Tannin-Based Natural Dye for DSSC: Polymerization Strategies to Maximize Efficiency

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Abstract

Dye-sensitized solar cells (DSSCs) use dyes to absorb sunlight. Tannin is an eco-friendly natural dye alternative. However, the efficiency of tannin-based DSSCs is still low due to the limited number of conjugated double bonds. This study aims to improve the efficiency of DSSCs by polymerizing tannin in two steps: Formaldehyde condensation under acidic conditions and glutaraldehyde crosslinking in an alkaline medium. Parameter variations included initiator concentration (KOH vs. NaOH), crosslinking agent volume, polymerization time and temperature, and tannin monomer concentration. Characterization by FTIR and UV-Vis spectroscopy showed an increase in light absorption after polymerization as a bathochromic effect. The best results were obtained at 120 °C, 2% NaOH initiator, 2.5 mL glutaraldehyde volume and 90 min reaction time, with DSSC efficiency reaching 9.18%, a fourfold increase compared to pure tannin (2.18%). This study shows that tannin polymerization significantly improves the efficiency of DSSCs, so it has the potential to be developed as a more efficient natural dye for photovoltaic applications.
Keywords: *crosslinking agent, dye, dye-sensitized solar cell (DSSC), natural dye, photovoltaic performance, poly-tannin, tannin polymerization*

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Highlights

1. Tannin polymerization significantly enhances DSSC efficiency, achieving up to 9.18%, a fourfold increase compared to unmodified tannin (2.18%).
2. Dual-step polymerization using formaldehyde condensation and glutaraldehyde crosslinking increases conjugated double bonds, resulting in bathochromic shifts and wider visible light absorption (200–700 nm).
3. Optimal polymerization conditions were identified: 120°C, 2% NaOH initiator, 2.5 mL glutaraldehyde, and 90 minutes reaction time, yielding the best photovoltaic performance.
4. Systematic study on initiator types (NaOH vs. KOH), monomer concentration, crosslinker volume, and polymerization time provided clear structure-property-performance relationships for DSSC application.
5. Poly-tannin demonstrated higher viscosity and density, indicating increased molecular weight and stability, enhancing dye adsorption and electron transfer on TiO_2 photoanodes.

Introduction

Energy is an essential part of everyday life (Chien et al., 2023; Dorahaki et al., 2018; Malinauskaite et al., 2019; Millward-Hopkins et al., 2020; Piao & Managi, 2023). Fossil fuels, as the main source of energy, are becoming increasingly limited and have a negative impact on the environment due to greenhouse gas emissions (Achakulwisut et al., 2023; Dorahaki et al., 2018; Friedlingstein et al., 2023; Müller et al., 2023; Piao & Managi, 2023; Weir et al., 2021). As a result, research into renewable energy is expanding, particularly solar energy, which is recognized as one of the most abundant and environmentally beneficial energy sources (Elalfy et al., 2024; Gul et al., 2016; Hossain et al., 2020; Kabir et al., 2018; Nijsse et al., 2023; Shahsavari & Akbari, 2018; Yang et al., 2017).

Dye-sensitised solar cells (DSSCs) are a future technology that continues to be developed as an alternative to solar energy due to their lower production costs compared to silicon-based solar cells (Badawy et al., 2024; Hamed et al., 2017; Hariningtias & Setiarso, 2021; Onah et al., 2024; Plebankiewicz et al., 2024; Rahman et al., 2023). DSSCs work by using dyes to absorb light and convert photon energy into electrical energy through TiO_2 semiconductors (Badawy et al., 2024; Gong et al., 2017; Khan et al., 2023; Michaels et al., 2020a; Rahman et al., 2023; Sharma et al., 2018; Wu et al., 2015). The selection of dyes with optimal light absorption in the visible spectrum, high stability, and environmental friendliness is a major challenge in DSSC development (Ammar et al., 2019; Coppola et al., 2023; Dragonetti & Colombo, 2021; Narvaez et al., 2021; Talwekar & Tiwari, 2022; Ye et al., 2015).

Most DSSC research uses complex metal dyes, such as ruthenium (Ru), which are known for their high efficiency but have high production costs and the potential to pollute the environment (Badawy et al., 2024; Barichello et al., 2024; Fagnani et al., 2023a, 2023b; Fetouh et al., 2024; Mathew et al., 2014; Michaels et al., 2020b; Sharma et al., 2018). A more environmentally friendly alternative is natural organic matter-based dyes, such as anthocyanins, chlorophyll and tannins (D'Amico et al., 2023; Mahajan et al., 2024; Malhotra et al., 2024; Richhariya et al., 2017; Triyanto et al., 2024; Zafar Iqbal, 2017). Tannins are polyphenolic compounds that can interact with visible light through their conjugated double-bond structure (Das et al., 2020; Haryatmi & Susilowati, 2022; Nurosyid et al., 2024; Suyitno et al., 2024; Swanson, 2003; Upneja et al., 2024). However, the effectiveness of tannin-based DSSCs remains lower than that of metal-based dyes due to the limited number of double bonds accessible for light absorption (Bekele & Sintayehu, 2022; da Conceição et al., 2023a, 2023b; Dhorkule et al., 2024).

A polymerization process can modify the tannin structure to improve the efficiency of tannin-based DSSCs (Das et al., 2020; Vera & Urbano, 2021). Polymerization of tannins aims to increase the number of conjugated double bonds, thereby increasing photon absorption in the visible spectrum (Das et al., 2020; Koopmann et al., 2020; Vera & Urbano, 2021). This happens through a condensation reaction in an alkaline medium, such as formaldehyde and a cross-linking agent (glutaraldehyde). Although this strategy has the potential to improve the efficiency of DSSCs, few studies have investigated the impact of polymerization parameters on DSSC efficiency.

The purpose of this study was to find the best polymerization conditions for tannic acid by changing the initiator concentration (KOH and NaOH), the amount of crosslinker (glutaraldehyde), the polymerization time, the polymerization temperature, and the concentration of tannic acid monomer. The efficiency of DSSCs produced under different polymerization settings was examined to find the optimal combination of parameters that could improve the energy conversion efficiency. The application of tannic acid-based polymer resins synthesized under various polymerization conditions for use in dye-sensitized solar cells (DSSCs) is a new field of research. Although tannins have been studied for various applications, their systematic optimization as polymeric materials for DSSC photoanodes is still limited in the literature. Furthermore, a direct correlation between polymer structure (adjusted by polymerization parameters) and its impact on light absorption and energy conversion efficiency will provide valuable insights into material design for eco-friendly and bio-based solar energy devices.

Research Methods

This research used tannic acid (Brataco, technical grade), glutaraldehyde (GA, Merck, 25% in water), filter paper (Whatman No. 1), ITO glass (Sigma-Aldrich, surface resistance ~15 Ω/sq), distilled water, double-distilled water (aquabidest, Ikapharmindo, p.a.), formaldehyde 37% (Merck, p.a.), potassium hydroxide (KOH, Merck, ≥85%, pellets), sodium hydroxide (NaOH, Merck, ≥98%, pellets), hydrochloric acid 36% (Merck, p.a.), universal pH indicator paper (Merck), alcohol 70% (Indo Alcohol), aluminum foil (Reynolds), potassium iodide and iodine (KI/I_2, Merck, p.a.), polyethylene glycol (PEG 400, Merck), acetonitrile (Merck, p.a., ≥99.8%), methanol (Merck, p.a., ≥99.9%), titanium dioxide TiO_2 Degussa P-25 (Evonik, anatase/rutile ~70:30), ferrous sulfate heptahydrate ($FeSO_4·7H_2O$, Merck, p.a.), and carbon derived from wax (locally synthesized via pyrolysis of paraffin-based candle wax).

