ecofriendly and efficient green energy resources for sustainable development of a clean society [1-4]. Thus, entire world is looking towards a renewable energy source. The global energy requirement can be fulfilling by solar energy because, it is freely available in nature [5], mother of all other renewable energy and one of the best green and clean alternative sources of energy. If solar energy is harvested properly, it will definitely fulfill all future energy requirement with remarkable change in environment.

Different solar cells like dye-sensitized solar cells [6-11], polymer solar cells [12-15], photovoltaic cells [16-20], solar energy driven electrochemical cell [21-23], electroluminescent devices [24-30], optical logical elements [31-33] etc. work on conversion of solar energy into electrical energy. But these cells have zero capacity to store energy and only photogalvanic cell has remarkable potential to convert and store solar energy into electrical energy simultaneously. Photogalvanic cell (PG cell) is an electrochemical device which work on

photogalvanic effect [34]. The main constituent use in fabrication of photogalvanic cells are photosensitizer, reductant, surfactant, electrode in acidic or alkaline medium. Out of all these components, photosensitizer play the role of solar energy harvesting species. However, reductant is the source of electron and surfactant work as to solubilize the photosensitizer and application of it is totally desirable. The overall performance of PG cells mainly depends on photosensitizer. In order to improve the efficiency of PG cells from time-to-time different synthetic photosensitizers have been exploited in various photogalvanic cells like Methylene blue [35], Toluidine blue [36], Brilliant cresyl blue [37], Nile blue [38] etc. But it was observed that these photosensitizers are very injurious to health of living organism and lower safety standards. So, to deal with the drawbacks associated with synthetic dyes, the use of a safe and ecofriendly photosensitizer is urgent requirement of environment. Hence, natural photosensitizers have gain attention as cheap, high abundance, ecofriendly sustainable sensitizer for use in photogalvanic cell because of their low toxicity and biodegradability. The use and disposal of the natural dye is supposed to be more eco-friendly in comparison to synthetic photosensitizers. Hence, this review represents the collection of recent growth in the application of natural photosensitizers in photogalvanic cell.

Working principle of photogalvanic cell

A photogalvanic cell is a dilute solution-based dye sensitized solar cell that directly converts solar energy into electrical energy through photoinduced redox process. The significant constituent of photogalvanic cells photosensitizer, a redox couple, electrode that immersed in an electrolyte solution. The photosensitizer absorbs the photons from the light that fall on it and become excited.

The excited photosensitizer then transfers an electron to the reductant, which cause the formation of reduced and oxidized species. This photoinduced redox reaction causes a concentration gradient within two electrodes. The oxidation reaction occurs at illuminated electrode, while at dark electrode, the reduction reaction takes place. This developed potential difference bring electrons flow through the external circuit from one to another electrode. This continuous photochemical reaction generates electricity. The current decreases and reaction slow down on removal of light source.

Mechanism of energy absorption by photosensitizer

In photogalvanic cell, the photosensitizer plays a crucial role in converting incident light energy into electrical energy through a sequence of photophysical and electrochemical processes. Unlike conventional photovoltaic devices that operate by semiconductor bandgap excitation, photogalvanic cells harness the photo-induced redox chemistry of molecular dyes or pigments dissolved in an electrolyte solution.

Photon Absorption and Excitation

When sunlight strikes the electrolyte, photons are absorbed by the photosensitizer molecules present in the solution. These molecules possess conjugated electronic structures that allow them to absorb light efficiently in the visible region. Upon absorption of a photon with energy the dye absorption threshold, an electron in the photosensitizer is promoted from the ground electronic state (S) to a higher excited state (S*):



This process converts the energy of the photons into electronic excitation energy within the dye molecule.

Photoinduced electron transfer

Once the photosensitizer is in its excited state (S^*), it becomes a stronger oxidizing or reducing agent compared to its ground state. It can accept or donate an electron to a suitable species in the electrolyte. In most photogalvanic system, the excited dye interacts with a reducing agent present in the solution, resulting in electron transfer:



Here, the excited photosensitizer is chemically reduced and the reductant is oxidized. This step effectively stores the absorption light energy in the form of chemical potential.

Charge separation and electron flow

The reduced photosensitizer (S^-) diffuse toward the illuminated electrode (photoelectrode). The oxidized reductant (R^+) diffuses toward the dark electrode.

