**Analysis of Different Dyes on ZnO nanoparticles layer for Solar Cell Applications**

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Chapter II

LITERATURE REVIEW

ABSTRACT

Production of dye sensitized solar cell using ZnO nanoparticles layer offer several advantages for potentially low-cost manufacturing and appropriate for cost-effective industrial production in future. The production of dye-sensitized solar cells (DSSCs) using ZnO nanoparticles and natural dyes extracted from Bougainvillea flower with red, violet and Nephelium mutabile Labill. The aims are to create a photoanode for DSSCs by forming a ZnO thin film with organic dyes through an immersion method. The fabricated electrode is coated onto a glass substrate using the doctor blade technique, and the electrode is then immersed into the dye solution. The fabricated solar cell's performance is analyzed in terms of its ability to convert sunlight into electricity. Parameters such as efficiency, current-voltage characteristics, and power output are measured and evaluated.

**Keywords**— dye sensitized solar cell; fabricate; characteristics.

**I. Introduction**

Solar irradiation is an abundant and virtually unlimited energy source, and it is believed that a large portion of the world's electricity demands can be met through the development of solar power technologies. This underscores the importance of continued research and development of renewable energy technologies to address the world's growing energy demands while mitigating the negative impacts of fossil fuel consumption. Inorganic silicon semiconductors were indeed the most widely used materials for commercially available solar cells. Silicon solar cells have been proven to be efficient and durable, making them a dominant technology in the solar industry. However, they do have certain drawbacks, including their relatively high production costs and the environmental impact associated with their manufacturing process. Due to their comparatively low cost of production and potential efficiency, hybrid solar cells seem to be very promising and cost-effective choices for photovoltaic energy sectors. Solar cell construction procedures based on natural anthocyanin colours derived from berries were pioneered in DSSC research in 1998 [1]. Natural pigments extracted from fruits and vegetables [2-3], such as chlorophyll and anthocyanins, have been thoroughly studied as DSSCs sensitizer. Dye sensitized solar cells (DSSCs) have been given considerable attention in recent years [4].

**II. Solar cell**

A solar cell, also known as a photovoltaic cell, is a device that converts sunlight directly into electricity through the photovoltaic effect. This effect involves the generation of an electric current or voltage in a material when it's exposed to light. Solar cells are a fundamental component of solar panels, which are used to harness solar energy for various applications, including residential, commercial, and industrial power generation.

The basic structure of a solar cell typically consists of semiconductor materials, most commonly silicon, though other materials like thin-film compounds and organic materials can also be used. When photons (particles of light) strike the surface of the solar cell, they can impart enough energy to the semiconductor material's electrons, allowing them to move and create an electric current.

Photons from sunlight are absorbed by the semiconductor material of the solar cell. The absorbed photons provide enough energy to free electrons from their atoms, creating electron-hole pairs. Electrons become negatively charged, while the holes left behind are positively charged. The electric field present within the semiconductor material causes the separated electrons and holes to move in opposite directions. This results in an electric current. Conductive metal contacts on the surface of the solar cell capture the moving electrons and transfer them as usable electric current to external circuits.

**III. Photovoltaic Cell Generations**

Photovoltaic (PV) cells play a crucial role in converting sunlight into electricity using the photovoltaic effect. As technology has advanced, different generations of photovoltaic technologies have emerged, each with varying materials, manufacturing methods, and efficiency levels. The categorization into generations helps track the evolution of these technologies. This is overview of the four major generations of PV technologies which is shown in figure 1.

First generation of photovoltaic are typically made using a crystalline silicon wafer. Consist of cells made from fairly thick (100s of μm thick) wafers of monocrystalline or multicrystalline silicon. Comprising of a large-area, single layer p-n junction diode. In 1972 for the first-time chlorophyll-sensitized zinc oxide (ZnO) electrode was synthesized through electron injection of excited dye molecules into a wide band gap of semiconductor, photons were converted into electricity [5]. Due to expensive manufacturing technology the researchers began give attention to third generation of DSSC. In 1991, Oregan and Gratzel expand the first dye-sensitized nanocrystalline solar cells whose photoelectric energy conversion rate reached 7.1% and incident photon to current conversion efficiency was about 80% [6]. This generation includes the traditional crystalline silicon solar cells, both monocrystalline and polycrystallineand gallium arsenide (GaAs).