The polymerization process of tannin increases the number of conjugated double bonds, increasing the absorption of photons in the visible spectrum. Tannin was mixed with an acid catalyst solution (HCl and formaldehyde) and condensed at 200 °C for 2 hours under magnetic stirring to form tannin-formaldehyde resin. The resulting resin was filtered, washed, and dried at 80°C. Next, the dried resin was dissolved in a base solution (KOH/NaOH) with different concentrations, heated at 60–70°C, and glutaraldehyde was added as a cross-linking agent, forming poly-tannin-glutaraldehyde resin (PTGR). The mixture was further heated before being cooled.

Characterization was carried out using FTIR and UV-Vis spectroscopy to analyze changes in functional groups and absorption spectra, as well as to measure the density and viscosity of the solution. ITO glass was prepared by cutting, ultrasonic cleaning, and resistance measurement to determine electrical conductivity. A nanocrystalline TiO_2 layer was deposited on ITO glass and heated at 100°C for 30 min. The electrolyte solution was prepared from KI/I_2 in acetonitrile with PEG added to improve ionic conductivity. The carbon counter electrode was prepared by coating the ITO glass with a carbon layer from a burning candle and heated to improve adhesion. The synthesized dye was applied to the TiO_2 layer by immersion for 30 min, dried, and then superimposed with the carbon electrode to form a sandwich structure with offsets at the ends for electrical contact. Two drops of electrolyte solution were added before the solar cell was fully assembled.

The performance of the DSSC was tested using a 24 W/m² UV lamp as the light source. The voltage and current were measured by a digital multimeter, and the energy conversion efficiency was calculated based on its photovoltaic response. The use of UV lamps is because although it does contain more visible light components, UV radiation has a higher photon energy and can cause structural damage to solar cell materials, such as degradation of the protective layer, formation of surface defects, as well as a significant decrease in device efficiency (Sinha et al., 2023). Thus, testing with UV lamps is often used as an accelerated aging test method to predict the durability and reliability of materials against long-term exposure to sunlight, as the destructive effects of UV can accelerate the degradation process that usually takes place over many years under natural sunlight. Thus, while analysis using the visible light spectrum is also important to mimic real conditions, the use of UV lamps remains scientifically relevant to evaluate material durability and study the degradation mechanisms that may occur in solar cells.

Results and Discussion

Dye characterization

Dye characterization using Fourier Transform Infrared (FTIR) was used in this study to detect functional groups and types of chemical bonds in tannins before and after polymerization into poly-tannins. The purpose of this study is to better understand the chemical structure changes that occur throughout the polymerization process, specifically in the creation of poly-tannin glutaraldehyde resin (PTGR). Tannin polymerization was carried out in an alkaline medium (NaOH) with glutaraldehyde as a cross-linking agent, producing resins with more complicated structures. FTIR characterization was used to detect changes in infrared absorption spectra, indicating functional group alteration during polymerization. The results are shown in Figure 1 and Table 1.

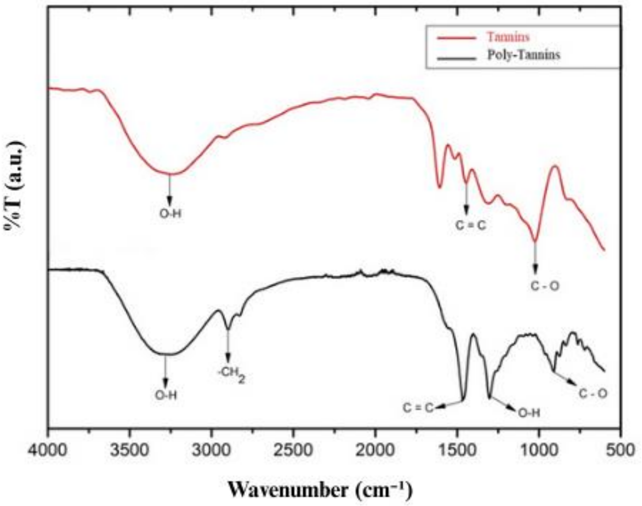

Figure 1. FTIR spectra of pure tannins and poly-tannin glutaraldehyde resin (PTGR), highlighting functional group changes after crosslinking.

Table 1. Functional group assignments and corresponding wave numbers observed in FTIR spectra of tannins and PTGR.

Functional groups	**Data Interpretation (cm^{-1})**		
	Tanin	**Poli-Tanin**	**Literature Data**
O-H phenol	3240.56	3318.58	3600–3200
CH$_2$ methylene	-	2942.46	2700–3000
C=C aromatic	1513.55	1549.83	1500–1675
C-O aromatic	1024.64	1021.33	1000–1100
C=O carbonyl	1606.49	1635.66	1600–1820

FTIR spectra were analyzed at 600–4000 cm^{-1} for pure tannins and 500–4000 cm^{-1} for poly-tannin. The spectra revealed considerable changes in the chemical structure of tannins after polymerization. Pure tannin contains three major groups: phenolic (-OH) at 3240.56 cm^{-1}, carbonyl (C=O) at 1606.49 cm^{-1}, and aromatic (C=C and C-O) at 1513.55 cm-^{1} and 1024.64 cm^{-1}. After polymerization, the infrared spectrum shifts, indicating a change in chemical structure. The phenol (-OH) group had the biggest shift from 3240.56 cm^{-1} to 3318.58 cm^{-1}, showing a change in hydrogen bonding interactions caused by polymerization. In addition, two new peaks appeared at 2942.46 cm^{-1} and 2877 cm^{-1}, corresponding to vibrations of the methylene bridge ($-CH_2$) formed during the reaction between tannin and formaldehyde. A decrease in carbonyl (C=O) intensity was also observed, indicating a change in the chemical structure of the tannin after polymerization.

The dyes were also characterized using a UV-Vis spectrophotometer to see how polymerization affected the optical characteristics of the tannins. The findings revealed a bathochromic impact. The bathochromic effect results from the interaction of the chromophore (light-absorbing group) and the autochrome (substituent group that enhances the optical effect). The addition of electrons to the poly-tannin structure during polymerization causes an absorbance change to higher wavelengths (redshift). The wavelength of maximum absorption shifts from 275 nm to 456 nm from pure tannin to poly-tannins, as shown in Table 2 and Figure 2. Furthermore, poly-tannin absorbs light in a broader range than pure tannin. Tannin absorbs light from 200 to 400 nm, while poly-tannin absorbs light between 200 and 700 nm. This demonstrates that poly-tannin absorbs more light in the visible wavelength range, which will increase its potential efficiency in DSSCs. Poly-tannin is projected to be more efficient than pure tannin in DSSC applications due to its increased absorption in the visible light area and wider spectrum. Overall, the UV-Vis characterization data indicate that tannin polymerization improves light absorption, which is an important component in improving dyes' efficiency as photosensitizers in DSSCs.

Table 2. UV-Vis absorbance data of tannins and poly-tannin glutaraldehyde resin (PTGR), showing changes in peak position and intensity after polymerization.

