ANALYSIS OF DIFFERENT DYES ON ZnO NANOPARTICLES LAYER FOR SOLAR CELL APPLICATIONS

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.

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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 colors derived from berries were pioneered in DSSC research in 1998 [1]. Chlorophyll and anthocyanins, derived from fruits and vegetables, have been the subject of comprehensive studies as sensitizers for DSSCs [2-3]. Dye-sensitized solar cells (DSSCs) have garnered substantial interest in the past few years [4].

II. SOLAR CELL

In the realm of renewable energy, a solar cell, also called a photovoltaic cell, is a mechanism employed to convert sunlight into electrical power 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 panels rely on solar cells as their essential component, allowing the conversion of solar energy into power for residential, commercial, and industrial needs.

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

Utilizing the photovoltaic effect, photovoltaic (PV) cells play an indispensable role in transforming sunlight into electrical energy. 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.

The initial generation of photovoltaic cells typically employs crystalline silicon wafers and comprises cells made from relatively thick wafers of either monocrystalline or multicrystalline silicon, often measuring hundreds of micrometers in thickness. Incorporating a single-layer p-n junction diode, these photovoltaic cells have a substantial surface area. In 1972, researchers successfully synthesized a chlorophyll-sensitized zinc oxide (ZnO) electrode. This breakthrough enabled the conversion of photons into electricity by injecting excited dye molecules' electrons into the wide bandgap semiconductor [5]. Due to expensive manufacturing technology the researchers began give attention to third generation of DSSC. In 1991, Oregan and Gratzel were pioneers in the development of the initial dye-sensitized nanocrystalline solar cells, achieving a remarkable photoelectric energy conversion rate of 7.1% and an incident photon-to-current conversion efficiency of approximately 80% [6]. This generation includes the traditional crystalline silicon solar cells, both monocrystalline and polycrystalline and gallium arsenide (GaAs).

Second-generation solar cells were introduced as a response to the high material consumption and cost associated with silicon solar cells. To address this, the maximum film thickness for this generation was reduced to a range spanning from a few nanometers to tens of micrometers, significantly minimizing material usage. 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 of solar cell technology encompasses a range of speculative and advanced concepts, leveraging the cost-effectiveness of thin film polymers while harnessing the durability of cutting-edge materials. These materials include innovative inorganic nanostructures such as metal oxides and metal nanoparticles, as well as organic-based nanomaterials like graphene, carbon nanotubes, and graphene derivatives [7].