Second-generation solar cells were introducing as a response to high material usage and cost of silicon solar cell. To reducing the material usage the maximum film thickness for this generation was brought down to a few nanometers to tens of micrometers. Thin-film technologies use much thinner semiconductor layers than crystalline silicon cells, which reduces material costs. Thin-film technologies use much thinner semiconductor layers than crystalline silicon cells, which reduces material costs. They include microcrystalline silicon (µc-Si) and amorphous silicon (a-Si), cadmium telluride (CdTe), and copper indium gallium selenide (CIGS) cells.

Third-generation solar cells are solution excellent potential for large-scale solar electricity generation. It is very different from the previous semiconductor devices. The devices are including nanocrystalline “films,” quantum dots, dye-sensitized solar cells and solar cells based on organic polymers.

The fourth generation encompasses more speculative and advanced concepts includes the low flexibility or low cost of thin film polymers along with the durability of “innovative inorganic nanostructures such as metal oxides and metal nanoparticles or organic-based nanomaterials such as graphene, carbon nanotubes and graphene derivatives [7].



**Figure 1: The generations of various photovoltaic cells**

**IV. Dye-Sensitized Solar Cell (DSSC)**

A dye-sensitized solar cell (DSSC), is a type of thin-film solar cell that converts sunlight into electricity using a mechanism inspired by natural photosynthesis. DSSCs are an alternative to traditional silicon-based solar cells and offer several advantages, such as lower manufacturing costs and the ability to work efficiently in low-light conditions. Dye-Sensitized Photovoltaic Cells (DSSCs) are part of the third generation of photovoltaic technologies, and they often utilize conjugated polymers and organic semiconductors as advanced materials in their construction. Polymer/organic photovoltaic cells are further classified as dye-sensitized organic photovoltaic cells (DSSCs), photoelectrochemical photovoltaic cells, and plastic (polymer) and organic photovoltaic devices (OPVDs), with different operating mechanisms [8]. A schematic of dye-sensitized organic photovoltaic cells (DSSCs) is shown in Figure 2.



**Figure 2: A schematic of dye-sensitized organic photovoltaic cells**

**V. The materials of Dye-Sensitized Solar Cell (DSSC)**

**V.I. Subtract DSSC**

The commonly used substrate is transparent conductive oxide (TCO) has special characteristics due to its high transparency and low resistance. TCO has a wide band gap, consisting of indium tin oxide (ITO), aluminum zinc oxide (AZO) and fluorine tin oxide (FTO) because of high electrical conductivity. Transparent and Conductive Substrate DSSCs are typically constructed with two sheets of conductive transparent materials, which help a substrate for the deposition of the semiconductor and catalyst, acting also as current collectors. Substrates must be highly transparent (transparency > 80%) to allow the passage of maximum sunlight to the active area of the cell. The electrical conductivity of the substrates should also be high for efficient charge transfer and to minimize energy loss. These two characteristics of substrate dictate the efficiency of DSSCs [9,10]. FTO and ITO are most often used as DSSC, where the sintering process of the oxide layer on the substrate is heated to 450-500°C, the materials have good conductivity and do not suffer from defects or defects at that temperature range [11]

**V.II Nanoparticle electrodes**

Oxide semiconductors are indeed preferred in photoelectrochemical applications due to their exceptional stability against photo-corrosion when exposed to light within their band gap [8]. Furthermore, the band gap of a semiconductor determines the energy of photons it can absorb and convert into electron-hole pairs. Oxide semiconductors often have wide band gaps (>3 eV), allowing them to absorb high-energy photons.