Dye	Maximum wavelength (nm)	Absorbance	Absorption Area (nm)
Poly-Tannins	456	0.259	200–700
Tannins	275	0.250	200–400

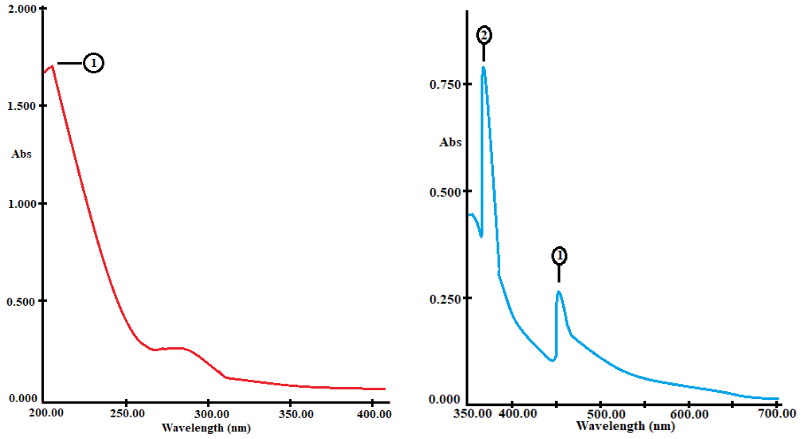

Figure 2. UV-Vis spectra of tannins and poly-tannin glutaraldehyde resin (PTGR), showing changes in absorbance peaks after polymerization.

The difference in density and viscosity between pure tannin and poly-tannin can also be used to measure the completion of polymerization. According to Figure 3, viscosity and density values increase dramatically after tannin polymerization to poly-tannin. The viscosity of poly-tannin was 9.13774 poise, significantly higher than that of pure tannin, which was only 1.83007 poise. This rise causes the solution to flow more slowly than pure tannin. The greater viscosity value also implies that poly-tannin has a higher molecular weight due to the longer polymer chains formed during the polymerization process.

The density of pure tannin increased from 1.04112 g/cm³ to 1.102 g/cm³ for poly-tannin, a difference of 0.06088 g/cm³. This shows that poly-tannin has a larger density, which is due to the increase in intermolecular bonding after polymerization. As poly-tannins' molecular weight grows, the interactions between molecules get stronger, resulting in a considerable increase in viscosity. Taken together, these characterization data demonstrate that the tannin polymerization was successful in producing a poly-tannin with a more complicated structure and a larger molecular weight, resulting in an increase in density and viscosity. This implies that poly-tannins may have a higher potential as a dye in DSSC applications than pure tannin.

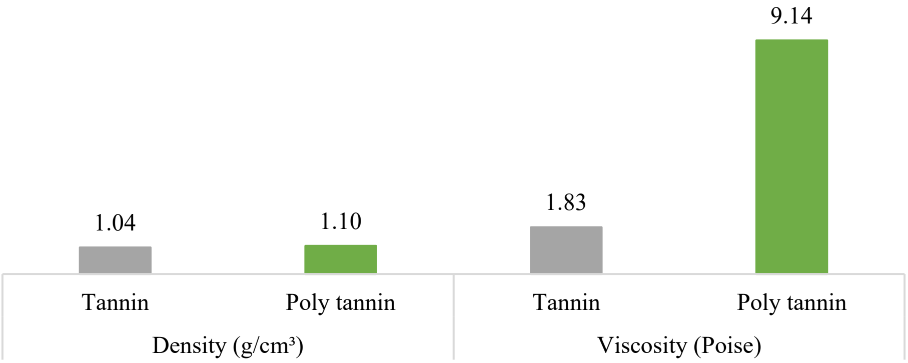

Figure 3. Comparison of density and viscosity between tannins and PTGR, showing the effect of crosslinking on the physical properties of the resin.

The effect of the crosslinking agent volume

Cross-linking agents play an important role in tannin polymerization by influencing the creation of links between polymer chains. This study used glutaraldehyde as a cross-linking agent. It combines with hydroxyl (-OH) groups on tannins via an aldol reaction or Schiff condensation reaction mechanism, generating methylene (-CH_2-) bridges between tannin molecules. The results are presented in Figure 4. In general, the amount of cross-linking agent affects the length and degree of branching of the poly-tannin chain formed: low and excessive crosslinker volume.

Low crosslinker volume (≤ 0.5 mL) is when the amount of free radicals generated is small, so only a small fraction of the tannin monomers can bond. This results in a polymer with a short structure, which is less effective in forming double bond conjugates, reducing photon uptake and lowering DSSC efficiency (1.85%). The volume of crosslinker increases (up to 2.5 mL): More free radicals are generated, increasing polymerization and producing poly-tannin with longer, branched chains. This structure is more optimal for forming a conjugated double bond system, which plays a role in increasing light absorption and electron transfer in DSSCs. Therefore, the efficiency of the DSSC reached a maximum value of 7.01% at a volume of 2.5 mL of glutaraldehyde.

Excessive crosslinker volume (>2.5ml) means excessive addition of glutaraldehyde causes the polymerization reaction to become uncontrolled, resulting in an overly dense polymer network. As a result, the mobility of electrons in the system is reduced and charge transfer in the DSSC is inhibited, leading to a decrease in efficiency at volumes of 3.5 mL and 4.5 mL. These results indicate that the optimum volume of cross-linking agent in tannin polymerization for DSSCs is 2.5 mL, because at this condition, poly-tannin has a good balance between chain length, conjugation degree and electron transfer capability.

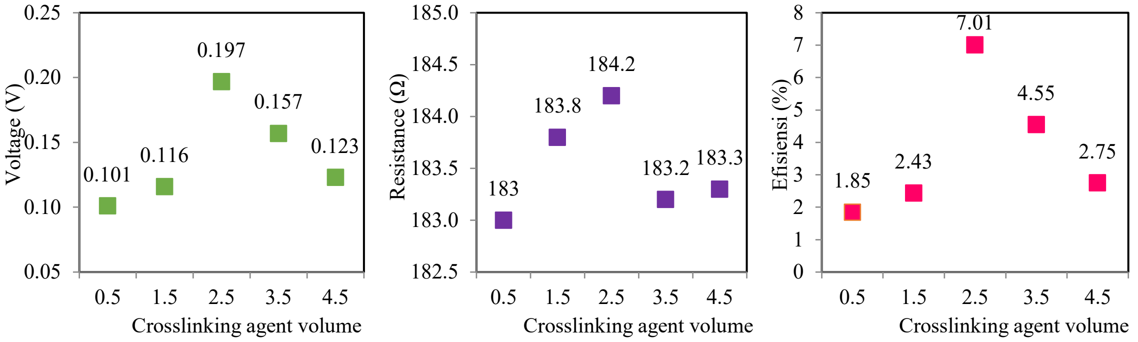

Figure 4. Influence of varying glutaraldehyde volumes as a crosslinking agent on DSSC performance parameters: open-circuit voltage, internal resistance, and overall efficiency.

The effect of initiator concentration (comparison between KOH and NAOH)

Initiators have an important role in tannin polymerization by forming free radicals that initiate polymer chain propagation reactions. In this study, two types of basic initiators were used, potassium hydroxide (KOH) and sodium hydroxide (NaOH). The initiator's main role is to aid in the opening of epoxy groups on glutaraldehyde, which improves the reactivity of tannins in the polymerization step. The amount of free radicals produced, the length of the polymer chain, and the degree of conjugation in the poly-tannin are all affected by the initiator concentration, which ultimately determines the effectiveness of the dye-sensitized solar cell (DSSC). In this experiment, the KOH concentration variations tested were 1%, 1.5%, 2%, 3%, 4%, and 5%, while the NaOH variations were 0.5%, 1.5%, 2.5%, 3.5%, and 4.5%.