Electrode reactions and current generation

- At the illuminated electrode:



- At the dark electrode



Regeneration of reactants

Both the photosensitizer and reductant are regenerated, allowing continuous operation of the cell as long as light is available.

Overall principle

Light \longrightarrow **excited photosensitizer** \longrightarrow **Electron transfer from reductant** \longrightarrow **Charge separation** \longrightarrow **electrical energy**

The reduced dye species diffuse to the illuminated electrode

Role of photosensitizer, reductant, surfactant and electrode

When photogalvanic cell irradiated with photons, photosensitizer excited by absorbing photons from ground state to excited state. Then photosensitizer transfer an electron to the electrode from the reductant. It initiates the photochemical redox reaction that generates the electric energy. Hence, photosensitizer play the significance role in photogalvanic cell. Some useful natural photosensitizers are chlorophyll [39], anthocyanins [40] and synthetic photosensitizers are methylene blue [41], thionine [42], etc. After studying various photogalvanic system it was concluded that only a suitable concentration of photosensitizer is valuable for photochemical reaction. Lower concentration of photosensitizer causes fall in photo potential and photocurrent because smaller amount of photosensitizer molecules is available for excitation and donation of the electrons to the platinum electrode. While higher concentration of photosensitizer absorbs maximum portion of sunlight and also induced decrease in photo potential and photocurrent. The reductant function as electron donor and regenerates the photosensitizer. It donates an electron to the oxidized photosensitizer. It stops everlasting degradation of the photosensitizer and keeps constant electrons flow in the system.

Example of common reductants are EDTA [43], oxalic acid [44], ascorbic acid [45], etc. The concentration of reductant also follows the same trend as the concentration of dye. The lower concentration of reductant causes decrease in photo potential and photocurrent due to fewer number of reductants will be present for electron donation to dye molecule. While, higher concentration of reductant molecule cause hinders the photosensitizer molecule resulted decrease in overall performance of the cell.

The application of surfactant molecule is optional however; use of surfactant molecule is found to enhance the electrical output of the cell by solubilizing the dye molecule [46-47]. Surfactant molecule interacts with the photosensitizer through the coulombic interaction or charge transfer reaction and solubilize the photosensitizer, which enhances the photovoltage and photo potential of the cell. As the concentration enhances, the photocurrent and photo potential increases reach a maximum and then decreases. The photogalvanic cell contain two chambers, a dark chamber, act as cathode and an illuminate chamber that act as anode. Hence, in this modified cell, electron flow from illuminated to dark chamber by external circuit. In order to achieve higher electrical performance various workers from time to time applied different electrodes. However, in current time Pt electrode is applied as working electrode and saturated calomel electrode applied as reference electrode.

Types of Photosensitizers

Dyes are colored substances that have been used from ancient time to color fibres, foodstuffs, paper, leather etc. In Indian history dyes appear in Vedic period in ‘Atharva veda’ find in word ‘rang’ for color and ‘ranjak’ for dye. Credit for the use of dye for the first time goes to A. Dyes have huge chemical and structural diversity which enable it vast application not only in coloring but also in photocatalysis, solar cells, waste water treatment, sensors and pharmaceutical industries etc. When dye molecule is added to chemical system it absorbs the sunlight and transfer the energy of excitation. In photogalvanic cells, previous time, Thionine dye was frequently applied till 1980. After it a number of various photosensitizers have been applied from different classes. The photosensitizers are significant constituent that absorb light and initiates the electron transfer reaction. These photosensitizers mainly classified on the basis of their chemical nature. Classification chart of photosensitizer which have been used in different photogalvanic cells from time to time given below in **Table 1**.

S. No.	Types of photosensitizers	Example	Characteristic features	Ref.
1.	Inorganic complexes	$\text{Ru}(\text{bpy})_3^{2+}$, Fe complexes	Hight stability, selective absorption	[48, 49]
2.	Organic dyes	Cationic dyes such as Methylene blue, Thionine, Brilliant cresyl blue, Nile blue	Strong visible light absorption	[50]
		Anionic dyes such as Eosin, Rose Bengal	High efficiency	[51]
3.	Semiconductor sensitizers	TiO_2 , ZnO, CdS	Act as sensitizer and charge separator	[52]

4.	Natural sensitizers	Chlorophyll, Anthocyanins	Eco friendly, low cost	[53]
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Table 1: Classification chart of photosensitizers used in photogalvanic cells.