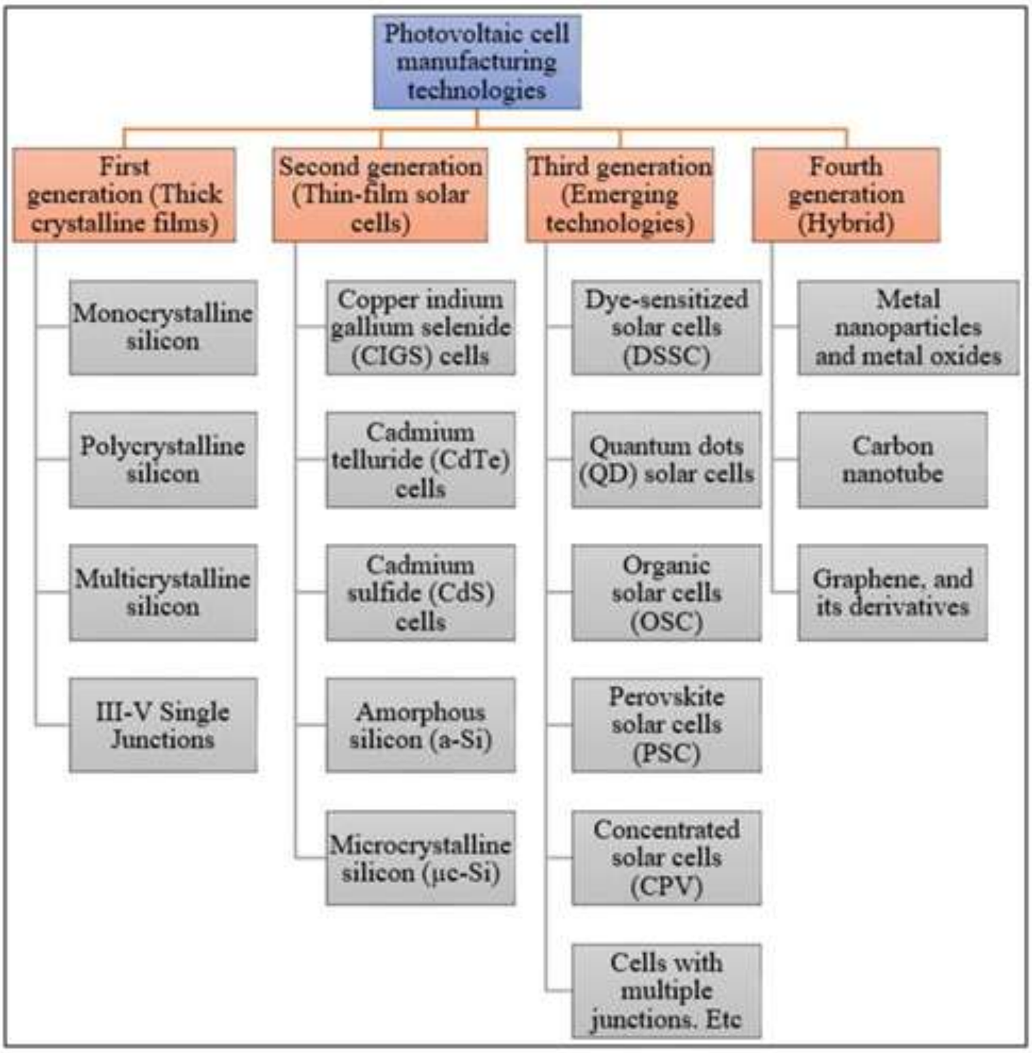

Figure 1: The generations of various photovoltaic cells

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 which frequently use organic semiconductors and conjugated polymers materials in their construction. Organic/polymer photovoltaic cells can be categorized into three main types: photoelectrochemical photovoltaic cells, and plastic (polymer) and organic photovoltaic devices (OPVDs), dye-sensitized organic photovoltaic cells (DSSCs), with different operating mechanisms [8]. Figure 2 illustrates a schematic of dye-sensitized organic photovoltaic cells (DSSCs).