The experimental findings revealed that KOH at 1% concentration had the lowest DSSC effectiveness of 1.25%. This low efficiency is due to the tiny quantity of free radicals generated, which causes polymerization to take place inefficiently, resulting in short poly-tannin chains and less effective light absorption. As the KOH concentration increased, so did the DSSC's efficiency, peaking at 7.01% at 2%. This suggests that the amount of free radicals produced is sufficient to optimally drive polymerization without triggering unwanted side reactions. However, as the KOH concentration was increased to 3%, 4%, and 5%, the DSSC efficiency decreased to 6.38%, 3.80%, and 3.83%, respectively. This decrease is likely due to the excess of free radicals that cause premature termination of the polymer chain, so that the poly-tannin structure formed becomes shorter and less effective in absorbing light. This phenomenon has also been reported in previous studies, stating that an excess of free radicals in the polymerization system can cause the polymer chain growth to terminate faster, resulting in shorter and less stable polymer structures in photovoltaic systems.

Meanwhile, when NaOH was used as the initiator, the same trend was also observed, but with a different pattern of concentration variation. The DSSC efficiency increases with increasing initiator concentration until it reaches a maximum value of 7.3% at 1.5% NaOH, which is slightly higher than KOH. This efficiency is probably higher because NaOH has stronger basic properties than KOH, so it is more effective in accelerating the condensation reaction of tannins with glutaraldehyde, resulting in poly-tannin with a higher degree of conjugation and better light absorption ability. However, increasing the NaOH content to 2.5%, 3.5%, and 4.5% resulted in DSSC efficiency decreases of 3.78%, 3.52%, and 3.83%. This drop is most likely due to the production of poly-tannin homopolymers that are too reactive, causing the conjugated double bond structure to become unstable and reducing photon absorption.

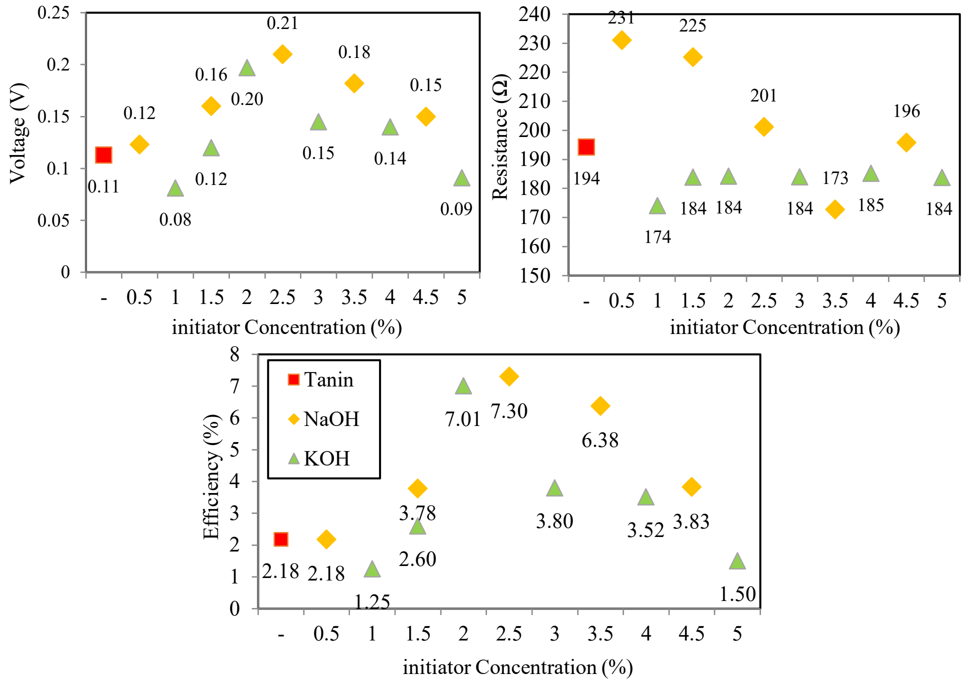

Figure 5. Voltage, resistance, and efficiency measurements from DSSC in response to variations in initiator concentration

Additionally, the difference in solution viscosity is another factor that affects DSSC efficiency. In this study, the solution with an initiator concentration of 1.5% NaOH exhibits a higher viscosity than the other variations, indicating that the polymer structure formed is longer and more complex. This increase in viscosity corresponds to an increase in the molecular weight of poly-tannin, which is in line with previous studies showing that higher viscosity may indicate the formation of longer and more branched polymer chains, which contributes to an increase in DSSC efficiency.

The results are presented in Figure 5. Overall, NaOH proved to be more effective than KOH as an initiator in the polymerization of tannins, as it produced poly-tannins with better conjugated structures, thereby improving the light absorption and efficiency of DSSCs. However, selecting the right initiator concentration is crucial to avoid side reactions that lead to the formation of too short or too branched polymers. The results of this study showed that the optimal condition for tannin polymerization in DSSCs was 1.5% NaOH, which resulted in the highest efficiency of 7.3%. For KOH, the optimal condition was 2%, with a corresponding efficiency of 7.01%.

The effect of polymerization time

Polymerization time is one of the important factors in determining the poly-tannin chain length, degree of cross-linking and polymer stability, all of which contribute to the efficiency of DSSCs. In this study, the polymerization time variations tested were 45, 60, 75, 90 and 115 minutes.

The experimental results show that the efficiency of DSSCs initially increases with increasing polymerization time but decreases after reaching the optimum condition. The results can be seen in Figure 6. At a polymerization time of 45 minutes, the efficiency of the DSSC was still low (2.93%), likely due to incompletely formed polymer chains, which resulted in a poly-tannin structure that was still too dilute and less conjugated to absorb light effectively. The efficiency of the DSSC increased with time, reaching a maximum of 7.81% at 90 minutes. This increase indicates that currently the polymer chains have developed long enough to have an optimum degree of conjugation, allowing more effective light absorption and improving electron transfer in the DSSC.

Extending polymerization to 115 min reduced efficiency to 6.42%. This decrease is most likely due to the significantly increased viscosity of the poly-tannin solution, which makes it more difficult for the poly-tannin to be absorbed onto the TiO_2 semiconductor surface. When the poly-tannin solution is too viscous, the dispersion of the dye becomes uneven, preventing optimal interaction between the poly-tannin and TiO_2. This phenomenon is also supported by previous studies showing that over-polymerization can lead to polymer aggregation, which inhibits electron diffusion and ultimately reduces the efficiency of the DSSC.

We conclude that the optimal polymerization time to produce poly-tannin with the highest DSSC efficiency is 90 min. The polymer chains are long enough to increase light absorption but have not yet reached a viscosity level that inhibits adsorption onto TiO_2. This time was used as the basis for further parameter variation tests.

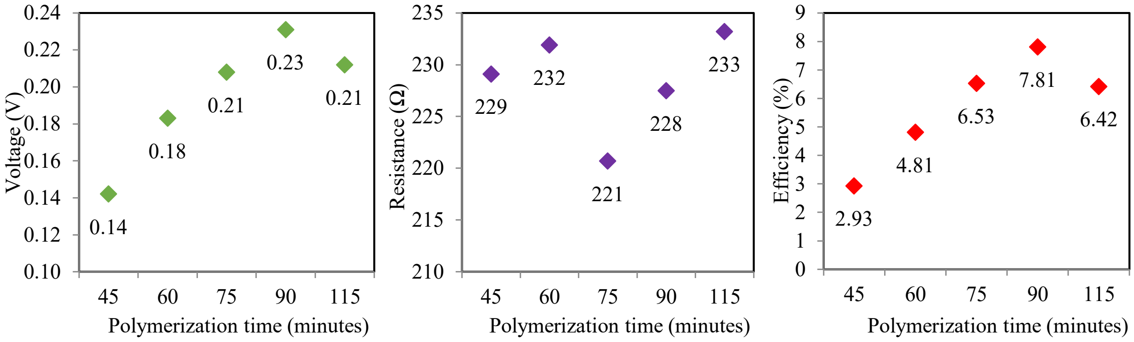

Figure 6. Voltage, resistance, and efficiency of DSSC as a function of polymerization time

The effect of tannin monomer concentration

This Figure indicates that a monomer concentration of 0.15 M produces a DSSC efficiency of 3.33%. This low efficiency is caused by the yield of poly-tannin glutaraldehyde (PTGR), which remains very dilute at low concentrations. Consequently, the polymer structure formed is small, and the cross-links formed with glutaraldehyde are still limited. This leads to a low number of conjugated double bonds, resulting in sub-optimal light absorption and lower DSSC efficiency. The results can be seen in Figure 7.

