



Effect of Gel Electrolyte, Paste and Electrode on the Efficiency of Dye-Sensitized Solar Cell using Schiff Base Dye Compound

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Received: 12 September 2022;

Accepted: 28 October 2022;

Published online: 30 January 2023;

AJC-21111

The low cost and ease of production have led to widespread adoption of dye-sensitized solar cells (DSSCs). Therefore, this study aims to synthesize Schiff base compounds from salicylaldehyde and ethylenediamine as a sensitizer in DSSC. The Schiff base compound was synthesized using the condensation method with mol ratio of 1:1 and the results showed yellow crystals with a yield of 81.14%. Furthermore, the UV-Vis spectrometer analysis showed that the Schiff base compound has bathochromic shift with a maximum wavelength change from 324 and 328 nm to 335 nm with transition $n \rightarrow \pi$, while the IR spectrum at wavenumber of 1610 cm^{-1} indicated the presence of an azomethine group ($-\text{C}=\text{N}-$). The TG-DTA analysis showed a mass loss stage of the Schiff base molecule at 97.2% in the temperature range of 180-300 °C. Based on UV-Vis, IR and TG-DTA data, the synthesized Schiff base has the potential to be used as a sensitizer in DSSC. The fabrication was then carried out using two variations of semiconductor namely TiO_2 and ZnO , three variations of PEG gel electrolyte with 0.05 M, 0.1 M and 0.15 M, as well as three counter electrodes including graphite from a pencil, candle flame and a combination of both. Based on the results, DSSC based on TiO_2 semiconductor with 0.15 M PEG gel electrolyte and candle flame counter electrode produced the highest efficiency of 0.29 % with maximum voltage (V_{max}) of 370 mV and maximum current strength (I_{max}) of 0.8 mA.

Keywords: Counter electrode, DSSC, Schiff base, Sensitizer.

INTRODUCTION

When compared to other countries, Indonesia receives more heat due to its location on the equator and its consequently high potential for developing solar energy [1]. Subsequently, its application needs solar cells that directly convert photons into electrical energy and store it in batteries [2]. These cells are classified into three generations *viz.* silicon semiconductor materials, thin-film silicon-based cells and dye-sensitized solar cells (DSSCs), which are widely used since the methodology is easy and inexpensive and the efficiency may be raised [2].

The DSSC series consists of four components, namely the working electrode, dye, electrolyte and comparison electrode [3]. Light absorption is then carried out by dye molecules and charge separation is conducted with inorganic nanocrystalline semiconductors, which have a wide bandgap [4]. These semiconductors increase the number of electrons flowing from the conduction to the valence band, thereby increasing the photo-

catalyst reaction space and absorption by dye as well as broadening the spectrum [4,5].

The dye acts as a sensitizer, hence absorbs photons directly from the sunlight and converts into the electrical energy [5,6]. Meanwhile, the majority of the dyes widely used are produced from organic or inorganic materials [5,7]. Synthetic dyes generally use a ruthenium based metal-organic complex, the best sensitizer in DSSC produces an efficiency up to 11% and has high stability [8]. However, its manufacturing process is rather expensive and contains heavy metals which are environmentally hazardous. As a result, synthetic/natural organic dyes have the potential to replace ruthenium complexes since they are more chemically and thermally stable, are not easily destroyed, are less expensive and the production process is simpler [7].

Schiff bases are the compounds that have an azomethine group ($-\text{C}=\text{N}-$) obtained from the condensation of aldehydes or ketones with primary amines, hence, they have a flexible and diverse structure. Besides, the formation might occur in

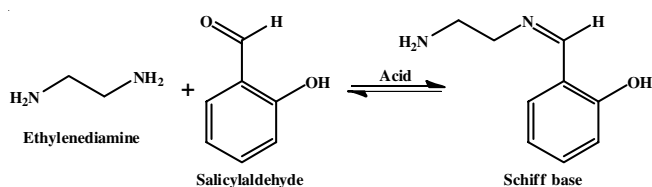
an acidic or alkaline atmosphere. Schiff bases formed from the aromatic aldehydes are more stable than the aliphatic types because they have a long conjugation bond system [9]. Schiff base metal complexes have potential photosensitizing behaviour, due to their photophysical properties [10]. The high thermal and moisture stabilities of Schiff base transition metal complexes are useful for their application as photosensitizers. The power conversion efficiency of 0.4% was obtained when using the Schiff base synthesized from salicylaldehyde and ethylenediamine as sensitizer in DSSC [11]. Dadkhah *et al.* [12] also synthesized a metal-free organic dye in the form of Schiff base from similar components and demonstrated the power conversion efficiency of 0.3%.

This work aims to synthesize Schiff base from salicylaldehyde and ethylenediamine through condensation under acidic conditions. The products obtained were characterized using UV-Vis and IR spectrophotometer as well as DTA-TGA technique. The synthesized Schiff base as a sensitizer was also applied as different gel electrolyte and paste solutions in dye-sensitized solar cells (DSSCs) as well as reference electrodes.