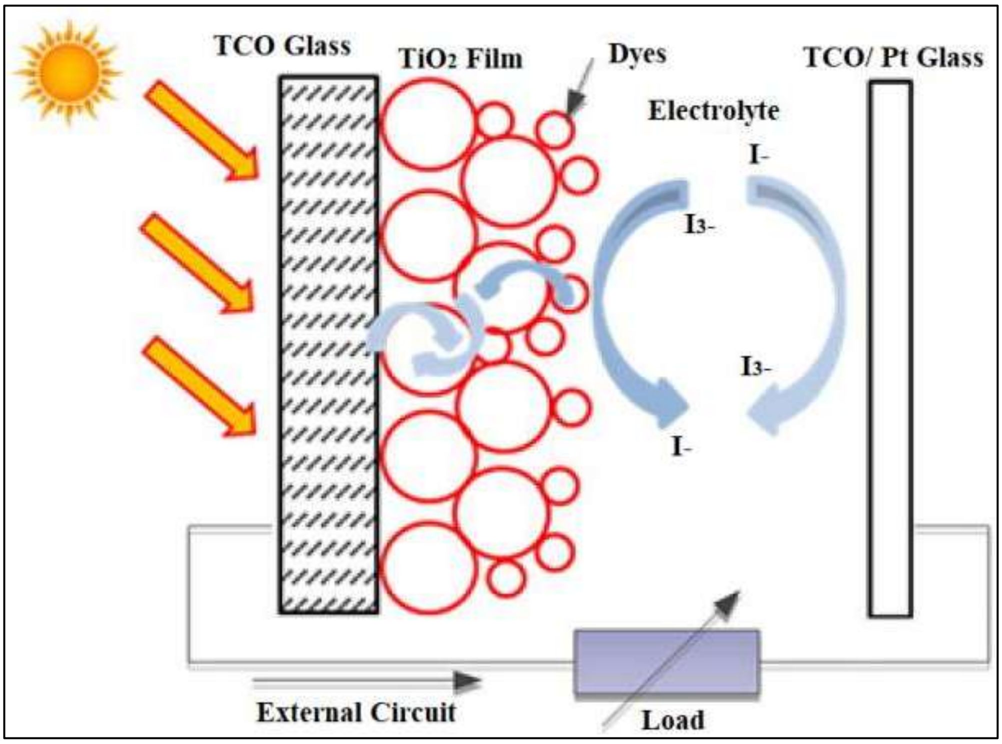

Figure 2: A schematic representation of dye-activated organic photovoltaic cells

V. THE MATERIALS OF DYE-SENSITIZED SOLAR CELL (DSSC)

1. **Subtract DSSC:** The commonly used substrate is transparent conductive oxide (TCO) has special characteristics due to its high transparency and low resistance. Transparent conductive oxides (TCOs) are chosen for their high electrical conductivity and possess a wide band gap. Common materials in this category include indium tin oxide (ITO), aluminum zinc oxide (AZO), and fluorine tin oxide (FTO). Transparent and Conductive Substrate Dye-Sensitized Solar Cells (DSSCs) are commonly built using a dual-layered structure comprising two sheets of conductive transparent materials. These sheets not only serve as the substrate for depositing the semiconductor and catalyst but also act as effective current collectors in the solar cell assembly. Highly transparent substrates (transparency > 80%) are essential to facilitate the unimpeded passage of maximum sunlight to the active region of the cell. In addition to high transparency, it is crucial for the substrates to exhibit excellent electrical conductivity. These substrate characteristics are vital for ensuring efficient charge transfer and mitigating energy loss. The performance of DSSCs hinges on the presence of these two substrate features [9,10]. FTO and ITO are commonly used as DSSC. When the sintering process is applied to the oxide layer on the substrate and heated to temperatures ranging from 450 to 500°C, the materials exhibit robust conductivity and remain free from defects within this temperature range [11]

2. **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]. In addition, a semiconductor's band gap 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 one of 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 recognized as a direct wide band gap semiconductor material, with an energy gap (Eg) of 3.37 eV at room temperature. Remarkably, it boasts a significant exciton binding energy of 60 meV. The efficiency of conversion in ZnO-based Dye-Sensitized Solar Cells (DSSCs) is largely determined by the extent of dye adsorption and the efficiency of electron diffusion. These two factors play a pivotal role in achieving optimal conversion rates [13]. ZnO aggregates containing smaller-sized ZnO nanocrystals exhibit an enhanced ability for dye loading. Conversely, ZnO aggregates comprising larger-sized ZnO nanocrystals may present distinct characteristics [14].

- **Binder:** In the formulation of the photoanode, a binder is frequently employed to enhance the nanocrystalline structure and increase the specific surface area of semiconductor materials 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 plays a crucial role in improving the adhesion of the ZnO/TiO2 layer to both the substrate and the various layers within the Dye-Sensitized Solar Cell (DSSC). The summary of Binder for Pothoanode are shown in table 1.

Table 1: Summary of Binder for Pothoanode

No	Binders/ Photoanodes	Efficiency	Ref
1	TiO_2, 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]

VI. DYE

The “dye” in (DSSCs), refers to a light-absorbing molecule that is essential in capturing photons from sunlight and initiating the photovoltaic process. The dye is a critical component in DSSCs' ability 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 levels of energy. The dye molecule becomes exited and entered a higher energy state after absorbs light. This energy is used to generate an electron-hole pair (exciton) within the dye molecule. Upon excitation, the electron and the positively charged hole within the dye become spatially separated. The excited electron is effectively transferred from the dye molecule to the conduction band of the semiconductor material

1. **Inorganic dyes:** In dye-sensitized solar cells (DSSCs), inorganic dyes can also be utilized 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 well-known for their excellent efficiency, albeit at a high cost and a difficult purification process. Nonetheless, they have routinely shown excellent outcomes.Until now, DSSCs using Ru bipyridyl complexes as photosensitizers, such as N3, N719, and the black Ruthenium dye, have achieved power conversion efficiencies of up to 11% [20] comparing to just 1% a decade ago. At present, Ruthenium dyes are recognized as the best option for producing highly efficient DSSCs.

2. **Organic Dyes:** Organic dye-sensitized solar cells (DSSCs) generally exhibit lower power conversion efficiency than metal complex-sensitized solar cells. However, pure organic dyes offer numerous benefits when used in DSSCs, including a high absorption coefficient, low cost, and convenient control of redox potential. To further reduce the cost of dyes for DSSCs, metal free organic dyes are strongly desired. Emerging photosensitizers such as coumarin, cyanine, merocyanine, indoline, triphenylamine, hemicyanine, dialkylaniline, phenothiazine, tetrahydroquinoline, and carbazole-based dyes have shown impressive solar-to-electrical power conversion efficiencies ranging from 5% to 9% over the last few years.