Increasing the monomer concentration leads to higher efficiency, reaching 8.33% at a monomer concentration of 0.45 M. This increase occurs because the higher the monomer concentration, the more tannin units are available for cross-linking with glutaraldehyde, resulting in poly-tannin with a longer and more stable structure. This structure increases the number of conjugated double bonds, which contributes to increased light absorption and electron transfer efficiency in DSSCs.

At 0.55M, the efficiency dropped as low as 6.30%. This decrease is probably due to the formation of tannin homopolymers in which the tannin molecules begin to bind to each other without the involvement of the cross-linking agent (glutaraldehyde). When homopolymers are formed, the polymer structure becomes stiffer and too large, inhibiting the diffusion of poly-tannin into the pores of TiO_2. In addition, the increase in solution viscosity at high monomer concentrations also contributes to the decrease in DSSC efficiency, as the more viscous poly-tannin is more difficult to penetrate and bond to the semiconductor surface effectively.

Previous studies have also shown that increasing the monomer concentration during polymerization tends to increase the molecular weight of the polymer. However, if the concentration is too high, homopolymerization can occur, hindering charge transfer and reducing the material's efficiency in photovoltaic applications. In addition, an excess of homopolymer can lead to poly-tannin precipitation, which causes aggregation of the material in solution, reducing the light absorption efficiency of the DSSC.

The results indicate that the optimum concentration of tannin monomer to improve the efficiency of DSSC was 0.45M, due to the production of a stable poly-tannin conformation, sufficient length and optimum conjugation. Concentrations higher than this are likely to cause polymer aggregation and increased viscosity, which inhibits dye adsorption and reduces the efficiency of the DSSC.

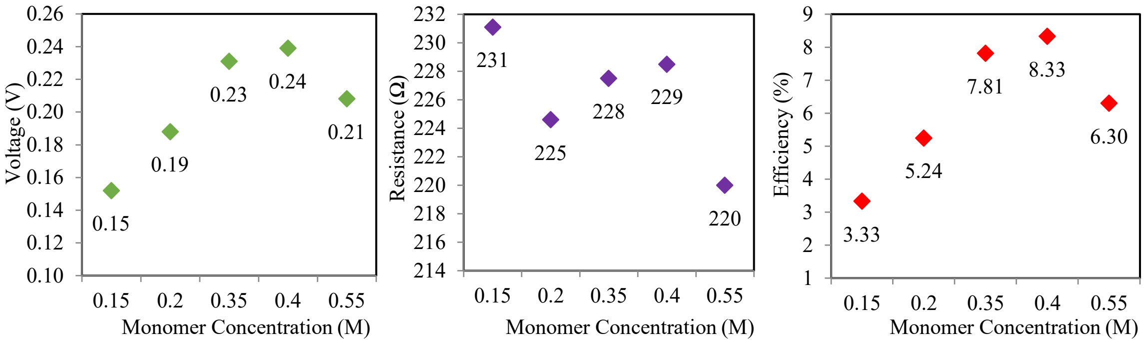

Figure 7. The Effects of Tannin Monomer Concentration on Voltage, Resistance, and DSSC Efficiency

The effect of polymerization temperature

Polymerization temperatures in the range of 100 to 140°C are considered ideal because at these temperatures the tannin polymerization reaction takes place optimally-the energy provided is sufficient to activate the formation of bonds between tannin molecules without causing degradation of the main chemical structure. At this temperature, the condensation process is efficient, resulting in poly-tannins with high molecular weight, good thermal stability, and desirable physical and chemical properties. If the temperature is too low, the reaction is slow, and the polymer formed is less perfect. Conversely, at too high a temperature, the tannins can be damaged or degraded, reducing the quality and yield of the polymer produced.

Previous research shows that tannin polymerization temperatures above 150°C are not recommended because in that temperature range, thermal degradation of the tannin structure begins to occur, especially in raw tannin extracts that still contain carbohydrates. Thermogravimetric studies (TGA) show that tannins with high carbohydrate content begin to degrade at around 150°C, while pure tannins only begin to degrade at around 200°C (Pizzi et al., 2024). In addition, other studies have found that the curing reaction of tannins with formaldehyde is optimal in the range of 100–120 °C, and that at temperatures above 150 °C, there is no increase in reaction, but rather an early indication of degradation before the main decomposition peak above 190 °C (Lisperguer et al., 2016). Thus, keeping the polymerization temperature below 140-150 °C is very important for the process to run efficiently without damaging the chemical structure of tannins and maintaining the quality of the poly-tannins produced.

The highest efficiency of 9.18% is obtained at a temperature of 120 °C, while the lowest efficiency is achieved at a temperature of 140 °C. The complete results are presented in Figure 8. The trend shows that efficiency increases with increasing temperature but decreases when it reaches the optimum point. This trend indicates that the efficiency of the DSSC increases with increasing temperature but decreases after reaching the optimum point. At too low a temperature, the polymerization reaction is slow and sub-optimal because the activation energy required for the condensation process between tannin and glutaraldehyde has not been reached. As a result, few monomers are cross-linked and the poly-tannin structure formed does not have enough conjugated double bonds to increase light absorption.

As the temperature increases, the collision rate between molecules increases, allowing more tannin monomers to react with the cross-linking agent. This produces poly-tannin with a longer and more stable polymer chain, which ultimately increases the efficiency of the DSSC. However, when the polymerization temperature exceeds 120°C, the efficiency of the DSSC begins to decrease. This decrease is due to the structural degradation of poly-tannin, where high temperatures can cause damage to the tannin functional groups, reducing the effectiveness of the double bonds in absorbing photons. In addition, unwanted side reactions can occur, resulting in a polymer structure that is too rigid and inhibits charge transfer in DSSCs. Increasing the viscosity of the solution is also an important factor, as a solution that is too thick will be difficult to absorb into the pores of the TiO_2 semiconductor, thereby reducing the energy conversion efficiency.

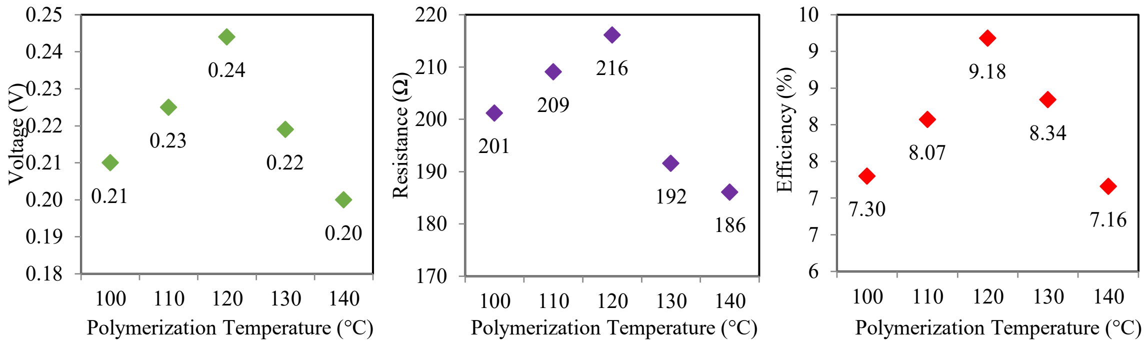

Figure 8. Voltage, resistance, and efficiency to temperature variation in the polymerization process

The results of all tests are collected in Figure 9. The comparison between ordinary tannin and poly-tannin as dyes in DSSC shows that ordinary tannin has an efficiency of only 2.18%, much lower than poly-tannin, which has undergone optimal polymerization with an efficiency of 9.18%. This indicates that modifying the tannin structure through polymerization under suitable conditions can enhance the efficiency of DSSC by more than four times. However, if polymerization is carried out under inappropriate conditions, the efficiency of DSSC may vary and even be lower than using tannin without polymerization. Therefore, the optimal polymerization temperature is very important to ensure that the poly-tannin structure formed has the best balance between chain length, degree of conjugation and adsorption ability to TiO_2.