EXPERIMENTAL

The chemicals and solvents *viz.* ethanol, 96% alcohol, salicylaldehyde, ethylenediamine, TiO₂ powder, Whatman 42 filter paper, polyethylene glycol (PEG) 6000, acetonitrile, potassium iodide, iodine (I₂), indium tin oxide (ITO) glass measuring 2 cm × 2 cm × 1 mm were procured from Merck, USA.

Synthesis of Schiff base: Salicylaldehyde (1.15 mL, 0.01 mol) and ethylenediamine 0.66 mL (0.01 mol) were mixed in 10 mL ethanol. The mixture was refluxed for 2 h at 78 °C and then allowed to stand until crystals were formed (**Scheme-I**). The obtained yellow crystals were filtered, washed with distilled water and dried in a desiccator (Yield: 2.6631 g; 81.14%).



Scheme-I: Synthetic route of Schiff base

Dye-sensitized solar cell (DSSC) fabrication: A paste of 0.5 g TiO₂ was prepared by adding 2 mL of ethanol and then stirred with a magnetic stirrer for 15 min to form a paste, then 0.5 g of dye from the synthesized Schiff base was added. The mixture was homogenized with a magnetic stirrer for another 15 min until the dye was evenly distributed.

The second variation of the paste containing ZnO was prepared with 3.5 g of ZnCl₂ and 3.6 mL of NH₃ in a beaker and stirred. The mixture was placed into a furnace and heated at 100 °C with a holding time of 24 h. The refilled ZnO was weighed up to 0.5 g, placed in a beaker, supplemented with 2 mL of ethanol and stirred using a magnetic stirrer for 15 min. Moreover, the paste was added with 0.5 g of synthesized Schiff base and then homogenized with a magnetic stirrer for 15 min.

Six plates of ITO glass were thoroughly washed using 96% alcohol and the conductive side was covered with scotch tape, leaving a size of 1 cm × 1 cm. The layer of TiO₂ and ZnO₂ paste with Schiff base was then coated on the conductive side of the glasses using the doctor blade method and applied evenly. The paste layer was dried and flamed for 10 min respectively at 200 °C.

The electrolyte preparation was varied into three concentrations of PEG, namely, 0.05 M, 0.1 M and 0.15 M. The PEG 0.05 M gel electrolyte was prepared from 0.498 g KI and 0.076 g I₂ diluted into 6 mL acetonitrile. This mixture was added with 0.12 g of PEG 6000 and stirred with a magnetic stirrer until homogeneous. The 0.1 M and 0.15 M PEG electrolytes were prepared by the same procedure, but 2.4 g PEG 6000 was inserted to 0.1 M electrolyte, while 0.15 M was added with 4.8 g.

The comparison electrode preparation had three variations, carbon was prepared using 8B pencil, which was scratched onto the conductive parts of the ITO glass and then burned with a candle flame soot. Also, the working and comparison electrodes were arranged in the form of a sandwich structure with two sides and a 0.5 cm space for electrical contact. The other two sides were clamped together with paper clips, while the electrolyte solution was dropped on the sidelines of the DSSC series. Furthermore, DSSC current and voltage measurements were performed using a digital multimeter.

The electrolyte variation of both TiO₂ and ZnO₂ pastes, which produced the best result was used for DSSC fabrication with a variety of comparison electrodes. Meanwhile, the comparison electrode was prepared on the conductive side of ITO glass with three variations, namely from 8B pencil graphite, candle flame soot and a combination of both. The three pieces of ITO glasses used were previously covered with scotch tape, leaving a size of 1 cm × 1 cm.

RESULTS AND DISCUSSION

Chemistry: The Schiff base was synthesized from ethylenediamine as primary amine and salicylaldehyde as the carbonyl of aldehyde derivative using condensation method. In this reaction, salicylaldehyde acts as an electrophile while ethylenediamine functions as a nucleophile. The mechanism of the reaction involves two phases, addition and elimination, and yields a Schiff base product having an azomethine group (-C=N-). Initially, the carbonyl O atom of salicylaldehyde is protonated to enhance its positive partial charge and facilitate the nucleophile attack derived from ethylenediamine. This attack on the carbonyl carbon atom causes the double bond (*sp*²) C=O to break into a single bond (*sp*³) thereby forming a carbinolamine intermediate. In contrast, the water molecule is first released during the elimination reaction, which begins with protonation of the hydroxyl group. Also, there is a change in the character of carbon and nitrogen bonds from *sp*³ to *sp*² due to the contribution of electrons belonging to the group.