Zinc oxide (ZnO)

Zinc oxide (ZnO) has been among the first metal oxides explored for use in dye-sensitized solar cells (DSCs). ZnO possesses high electron mobility in its bulk form, which means that electrons can move relatively easily through the material [12]. Zinc oxide (ZnO) is a direct wide band gap semiconductor material (Eg = 3.37 eV at room temperature). It has a large excitation binding energy of 60 meV. The extent of dye adsorption and electron diffusion are the key factors that affect conversion efficiency for ZnO-based DSSCs [13]. ZnO aggregates with small-sized ZnO nanocrystals have a higher capability of dyeloading, while the ZnO aggregates with larger sized [14].

A. Binder

In dye-sensitized solar cells (DSSCs), a binder is often used in the formulation of the photoanode to enhance the nanocrystallinity and specific surface area of the semiconductor material, such as Zinc oxide (ZnO) and titanium dioxide (TiO2) and. The binder serves as a matrix that helps hold the nanocrystalline ZnO/TiO2 particles together, maintaining their structure and maximizing their surface area.

However, these nanoparticles can be prone to aggregation, which reduces their effectiveness. A binder helps prevent particle aggregation by creating a three-dimensional network that holds the nanoparticles in place and maintains the desired nanocrystalline structure.The binder helps ensure a uniform coating of the ZnO/TiO2 layer onto the substrate. This uniformity is crucial for consistent light absorption and charge separation within the DSSC. The binder improves the adhesion of the ZnO/TiO2 layer to the substrate and other layers of the DSSC. The summary of Binder for Pothoanode are shown in table 1.

|  |  |  |  |
| --- | --- | --- | --- |
| No | Binders/ Photoanodes | Efficiency | Ref |
| 1 | TiO2, ethyl cellulose | 4.47% | [15] |
| 2 | ZnO, Indium | 4.26% | [16] |
| 3 | TiO2, chitosan | 4.18%. | [17] |
| 4 | ZnO, ethyl cellulose | 3.68% | [18] |
| 5 | Tio, butanol, HCl | 0.31% | [19] |

Table 1: Summary of Binder for Pothoanode

**VI. Dye**

In Dye-Sensitized Solar Cells (DSSCs), the “dye” refers to a light-absorbing molecule that plays a crucial role in capturing photons of sunlight and initiating the photovoltaic process. The dye is a key component that allows DSSCs to convert light energy into electrical energy. The primary function of the dye in a DSSC is to absorb photons from sunlight. Different dyes are designed to absorb specific wavelengths of light, allowing them to efficiently harness solar energy. The absorbed photons transfer their energy to the dye molecule, exciting it to a higher energy state. After absorbing light, the dye molecule becomes excited and enters a higher energy state. This energy is used to generate an electron-hole pair (exciton) within the dye molecule. The excited electron and the positively charged hole are separated within the dye.The generated excited electron is injected from the dye molecule into the conduction band of the semiconductor material.

**A.Inorganic dyes**

Inorganic dyes can also be used in dye-sensitized solar cells (DSSCs), alongside organic dyes, to capture sunlight and initiate the photovoltaic process. Inorganic dyes often exhibit higher stability against photo-degradation and environmental factors. Ruthenium (Ru) dyes are characterized with high efficiency, expensive cost as well as their difficult purification and have reached the best results. Until now, DSSCs with Ru bipyridyl complexes (N3 and N719) and the black Ruthenium dye as photo sensitizers have achieved power conversion efficiencies up to 11% [20] compared to just 1% twenty years ago. Ruthenium dyes are considered the best dyes for the production of efficient DSSC currently