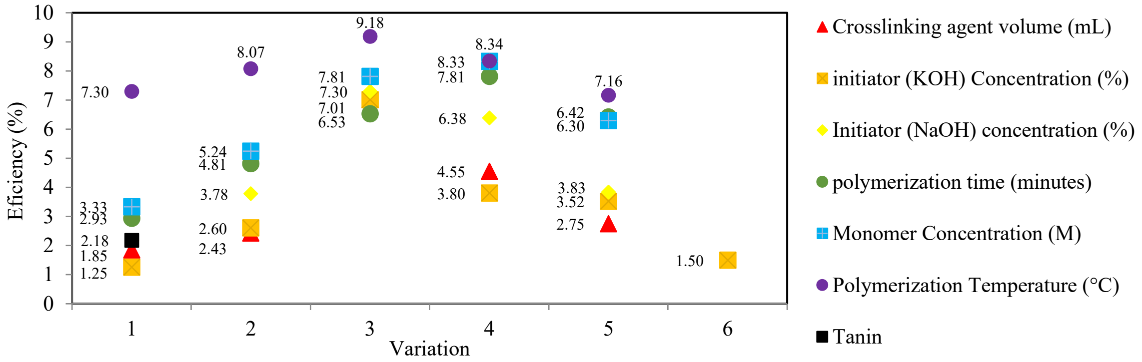

Figure 9. Comparison of DSSC efficiency across different experimental variables.

Conclusions

This study shows that tannin polymerization significantly improves the efficiency of dye-sensitised solar cells (DSSCs). Polymerization using formaldehyde and glutaraldehyde increases the number of conjugated double bonds, thereby increasing light absorption and energy conversion. The best results were obtained at a temperature of 120 °C, 2% NaOH initiator, 2.5 mL glutaraldehyde volume and 90 minutes reaction time, with DSSC efficiency reaching 9.18%, four times higher than pure tannin (2.18%). These results indicate that poly-tannin has the potential to be a more efficient natural dye in DSSC, providing a more environmentally friendly alternative to metal-based dyes.

Author Contributions

H designed the research conceptualization and methodology, performed data analysis, supervised the project, managed project administration, and secured the funding. **AAP**, **RGL**, and **WF** performed the data collection. **PP** conducted data analysis and visualization and wrote both the original draft and the revised version. All authors contributed and agreed to the final version of the manuscript.

Conflict of Interest

The authors have declared that there is no conflict of interest.

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References

Achakulwisut, P., Erickson, P., Guivarch, C., Schaeffer, R., Brutschin, E., & Pye, S. (2023). Global fossil fuel reduction pathways under different climate mitigation strategies and ambitions. *Nature Communications*, *14*(1), 5425. https://doi.org/10.1038/s41467-023-41105-z

Ammar, A. M., Mohamed, H. S. H., Yousef, M. M. K., Abdel-Hafez, G. M., Hassanien, A. S., & Khalil, A. S. G. (2019). Dye-Sensitized Solar Cells (DSSCs) Based on Extracted Natural Dyes. *Journal of Nanomaterials*, *2019*, 1–10. https://doi.org/10.1155/2019/1867271

Badawy, S. A., Abdel-Latif, E., & Elmorsy, M. R. (2024). Tandem dye-sensitized solar cells achieve 12.89% efficiency using novel organic sensitizers. *Scientific Reports*, *14*(1), 26072. https://doi.org/10.1038/s41598-024-75959-0

Barichello, J., Mariani, P., Vesce, L., Spadaro, D., Citro, I., Matteocci, F., Bartolotta, A., Di Carlo, A., & Calogero, G. (2024). Bifacial dye-sensitized solar cells for indoor and outdoor renewable energy-based application. *Journal of Materials Chemistry C*, *12*(7), 2317–2349. https://doi.org/10.1039/D3TC03220E

Bekele, E. T., & Sintayehu, Y. D. (2022). Recent Progress, Advancements, and Efficiency Improvement Techniques of Natural Plant Pigment-Based Photosensitizers for Dye-Sensitized Solar Cells. *Journal of Nanomaterials*, *2022*(1). https://doi.org/10.1155/2022/1024100

Chien, F., Huang, L., & Zhao, W. (2023). The influence of sustainable energy demands on energy efficiency: Evidence from China. *Journal of Innovation & Knowledge*, *8*(1), 100298. https://doi.org/10.1016/j.jik.2022.100298

Coppola, C., Parisi, M. L., & Sinicropi, A. (2023). The Role of Organic Compounds in Dye-Sensitized and Perovskite Solar Cells. *Energies*, *16*(2), 573. https://doi.org/10.3390/en16020573

da Conceição, L. R. B., da Cunha, H. O., Leite, A. M. B., Suresh Babu, R., Raja, S., Ribeiro, C., & de Barros, A. L. F. (2023a). Evaluation of Solar Conversion Efficiency in Dye-sensitized Solar Cells Using Natural Dyes Extracted from Alpinia purpurata and Alstroemeria Flower Petals as Novel Photosensitizers. *Colorants*, *2*(4), 618–631. https://doi.org/10.3390/colorants2040032

da Conceição, L. R. B., da Cunha, H. O., Leite, A. M. B., Suresh Babu, R., Raja, S., Ribeiro, C., & de Barros, A. L. F. (2023b). Evaluation of Solar Conversion Efficiency in Dye-sensitized Solar Cells Using Natural Dyes Extracted from Alpinia purpurata and Alstroemeria Flower Petals as Novel Photosensitizers. *Colorants*, *2*(4), 618–631. https://doi.org/10.3390/colorants2040032

D'Amico, F., de Jong, B., Bartolini, M., Franchi, D., Dessì, A., Zani, L., Yzeiri, X., Gatto, E., Santucci, A., Di Carlo, A., Reginato, G., Cinà, L., & Vesce, L. (2023). Recent Advances in Organic Dyes for Application in Dye-Sensitized Solar Cells under Indoor Lighting Conditions. *Materials*, *16*(23), 7338. https://doi.org/10.3390/ma16237338

Das, A. K., Islam, M. N., Faruk, M. O., Ashaduzzaman, M., & Dungani, R. (2020). Review on tannins: Extraction processes, applications and possibilities. *South African Journal of Botany*, *135*, 58–70.

https://doi.org/10.1016/J.SAJB.2020.08.008

Dhorkule, M., Lamrood, P., Ralegankar, S., Patole, S. P., Wagh, S. S., & Pathan, H. M. (2024). Unveiling the Efficiency of Dye-Sensitized Solar Cells: A Journey from Synthetic to Natural Dyes. *ES Food & Agroforestry*. https://doi.org/10.30919/esfaf1086

Dorahaki, S., Rashidinejad, M., Abdollahi, A., & Mollahassani-pour, M. (2018). A novel two-stage structure for coordination of energy efficiency and demand response in the smart grid environment. *International Journal of Electrical Power & Energy Systems*, *97*, 353–362. https://doi.org/10.1016/j.ijepes.2017.11.026