3. **Natural Dyes:** DSSCs are currently using natural dyes as sensitizers, which not only reduces manufacturing costs but also aligns with environmental sustainability aims. Natural dyes are mostly used for educational reasons due to their affordable price and environmental friendliness. Over the last few decades, a diverse range of fruits, flowers, vegetables, seeds, and plants have been investigated as potential sensitizers, providing an array of natural colors that can be extracted for DSSC applications. Extraction of dyes from natural sources is an easy method that has been widely researched and proven efficient as suitable sensitizers over the last many decades. Plant pigmentation occurs as a result of the electrical structure of pigments reacting with sunlight, causing changes in the wavelengths 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 accessible in the form of roots, tubers, and stems. The diverse range of sensitizing performances exhibited by anthocyanins derived from various plants has captured interest of researchers.This is attributed to their extraordinary ability to absorb light and convert it into electrons.

In recent years, academics have become increasingly interested in the use of dyes derived from natural resources. The application of natural dyes promising significant development within this technology. Natural dyes not only lower the cost compared to metal complex sensitizers but also offer more cost-effective alternative to the expensive chemical synthesis process via a simple extraction method. Natural dyes are abundant, easy to extract, and are not associated with any environmental threat, making them a safe and environmentally friendly matter. These natural dyes can be obtained from various parts of plants such as flower petals, leaves, roots, and barks, in the form of pigments like anthocyanin, carotenoid, flavonoid, and chlorophyll. Various natural dyes can be blended in proper ratios to create a dye sensitizer, providing an alternative approach to enhance band absorption and consequently enhance and boost the efficiency of Dye-Sensitized Solar Cells (DSSCs). Thus, natural dyes can be economically viable option. Optimal results can be achieved by blending the diverse pigments found in natural dyes. Table 1 summarizes the DSSC performance characteristics when utilizing various natural dyes.

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%	-The efficiency of dye-sensitized solar cells can be improved by altering the solvent used during dye preparation, adjusting the temperature at which the dye is extracted, and modifying the pH of the extraction process. -Ethanol has been identified as the preferred solvent for natural dyes in this context.	[21]
2	DSSCs	Tio2	-Pomegranate fruit	0.2%	- Pomegranate fruit juice contains anthocyanin natural pigment, which reduces bandgap energy.	[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 -Carya illinoensis -Roselle -Calumus draca -Rosa damascene -Rheum -Runica granatum	0.01% 0.039% 0.030% 0.025% 0.022% 0.004% 0.01% 0.009%	- Among the various extracts, safflower extract demonstrated the highest performance as a sensitizer.	[24]
5	DSSC	Tio2	Garcinia mangostana and Archidendron pauciflorum Garcinia mangostana and Archidendron pauciflorum	0.07% 0.38%	- Jering has the potential to be used as a sensitizer in dye-sensitized solar cells (DSSCs), and its performance can be improved in future studies by using suitable catalysts as co-adsorbents or dyes.	[25]

			Garcinia mangostana and Archidendron pauciflorum -Garcinia -Mangostana Archiden Pauciflorum			
6	DSSC	ZnO	-Purple Cabbage -Beet Root -Mixed	0.1015% 0.1788% 0.3824%	- Combining different dyes results in a broader absorption of the visible light spectrum compared to individual dyes	[26]
7	DSSC	ZnO	-Walnuts -Rhubarb -Pomegranate	0.0104% 0.0104% 0.0043%	- Among the three natural dye extracts, walnuts had the most efficient photosensitization exhibit.	[27]
8	DSSC	Tio2	-Buah naga merah -Daun pandan -Daun singkong -Bayam merah -Bayam merah + Singkong -Buah naga + pandan	0.00207% 0.00154% 0.00143% 0.00148% 0.00283% 0.00222%	- The highest efficiency comes from a mixture of dragon fruit and pandan leaf as a dye	[28]
9	DSSC	ZnO	-	2.14%	-The highest efficiency was achieved when the ZnO film was coated three times with N719 dye for a duration of 30 minutes	[29]
10	DSSC	Tio2	-MK Dyes (Alkyl-functionalized carbazole dyes)	8.3%	- The n-hexyl oligothiophene backbone of MK dyes significantly reduces charge recombination between electrons and I3- ions on the TiO2 electrode.	[30]