**B. Organic Dyes**

DSSC sensitized with organic dyes have power conversion efficiencies lower than those sensitized with metal complexes. However pure organic dyes have many benefits in their application of DSSC such as high absorption coefficient, lower cost, and easy control of redox potential. In order to obtain even cheaper dyes for DSSC, metal free organic dyes are strongly desired. In the last few years novel photosensitizers such as coumarin, cyanine, merocyanine, indoline, triphenylamine, hemicyanine dialkylaniline, phenothiazine, tetrahydroquinoline, and carbazole based dyes have reach solar to electrical power conversion efficiencies up to 5–9%

**C. Natural Dyes**

Currently in DSSC, dyes are replaced with natural dyes as sensitizer, which is can reduces the cost of fabrication and more environmentally. Natural dyes are exclusively used for educational purposes representing a low cost and environmentally friendly. Numerous fruits, flowers vegetables have been tested over the last decades as suitable sensitizers. Natural dye can be extracted from different types of flower, fruit, seeds and plants. Extraction of dye from natural source is easier and have been tested over the last decades as suitable sensitizers. Plant pigmentation occurs due to the electronic structure of the pigment are interact with sunlight to change the wavelengths that are either reflected or transmitted by the plant. Anthocyanins is colour water-soluble pigments belong to the phenolic group. The pigments are in glycosylated shapes. Anthocyanins is responsible for the colours in fruits and vegetables such as red, purple, and blue. It is also available in roots, tubers and stems. Anthocyanins from various plants give different sensitize performance. This situation has recent interest to researcher because of their capability to absorb light and transform it into electrons.

Recently dyes extracted from natural resources has become the new attract for researchers. Application of natural dyes is a promising development in the field of this technology. Natural dyes are reduced cost of metal complex sensitizers and also replace the expensive chemical synthesis process through simple extraction process. Natural dyes are readily available, easily extractable, safe material causes and no environment threat. This can be extracted from flowers petals, leaves, roots and barks in the form of anthocyanin, carotenoid, flavonoid and chlorophyll pigments. Numerous natural dyes can be combined in suitable proportions to form dye sensitizer. It can be an alternative to enhance the band absorption and as a result to improve and increase the efficiency of the DSSC. Thus, natural dyes can be economically viable option. By mixing the different pigments present in the natural dyes can give better results. The summary of the performance parameters of the DSSC using different natural dyes are shown in Table 1.

**Table 1: Summary of the performance parameters of the DSSC using different natural dyes**

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| **No** | **Sensitizer** | **semiconductor** | **Dye** | **Efficiency** | **Highlight** | **Ref** |
| 1 | DSSC | ZnO | -Beetroot-Rose -Strawberry | 0.1%0.08%0.22% | -Efficiency of the dye sensitized solar cells can be enhanced by changing the solvent used in the preparation of the dye, changing the dye extracting temperature and pH of the extract. -Ethanol is found to be the suitable solvent for natural dye. | [21] |
| 2 | DSSCs | Tio2 | -Pomegranate fruit | 0.2% | - The bandgap energy gets decreased due to anthocyanin natural dyeof pomegranate fruit juice | [22] |
| 3 | DSSC | ZnO | -Phytolacca icosandra Phyllanthus reticulatus | 2.76%4.62 | - Efficiency will increase by using ethanolic fruit extract | [23] |
| 4 | DSSC | ZnO | -Safflower -Senna -Calumus draca -Carya illinoensis-Rheum -Roselle -Rosa damascena -Runica granatum | 0.01%0.039%0.030%0.025%0.022%0.004%0.01%0.009% | -Safflower extract as a sensitizer showed the best performance among the other extracts.  | [24] |
| 5 | DSSC | Tio2 | Garcinia mangostana and Archidendron pauciorumGarcinia mangostana and Archidendron pauciorumGarcinia mangostana and Archidendron pauciorum-Garcinia -MangostanaArchiden Pauciflorum | 0.07%0.38% | - Jering have the capability to be used as DSSC sensitizer, but their performance can be improved in future works by added suitable catalyst as co-adsorbance or dye | [25] |
| 6 | DSSC | ZnO | -Purple Cabbage-Beet Root-Mixed | 0.1015%0.1788%0.3824% | -The mixed dye absorbs broader visible light spectrum as compare to individual dyes | [26] |
| 7 | DSSC | ZnO | -Walnuts-Rhubarb-Pomegranate | 0.0104%0.0104%0.0043% | -Walnuts possesses the best photosensitization effect among three extracts of natural dye. | [27] |
| 8 | DSSC | Tio2 | -Buah naga merah-Bayam merah-Daun pandan-Daun singkong-Buah naga + pandan-Bayam merah + singkong | 0.00207%0.00154%0.00143%0.00148%0.00283%0.00222% | -Efisiensi tertinggi berasal dari campuran dye buah naga-daun pandan yaitu 0,00283%. | [28] |
| 9 | DSSC | ZnO | - | 2.14% | -The present study confirmed that immersion time affects the content of dye loading and the efficiency of the DSSC. -ZnO film coated three times to thick in N719 dye for 30 min has the best efficiency. | [29] |
| 10 | DSSC | Tio2 | -MK Dyes (Alkyl-functionalized carbazole dyes) | 8.3% | -MK dyes presence of a n-hexyloligothiophene backbone, which prevents charge recombination between electrons and I3 - ions on the TiO2 electrode | [30] |