Dragonetti, C., & Colombo, A. (2021). Recent Advances in Dye-Sensitized Solar Cells. *Molecules*, *26*(9), 2461. https://doi.org/10.3390/molecules26092461

Elalfy, D. A., Gouda, E., Kotb, M. F., Bureš, V., & Sedhom, B. E. (2024). Comprehensive review of energy storage systems technologies, objectives, challenges, and future trends. *Energy Strategy Reviews*, *54*, 101482. https://doi.org/10.1016/j.esr.2024.101482

Fagnani, F., Colombo, A., Dragonetti, C., & Roberto, D. (2023a). Recent Investigations on the Use of Copper Complexes as Molecular Materials for Dye-Sensitized Solar Cells. *Molecules*, *29*(1), 6. https://doi.org/10.3390/molecules29010006

Fagnani, F., Colombo, A., Dragonetti, C., & Roberto, D. (2023b). Recent Investigations on the Use of Copper Complexes as Molecular Materials for Dye-Sensitized Solar Cells. *Molecules*, *29*(1), 6. https://doi.org/10.3390/molecules29010006

Fetouh, H. A., Dissouky, A. E., Salem, H. A., Fathy, M., Anis, B., & Hady Kashyout, A. E. (2024). Synthesis, characterization and evaluation of new alternative ruthenium complex for dye sensitized solar cells. *Scientific Reports*, *14*(1), 16718. https://doi.org/10.1038/s41598-024-66808-1

Friedlingstein, P., O'Sullivan, M., Jones, M. W., Andrew, R. M., Bakker, D. C. E., Hauck, J., Landschützer, P., Le Quéré, C., Luijkx, I. T., Peters, G. P., Peters, W., Pongratz, J., Schwingshackl, C., Sitch, S., Canadell, J. G., Ciais, P., Jackson, R. B., Alin, S. R., Anthoni, P., … Zheng, B. (2023). Global Carbon Budget 2023. *Earth System Science Data*, *15*(12), 5301–5369. https://doi.org/10.5194/essd-15-5301-2023

Gong, J., Sumathy, K., Qiao, Q., & Zhou, Z. (2017). Review on dye-sensitized solar cells (DSSCs): Advanced techniques and research trends. *Renewable and Sustainable Energy Reviews*, *68*, 234–246. https://doi.org/10.1016/j.rser.2016.09.097

Gul, M., Kotak, Y., & Muneer, T. (2016). Review on recent trend of solar photovoltaic technology. *Energy Exploration & Exploitation*, *34*(4), 485–526. https://doi.org/10.1177/0144598716650552

Hamed, N. K. A., Ahmad, M. K., Urus, N. S. T., Mohamad, F., Nafarizal, N., Ahmad, N., Soon, C. F., Ameruddin, A. S., Faridah, A. B., Shimomura, M., & Murakami, K. (2017). *Performance comparison between silicon solar panel and dye-sensitized solar panel in Malaysia*. 020029. https://doi.org/10.1063/1.5002047

Hariningtias, E. R., & Setiarso, P. (2021). Potensi Ekstrak Daun Salam

(Syzygium polyanthum) pada pH Asam Sebagai Sensitizer Pada Dye Sensitized Solar Cell (DSSC). *Jurnal Kimia Riset*, *6*(2), 109. https://doi.org/10.20473/jkr.v6i2.30506

Haryatmi, D., & Susilowati, I. T. (2022). Determining The Tannin Content in Pisang Ambon (Musa × paradisiaca L.) with the Potential as Anthelmintic. *Jurnal Kimia Riset*, *7*(2), 118–124. https://doi.org/10.20473/jkr.v7i2.28859

Hossain, E., Faruque, H., Sunny, Md., Mohammad, N., & Nawar, N. (2020). A Comprehensive Review on Energy Storage Systems: Types, Comparison, Current Scenario, Applications, Barriers, and Potential Solutions, Policies, and Future Prospects. *Energies*, *13*(14), 3651. https://doi.org/10.3390/en13143651

Kabir, E., Kumar, P., Kumar, S., Adelodun, A. A., & Kim, K.-H. (2018). Solar energy: Potential and future prospects. *Renewable and Sustainable Energy Reviews*, *82*, 894–900. https://doi.org/10.1016/j.rser.2017.09.094

Khan, M., Iqbal, M. A., Malik, M., Hashmi, S. U. M., Bakhsh, S., Sohail, M., Qamar, M. T., Al-Bahrani, M., Capangpangan, R. Y., Alguno, A. C., & Choi, J. R. (2023). Improving the efficiency of dye-sensitized solar cells based on rare-earth metal modified bismuth ferrites. *Scientific Reports*, *13*(1), 3123. https://doi.org/10.1038/s41598-023-30000-8

Koopmann, A.-K., Schuster, C., Torres-Rodríguez, J., Kain, S., Pertl-Obermeyer, H., Petutschnigg, A., & Hüsing, N. (2020). Tannin-Based Hybrid Materials and Their Applications: A Review. *Molecules*, *25*(21), 4910. https://doi.org/10.3390/molecules25214910

Lisperguer, J., Saravia, Y., & Vergara, E. (2016). Structure and Thermal Behavior of Tannins from Acacia dealbata Bark and Their Reactivity Toward Formaldehyde. *Journal of the Chilean Chemical Society*, *61*(4), 3188–3190. https://doi.org/10.4067/S0717-97072016000400007

Mahajan, U., Prajapat, K., Dhonde, M., Sahu, K., & Shirage, P. M. (2024). Natural dyes for dye-sensitized solar cells (DSSCs): An overview of extraction, characterization and performance. *Nano-Structures & Nano-Objects*, *37*, 101111. https://doi.org/10.1016/j.nanoso.2024.101111

Malhotra, S. S., Ahmed, M., Gupta, M. K., & Ansari, A. (2024). Metal-free and natural dye-sensitized solar cells: recent advancements and future perspectives. *Sustainable Energy & Fuels*, *8*(18), 4127–4163. https://doi.org/10.1039/D4SE00406J

Malinauskaite, J., Jouhara, H., Ahmad, L., Milani, M., Montorsi, L., & Venturelli, M. (2019). Energy efficiency in industry: EU and national policies in Italy and the UK. *Energy*, *172*, 255–269. https://doi.org/10.1016/j.energy.2019.01.130

Mathew, S., Yella, A., Gao, P., Humphry-Baker, R., Curchod, B. F. E., Ashari-Astani, N., Tavernelli, I., Rothlisberger, U., Nazeeruddin, Md. K., & Grätzel, M. (2014). Dye-sensitized solar cells with 13% efficiency achieved through the molecular engineering of porphyrin sensitizers. *Nature Chemistry*, *6*(3), 242–247. https://doi.org/10.1038/nchem.1861

Michaels, H., Rinderle, M., Freitag, R., Benesperi, I., Edvinsson, T., Socher, R., Gagliardi, A., & Freitag, M. (2020a). Dye-sensitized solar cells under ambient light powering machine learning: towards autonomous smart sensors for the internet of things. *Chemical Science*, *11*(11), 2895–2906. https://doi.org/10.1039/C9SC06145B

Michaels, H., Rinderle, M., Freitag, R., Benesperi, I., Edvinsson, T., Socher, R., Gagliardi, A., & Freitag, M. (2020b). Dye-sensitized solar cells under ambient light powering machine learning: towards autonomous smart sensors for the internet of things. *Chemical Science*, *11*(11), 2895–2906. https://doi.org/10.1039/C9SC06145B