VII. ELECTROLYTE

The electrolyte used in Dye-Sensitized Solar Cells (DSSCs) is typically a liquid or gel-like substance containing iodine (I^-) and triiodide (I_3 $^-$) serving as a redox mediator. Its primary function is to facilitate charge transport between the dye-sensitized semiconductor and the counter electrode, thereby closing the circuit and enabling the conversion of light energy into electrical energy.

Electrolytes in Dye- Sensitized Solar Cells (DSSCs) can be classified into three primary categories which is liquid electrolytes, quasi-solid electrolytes, and solid-state conductors [31]. The first generation of Dye-Sensitized Solar Cells (DSSCs) is reported efficiencies around 7-8% utilized a liquid electrolyte that contained an iodide/triiodide redox couple [32].

Liquid Electrolytes: The use of electrolytes based on liquid solvents in dye-sensitized solar cells (DSSCs) indeed offers several advantages that contribute to their popularity. Liquid electrolytes have a low viscosity, which allows them to flow readily and penetrate porous electrode materials, facilitating ion transport. They also have good connectivity and interaction at the electrode/electrolyte interface, resulting in relatively high ionic conductivity. These characteristics allow for efficient ion transport, are simple to make, and contribute to high conversion efficiency [33].

1. **Organic Solvent-Based Electrolytes:** Organic solvents play a pivotal role for serving as a medium for dissolving and facilitating the diffusion of ionic species, such as the iodide/triiodide redox couple. Solvents used in Dye-Sensitized Solar Cells (DSSCs) should possess qualities such as affordability, low toxicity, and minimal light absorption [34].

2. **Ionic Liquid-Based Electrolytes:** Electrolytes formulated with non-volatile and solvent-free ionic liquids (ILs) have garnered substantial interest because of their beneficial properties for Dye-Sensitized Solar Cells (DSSCs). The advantages of utilizing IL-based electrolytes encompass chemical and thermal stability, moderate ionic conductivity, and negligible vapor pressure [35].

VIII. COUNTER-ELECTRODE CATALYSTS

To achieve sufficiently rapid reaction kinetics for the reduction of triiodide at the cathode coated with Transparent Conductive Oxide (TCO), the application of a catalyst coating is necessary.

1. **Platinum:** Platinum has been almost completely utilized in the literature as a conventional and typically most efficient catalyst. Platinum (Pt) is a commonly used catalyst material for the counter electrodes in Dye-Sensitized Solar Cells (DSSCs). The counter electrode, often referred to as the cathode, is an essential component of DSSCs, as Its role in facilitating the regeneration of the redox couple is vital (such as iodide/triiodide ions) that shuttles charges between the electrolyte and the dye-sensitized semiconductor. The catalytic activity of the counter electrode is a critical factor for ensuring 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. As a result, it has been frequently applied as the counter electrode in various electrochemical tests [36].

2. **Carbon:** Carbon-based materials are being explored as potential catalysts for counter electrodes in various electrochemical systems, including Dye-Sensitized Solar Cells (DSSCs). While they may not possess the same level of catalytic activity as noble metals like platinum, carbon-based materials present distinct advantages in terms of cost-effectiveness, widespread availability, and environmental sustainability. The performance of photovoltaic cells utilizing carbon counter electrodes is on par with that of platinum. Consequently, cost-effective carbon counter electrodes prove to be suitable catalysts in cobalt-based Dye-Sensitized Solar Cells (DSCs). When the Pt catalyst was replaced with carbon black, the fill factor (FF) and overall photovoltaic performance improved significantly. [37].