**VII. Electrolyte**

The electrolyte in DSSCs is typically a liquid or gel-like substance consists of iodine (I⁻) and triiodide (I₃⁻) that serves as a redox mediator. It helps transport charge between the dye-sensitized semiconductor and the counter electrode, completing the circuit and allowing the conversion of light energy into electrical energy. Three main types of electrolytes can be categorized as liquid electrolytes, quasi-solid electrolytes, and solid-state conductors [31]. The first generation of Dye-Sensitized Solar Cells (DSSCs) with reported efficiencies of around 7-8% utilized a liquid electrolyte that contained an iodide/triiodide redox couple [32].

Liquid Electrolytes

The use of liquid solvent-based electrolytes in Dye-Sensitized Solar Cells (DSSCs) indeed offers several advantages that contribute to their popularity. Liquid electrolytes typically have low viscosity, which means they flow easily and can permeate through the pores of the porous electrode materials and facilitate ion transport, excellent connectivity interaction at the electrode/electrolyte interface, can exhibit relatively high ionic conductivity, allowing for efficient transport of ions and simple preparation methods, thereby rendering high conversion efficiency [33].

**A. Organic Solvent-Based Electrolytes**

Organic solvents play a crucial role in providing a medium for the dissolution and diffusion of the ionic species (such as the iodide/triiodide redox couple). The solvents in DSSCs should have low cost, low toxicity, and low light absorption [34].

1. **Ionic Liquid-Based Electrolytes**

Electrolytes based on non-volatile and solvent-free ionic liquids (ILs) has gained significant attention due to their advantageous properties for DSSCs. the advantages of using IL-based electrolytes include chemical and thermal stability, moderate ionic conductivity, and minimal vapor pressure [35].

**VIII. Counter-electrode catalysts**

For sufficiently fast reaction kinetics for the triiodide reduction reaction at the TCO coated cathode, a catalyst coating is needed.

1. **Platinum**

As a traditional and usually most efficient catalyst, platinum has been used almost exclusively in the literature. Platinum (Pt) is a commonly used catalyst material for counter electrodes in Dye-Sensitized Solar Cells (DSSCs). The counter electrode, often referred to as the cathode, is a critical component of DSSCs, as it plays a crucial role in the regeneration of the redox couple (such as iodide/triiodide ions) that shuttles charges between the electrolyte and the dye-sensitized semiconductor. The catalytic activity of the counter electrode is essential for efficient charge transfer at this interface.

Pt is often selected as the counter electrode material in electrochemical systems, including Dye-Sensitized Solar Cells (DSSCs), due to inertness towards oxidation and its excellent catalytic activity. In certain experimental setups, an ion-exchange membrane may not be necessary during the electrochemical measurements. Therefore, it has been prevalently applied as the counter electrode in various electrochemical tests [36].