Synthetic Photosensitizer and their drawback

Besides these applications synthetic dyes has toxic nature and adverse effect on all forms of life, finishing industries. Textile dyeing has created a huge pollution problem as it is one of the most chemically intensive industries on earth and No. 1 polluter of clean water (after agriculture). More than 8000 chemicals are used by industries in various processes of textiles manufacture including dyeing and printing. The chemicals which are used in this process are poisonous and damaging to human health directly or indirectly. Large quantity of water is needed for textile processing, dyeing and printing. Consumption of water in daily is an average sized textiles mill having a production of about 8000 kg of fabric per day is about 1.6 million liters and 16% of this is consumed in dyeing and 8% in printing. 17 to 20 percent of industrial water pollution comes from textiles dyeing and finishing treatment gives to fabric. Significant amount of environmental degradation and human illness have been caused by textiles effluent. Benzidine-based dyes increase the risk of cancer of the bladder and other organs in humans and were the major factor responsible for mutagenesis¹⁰⁰. Azo dye methyl yellow exhibits carcinogenicity through highly reactive metabolic intermediate that can interact with DNA and cause mutations. It was proved that benzidine was the major factor responsible such as *Staphylococcus aureus*. As a result of these harmful effects of synthetic dye world moved towards the use of natural dyes as it is biodegradable and ecofriendly in nature.

However, dyes have important properties to form complex with surfactant.

Although synthetic photosensitizers are efficient light absorbers and commonly used in various photogalvanic cells but, have different limitations such as they decompose after long exposure to light decreasing time period of cell. Synthetic photosensitizers have toxicity, photodegradation, high cost, partial stability, disposal problems, non-biodegradable and recombination losses, that prevent their long-term uses in photogalvanic cell. In **Table 2** given below show comparative study of synthetic and natural photosensitizers use in photogalvanic cell.

S. No.	Parameter	Synthetic photosensitizers	Natural photosensitizers
1.	Source	Synthetic chemical dyes and complexes	Originates from natural sources
2.	Example	Safranine, Thionine, Brilliant cresyl blue, Rose Bengal	Carotenoids, Anthocyanine, Chlorophyll
3.	Absorption of light	Strong absorption	Reasonable absorption
4.	Stability	Moderate, susceptible to photodegradation	Poor to moderate

5.	Photochemical efficiency	High	Low to moderate
6.	Harmfulness	Often toxic and non-degradable	Ecofriendly and nontoxic
8.	Disposal	Hazardous	Safe
9.	Sustainability	Low	High

Table 2 comparative study of synthetic and natural photosensitizers use in photogalvanic cell.

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How Natural Photosensitizer is better over synthetic photosensitizer

Natural photosensitizers are biodegradable and nontoxic in nature. They are derived from plants, biological waste, fruits, that make them renewable. In the preparation of natural dyes gentle chemical reactions are involved with no disposal problem. Natural dyes are eco-friendly obtained from renewable resources, biodegradable in nature, produce no health hazards, act as health cure Extraction of natural dyes are very easy and can be obtained by simple solvent extraction. Various literature suggests that if natural photosensitizers can combine with suitable reductants and electrolytes, it can produce comparable photocurrent and photovoltage to synthetic dye which are summarized in tabular form as given below.

S. No.	Natural Photosensitizer/ Source	Major Active Pigments	Cover wavelength (nm)	Reductant Used
1.	Spinach extract	Chlorophyll-a, Chlorophyll-b	430-453	EDTA, Ascorbic acid
2.	Algae extract	Chlorophyll	400-500	Oxalic acid
3.	Green leaf extract	Chlorophyll	400-450	Glucose
4.	Red cabbage extract	Anthocyanin	450-600	EDTA
5.	Beetroot extract	Betalain	400-600	Glucose
6.	Rose petal extract	Anthocyanin	450-600	Ascorbic acid
7.	Hibiscus flower	Anthocyanin		EDTA

8.	Turmeric extract	Curcumin	400-450	Glucose
9.	Neem leaf extract	Chlorophyll	400-450	Oxalic acid
10.	Spinach+Mint mixed extract	Chlorophyll		Ascorbic acid

Table 3 Shows all natural photosensitizers used in photogalvanic cell, their absorption maxima and references.