IX. UV-VIS SPECTROSCOPY

UV-Vis spectroscopy measures the absorption or transmission of distinct wavelengths of UV or visible light transmitted through a sample. This feature is impacted by the sample's composition, potentially providing information about the compounds and concentrations present in the sample. Light's energy is inversely proportional to its wavelength, with shorter wavelengths carrying more energy and longer wavelengths carrying less energy. To induce electrons in a material to transition to a higher energy state, a specific amount of energy is required which itg can detect as absorption. Electrons in various bonding environments within a material demand distinct amounts of energy to promote their transition. This condition causes absorption of light occurs at varying wavelengths in different materials. 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 detected in a UV-Vis absorption spectrum can be used to calculate the concentration of the sample under investigation. As an example, the concentration of a sample can be determined using the absorbance value at the peak wavelength [38] shown below:

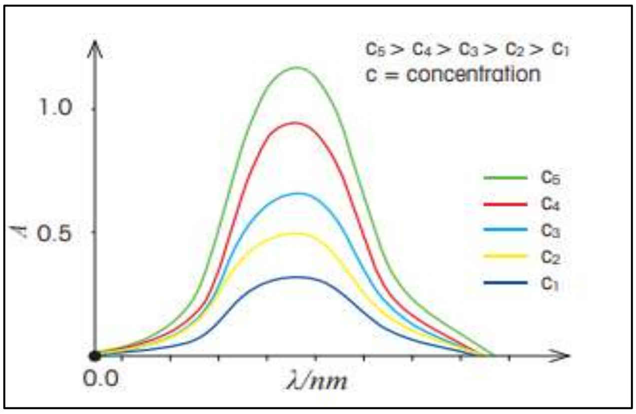

Figure 3: Higher concentrations result to higher absorbance value

X. X-RAY DIFFRACTION

X-ray diffraction techniques are extremely useful tool for analyzing of materials non-destructive, enabling the characterization of crystallographic structure, physical properties of materials, chemical composition, and thin films. X-ray diffraction (XRD) is a crucial tool for examining the structure of nanomaterials since its wavelength is on the atomic scale. The intensities recorded through XRD can provide precise, quantitative insights into atomic arrangements at interfaces. Additionally, it can be employed to measure various structural properties of crystalline phases, including phase composition, strain, grain size, and defect structure. It is also used to determine the thickness of thin films and to examine atomic configurations in amorphous materials such as polymers. Solid matter consists of two primary types of materials which is amorphous and crystalline. The atoms in a crystalline sample are arranged in an orderly manner, and the crystal may be explained by the lowest volume element if it is repeated in three dimensions [39]. The smallest volume element is called a unit cell. Three axes a, b, and c can be used to represent the dimensions of this unit cell. along with the angles between these axes denoted as α, β, and γ. Figure 4 shows a schematic illustration for unit cell..

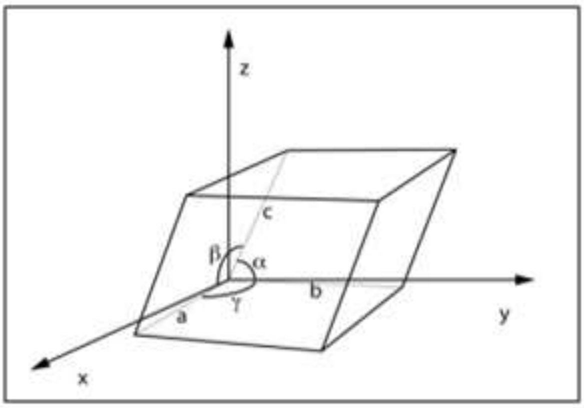

Figure 4: A unit cell from a three-dimensional lattice

XI. 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 influence 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. SEM analysis is not only employed for surface assessment but also serves as a valuable tool for characterizing particles, including wear debris generated during mechanical wear testing.

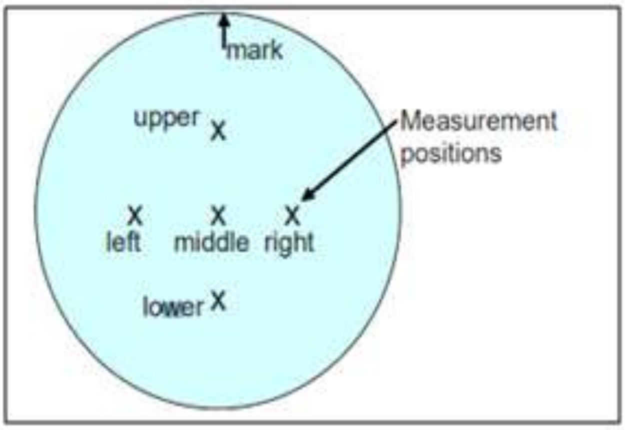

Figure 5: An example for a circular substrate with five distinct measurement position

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