1. **Carbon**

Carbon-based materials are being explored as counter-electrode catalysts in various electrochemical systems, including Dye-Sensitized Solar Cells (DSSCs). While not as catalytically active as noble metals like platinum, carbon-based materials offer advantages in terms of cost-effectiveness, availability, and environmental sustainability. The performance of photovoltaic using carbon counter electrodes is equivalent to that of platinum. Low cost carbon counter electrodesare therefore suitable catalysts in cobalt-based DSCs. The FF and thephotovoltaic performance improved significantly by changing thePt catalyst to carbon black [37].

**VIIII. UV-Vis spectroscopy**

UV-Vis spectroscopy is a technique to measures the number of discrete wavelengths of UV or visible light that are absorbed or transmitted through a sample. This property is influenced by the sample composition, potentially providing information about what substances and concentrations are present in the sample. Light has an amount of energy which is inversely proportional to its wavelength. shorter wavelengths of light bring more energy and longer wavelengths bring less energy. A specific amount of energy is needed to encourage electrons in a material to a higher energy state which can detect as absorption. Electrons in different bonding environments in a material require a different specific amount of energy to encourage the electrons. This condition causes absorption of light occurs for different wavelengths in different materials. Humans are able to see a spectrum of visible light, from approximate 380 nm, which is violet, to 780 nm, which is red. Thus, light can be defined by its wavelength, which can be useful in UV-Vis spectroscopy to analyse or identify different substances by locating the specific wavelengths corresponding to maximum absorbance. The absorbance peaks observed in a UV-Vis absorption spectrum can be used to quantify the concentration of the investigated sample, For example, the sample concentration can be calculated from the absorbance value of the peak [38] shown below:



**Figure 3: A higher concentration leads to higher absorbance value**

**IX. X-ray diffraction**

X-ray diffraction techniques are a very useful tool to study the characterization, non-destructively, the crystallographic structure, physical properties of materials, chemical composition and thin films. It can also be used to measure numerous structural properties of these crystalline phases such as phase composition, strain, grain size and defect structure. It also used to determine the thickness of thin films, as well as the atomic arrangements in amorphous materials such as polymers. Solid matter contains out of two types of material: amorphous and crystalline. In an amorphous sample the atoms are set in a random way, glasses are an example of amorphous materials. In acrystalline sample the atoms are arranged in ordered pattern and there is a smallest volume element that, repetition in three dimensions, can explained the crystal [39]. This smallest volume element is called a unit cell. The dimensions of this unit cell can be described by three axes namely: a, b and c and the angles between the axis are α, β and γ. A schematic diagram of the unit cell is given in Figure 4.



**Figure 4: A unit cell from a three-dimensional lattice**

X-ray diffraction (XRD) is useful method for the study of nanomaterials (materials with structural features of at least one dimension in the range of 1-100 nm). The wavelength of X-rays is on the atomic scale, so X-ray diffraction (XRD) is a primary tool for analysed the structure of nano-materials. The intensities measured using XRD can offer quantitative, accurate information on the atomic arrangements at interfaces.

**X. Scanning electron microscope (SEM)**

SEM show the microstructure of photoelectrode materials such as titanium dioxide nanoparticles. It can reveal the size, shape, and arrangement of these nanoparticles, providing insights into their morphology and how they affect the overall performance of the cell. Its can be used to observe the distribution of dye molecules on the surface of the photoelectrode for understand how the dye is adsorbed onto the semiconductor material and how it influences light absorption and its can be used to examine the surface morphologyof the counter electrode (often platinum or other materials). It helps researchers understand how the morphology of the counter electrode affects its catalytic activity and charge transfer properties. In addition to surface evaluation, SEM analysis is utilized for particle characterization, such as wear debris generated during mechanical wear testing



**Figure: 5 An example for a circular substrate with five distinct measurement position**

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