Industrial and educational research applications prefer natural photosensitizer over synthetic photosensitizer due to their low toxicity, renewability and ecofriendly nature.

Current Challenges with the use of Natural Photosensitizer

Since, natural photosensitizers are ecofriendly and nontoxic, however, there are various aspects which need to be notice. After studying extensive literatures, we have mention serious problem associated with several technical and scientific shortcomings that confine their extensive application. Natural photosensitizers undergo photodegradation on constant illumination that suppress photocurrent generation, it produces lower conversion efficiency of the cell due to faster recombination of photogenerated charge carrier. Most of the natural dyes don't absorb broad solar spectrum. In comparison to synthetic dye, they often absorb narrow range of wavelength for efficient light absorption which reduces the photocurrent generation. Extraction of natural photosensitizers is often a time-consuming process. These extracts may degrade easily by microbial growth, temperature sensitivity. Difficulty occurs in storing and reusing it. The solubility of natural dyes is very poor in common electrolytes, that decreases effective interaction with light and the redox species cause reduction in photocurrent generation and overall performance of the cell. Fabrication of photogalvanic cell with natural dye may also face challenges because extracted photosensitizers vary with extraction technique, origin, time, plant maturity etc. However, work in this direction is limited but comparative studies of crude chlorophyll extract and synthetic dyes produce low electrical output in photogalvanic cells.

These aspects may decrease the conversion efficiency and storage capacity of the cell. In recent time these challenges require a truthful effective research work towards this direction to make the natural photosensitizer apply in photogalvanic cell practical and commercially viable.

Method of Enhancement of efficiency of Natural Photosensitizer

Although efficiency of photogalvanic cells, fabricated with natural photosensitizers have low, but modification of the cell with some well organize ideal conditions may produce some fruitful outcomes. These modifications employ may enhance cell performance which are as follow.

Optimization of dye concentration: Determination of optimum concentration of photosensitizer by using different photogalvanic cells fabricated with various concentration of natural photosensitizer may ensures maximum absorption of solar spectrum. Low

concentration may decrease the photon captures, while high concentration of dye may initiate aggregation and self-quenching that decrease the efficiency of the cell.

Optimization of electrolyte concentration: Natural photosensitizers are very sensitive towards pH, by optimizing electrolyte concentration maintain the photosensitizer in its suitable photoactive form that may enhance the overall electrical output of the cell.

Application of suitable redox couples: Selection of reversible reductant may enhance donation of electron to the excited photosensitizer. Combination of effective electron donor-acceptor may enhance the charge separation and electrical output of the cell that avoid the back-electron transfer.

Use of surfactant: Application of surfactants such as SLS, CTAB, Tween 80, TritonX-100 may prevent the aggregation of dye molecule. Presence of surfactant solubilize and hence, stabilize the photosensitizer that increase the light harvesting efficiency of the cell.

Developed electrode materials: Application of electrode having high surface area such as platinum electrode, graphite, carbon nanotubes may enhance electron collection which increase overall performance of the cell.

Use of mixed natural photosensitizers: Literature study suggest that application of mixed photosensitizer absorb broad solar spectrum which enhances light harvesting capacity and overall performance of the cell. Although application of natural photosensitizer with suitable reductant that absorb broad solar spectrum cause enhance electrical output has not been commercialized, but a variety of combination of mixed natural photosensitizer that may increase the overall performance of the cell studied. Most of the processes in this direction are expected to operate, but the process established till date either have unfortunate efficiency, poor stability. Thus, it is matter of further more extensive research work on use of natural photosensitizer in photogalvanic cell to make it practically applicable in day-to-day life and commercially viable.

Conclusion

The extensive research work in this direction have proposed a number of facts to fabricate photogalvanic cell, its mechanism and features that influence the overall performance of the cell. Once, perfect combination of natural photosensitizers with suitable reductant has been established the photogalvanic cell shall be cost effective, ecofriendly source of energy and it shall be definitely sustainable alternative to solar cells with no toxic waste materials. In short, the method of development of natural photosensitizer offers low-cost production, easy assembly setups, eco-friendly technique with inherent storage capacity, but still there are a number of technical challenges and limitations in this field that must be overcome before these technologies can be useful in commercial life.

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Conflict of Interest

The authors declare no conflicts of interest regarding this manuscript.

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