Millward-Hopkins, J., Steinberger, J. K., Rao, N. D., & Oswald, Y. (2020). Providing decent living with minimum energy: A global scenario. *Global Environmental Change*, *65*, 102168. https://doi.org/10.1016/j.gloenvcha.2020.102168

Müller, J. D., Gruber, N., Carter, B., Feely, R., Ishii, M., Lange, N., Lauvset, S. K., Murata, A., Olsen, A., Pérez, F. F., Sabine, C., Tanhua, T., Wanninkhof, R., & Zhu, D. (2023). Decadal Trends in the Oceanic Storage of Anthropogenic Carbon From 1994 to 2014. *AGU Advances*, *4*(4). https://doi.org/10.1029/2023AV000875

Narvaez, G., Giraldo, L. F., Bressan, M., & Pantoja, A. (2021). Machine learning for site-adaptation and solar radiation forecasting. *Renewable Energy*, *167*, 333–342. https://doi.org/10.1016/j.renene.2020.11.089

Nijsse, F. J. M. M., Mercure, J.-F., Ameli, N., Larosa, F., Kothari, S., Rickman, J., Vercoulen, P., & Pollitt, H. (2023). The momentum of the solar energy transition. *Nature Communications*, *14*(1), 6542. https://doi.org/10.1038/s41467-023-41971-7

Nurosyid, F., Riyadi, U., Widiyandari, H., Iriani, Y., Khairuddin Khairuddin, & Suryana, R. (2024). Optoelectronic Properties of Combinations of Anthocyanin, Betalain, and Chlorophyll doped with Ag Metal as the Photosensitizers in Dye-Sensitized Solar Cell. *Evergreen*, *11*(3), 2135–2141. https://doi.org/10.5109/7236857

Onah, E. H., Lethole, N. L., & Mukumba, P. (2024). Luminescent Materials for Dye-Sensitized Solar Cells: Advances and Directions. *Applied Sciences*, *14*(20), 9202. https://doi.org/10.3390/app14209202

Piao, X., & Managi, S. (2023). Household energy-saving behavior, its consumption, and life satisfaction in 37 countries. *Scientific Reports*, *13*(1), 1382. https://doi.org/10.1038/s41598-023-28368-8

Pizzi, A., Laborie, M.-P., & Candan, Z. (2024). A Review on Sources, Extractions and Analysis Methods of a Sustainable Biomaterial: Tannins. *Journal of Renewable Materials*, *12*(3), 397–425. https://doi.org/10.32604/jrm.2023.046074

Plebankiewicz, I., Bogdanowicz, K. A., Kwaśnicki, P., Przybył, W., Skunik-Nuckowska, M., Kulesza, P. J., & Iwan, A. (2024). Inorganic–organic modular silicon and dye-sensitized solar cells and predicted role of artificial intelligence towards efficient and stable solar chargers based on supercapacitors. *Scientific Reports*, *14*(1), 6115. https://doi.org/10.1038/s41598-024-56302-z

Rahman, S., Haleem, A., Siddiq, M., Hussain, M. K., Qamar, S., Hameed, S., & Waris, M. (2023). Research on dye sensitized solar cells: recent advancement toward the various constituents of dye sensitized solar cells for efficiency enhancement and future prospects. *RSC Advances*, *13*(28), 19508–19529. https://doi.org/10.1039/D3RA00903C

Richhariya, G., Kumar, A., Tekasakul, P., & Gupta, B. (2017). Natural dyes for dye sensitized solar cell: A review. *Renewable and Sustainable Energy Reviews*, *69*, 705–718. https://doi.org/10.1016/j.rser.2016.11.198

Shahsavari, A., & Akbari, M. (2018). Potential of solar energy in developing countries for reducing energy-related emissions. *Renewable and Sustainable Energy Reviews*, *90*, 275–291. https://doi.org/10.1016/j.rser.2018.03.065

Sharma, K., Sharma, V., & Sharma, S. S. (2018). Dye-Sensitized Solar Cells: Fundamentals and Current Status. *Nanoscale Research Letters*, *13*(1), 381. https://doi.org/10.1186/s11671-018-2760-6

Sinha, A., Qian, J., Moffitt, S. L., Hurst, K., Terwilliger, K., Miller, D. C., Schelhas, L. T., & Hacke, P. (2023). UV-induced degradation of high-efficiency silicon PV modules with different cell architectures. *Progress in Photovoltaics: Research and Applications*, *31*(1), 36–51. https://doi.org/10.1002/pip.3606

Suyitno, S., Muqoffa, M., Marlina, A., Adriyanto, F., & Basuki, B. (2024). Unlocking the potential of anthocyanin-based dye-sensitized solar cells: Strategies for enhancing efficiency, stability, and economic viability. *Journal of Applied Research and Technology*, *22*(2), 308–326. https://doi.org/10.22201/icat.24486736e.2024.22.2.2298

Swanson, B. G. (2003). Tannins and Polyphenols. *Encyclopedia of Food Sciences and Nutrition*, 5729–5733. https://doi.org/10.1016/B0-12-227055-X/01178-0

Talwekar, R. H., & Tiwari, A. (2022). Optical property analysis of transition and alkaline metal doped MoS2 bulk layers for photo-sensor applications. *Materials Today: Proceedings*, *59*, 692–698. https://doi.org/10.1016/j.matpr.2021.12.222

Triyanto, A., Ali, N., Salleh, H., Setiawan, J., & Yatim, N. I. (2024). Development of natural dye photosensitizers for dye-sensitized solar cells: a review. *Environmental Science and Pollution Research*, *31*(22), 31679–31690. https://doi.org/10.1007/s11356-024-33360-4

Upneja, A., Kaur, K., & Gupta, N. (2024). Green synthesis of TiO2 nanoparticles for enhanced photovoltaic properties in dye-sensitized solar cells: a mini-review. *Journal of Coordination Chemistry*, *77*(22–24), 2527–2543. https://doi.org/10.1080/00958972.2024.2445212

Vera, M., & Urbano, B. F. (2021). Tannin polymerization: an overview. *Polymer Chemistry*, *12*(30), 4272–4290. https://doi.org/10.1039/D1PY00542A

Weir, B., Ott, L. E., Collatz, G. J., Kawa, S. R., Poulter, B., Chatterjee, A., Oda, T., & Pawson, S. (2021). Bias-correcting carbon fluxes derived from land-surface satellite data for retrospective and near-real-time assimilation systems. *Atmospheric Chemistry and Physics*, *21*(12), 9609–9628. https://doi.org/10.5194/acp-21-9609-2021

Wu, J., Lan, Z., Lin, J., Huang, M., Huang, Y., Fan, L., & Luo, G. (2015). Electrolytes in Dye-Sensitized Solar Cells. *Chemical Reviews*, *115*(5), 2136–2173. https://doi.org/10.1021/cr400675m

Yang, S., Fu, W., Zhang, Z., Chen, H., & Li, C.-Z. (2017). Recent advances in perovskite solar cells: efficiency, stability and lead-free perovskite. *Journal of Materials Chemistry A*, *5*(23), 11462–11482. https://doi.org/10.1039/C7TA00366H

Ye, M., Wen, X., Wang, M., Iocozzia, J., Zhang, N., Lin, C., & Lin, Z. (2015). Recent advances in dye-sensitized solar cells: from photoanodes, sensitizers and electrolytes to counter electrodes. *Materials Today*, *18*(3), 155–162. https://doi.org/10.1016/j.mattod.2014.09.001

Zafar Iqbal. (2017). Eco-friendly natural dyes as sensitizers for dye-sensitized solar cells (DSSCs). *International Journal of Biosciences (IJB)*, *11*(6), 151–158. https://doi.org/10.12692/ijb/11.6.151-158