UV-Vis studies: The synthesized Schiff base molecule has a UV-Vis spectrum (Agilent Cary 50 UV-Vis spectrophotometer) with three absorption peaks as shown in Fig. 1. An absorption at the wavelength of 215 nm is due to the influence of

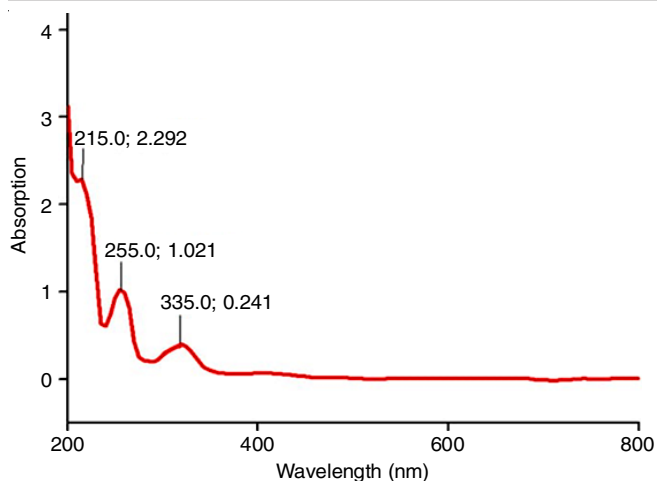


Fig. 1. UV-Vis spectrum of the synthesized Schiff base

solvent used (ethanol), while the absorption at 255 nm indicates the presence of a chromophore of benzene. The maximum wavelength absorption was occurred at 335 nm with an absorbance of 0.241 and a transition of $n \rightarrow \pi^*$. This indicates that Schiff base has been formed as demonstrated by a shift in absorption at the maximum wavelength of the constituent compounds.

IR studies: Fig. 2 shows the IR spectrum (Agilent Cary 630 IR spectrophotometer) of the synthesized Schiff base compound with an absorption peak for azomethine group ($-\text{C}=\text{N}-$) at 1610 cm^{-1} . This is consistent with previous research which stated that Schiff bases generally form absorption in the wavenumber region of $1660\text{--}1600 \text{ cm}^{-1}$ [13]. Furthermore, the Schiff base spectrum also exhibits the presence of C-H bonds in the 3049 cm^{-1} region and C=C bonds at 1572 cm^{-1} which corresponded to the wavenumbers for (C-H) aromatic sp^2 found at $3100\text{--}3000 \text{ cm}^{-1}$ and the (C=C) aromatic at $1600\text{--}1450 \text{ cm}^{-1}$.

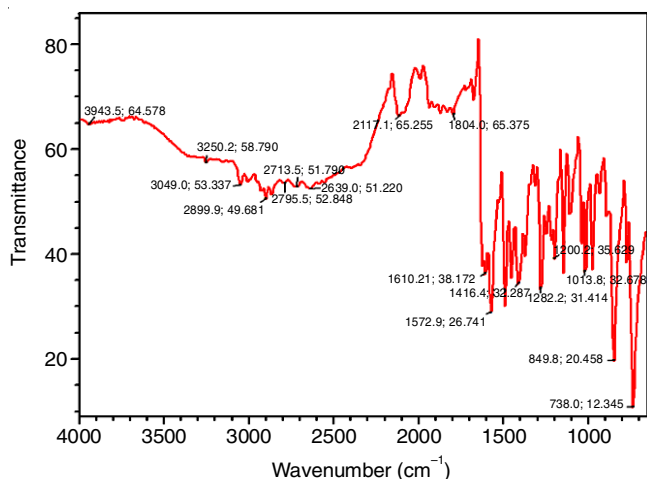


Fig. 2. IR spectrum of synthesized Schiff base

The absorption band of (C-N) to the aromatic ring is characterized by the appearance of a peak at 1282 cm^{-1} , which corresponds with the theoretical vibration (C-N) that appears at the absorption of $1350\text{--}1150 \text{ cm}^{-1}$ [13-15]. Meanwhile, the (NH) absorption band is characterized by the appearance of a peak at 849 cm^{-1} . This is in agreement with a study which reported

a strong absorption band at $920\text{--}720 \text{ cm}^{-1}$ and $3500\text{--}3300 \text{ cm}^{-1}$ [15]. The synthesized Schiff base exhibited an absorption band at 3189 cm^{-1} , which is due to the presence of (O-H) group of salicylaldehyde [13,14,16].

Thermal studies: Fig. 3 shows the DTA TG thermogram (DTA-TGA Shimadzu DTG 60) of the synthesized Schiff base compound. The DTA curve in Fig. 3 shows the presence of an endothermic peak at $121.2 \text{ }^\circ\text{C}$, indicating the release of water molecules present in the Schiff base molecule. Furthermore, an exothermic peak was formed at $288.2 \text{ }^\circ\text{C}$, which implies the degradation of the synthesized framework ($\text{C}_9\text{H}_{12}\text{N}_2\text{O}$) due to the small average bond energy value (73 kcal/mol) of the C-N bond. In the Schiff base compound, the C-N bond between the carbon atom and the amine group (R-NH_2) forms an imine. At the same time, the decomposition of Schiff base compound begins and ends at a higher temperature [15], since the C-N bond in the imine is substantially stronger because to the electron push from the alkyl group in salicylaldehyde. Furthermore, the TGA curve exhibits a sharp decline between the temperature range of $180\text{--}300 \text{ }^\circ\text{C}$. This shows that the synthesized Schiff base has undergone a one-step decomposition with a single mass loss of 97.2% , while the occurrence of weight loss between $180\text{--}300 \text{ }^\circ\text{C}$ indicates the thermal stability up to $180 \text{ }^\circ\text{C}$. This allows the synthesized Schiff base to be applied as a sensitizer in dye-sensitized solar cell (DSSC).

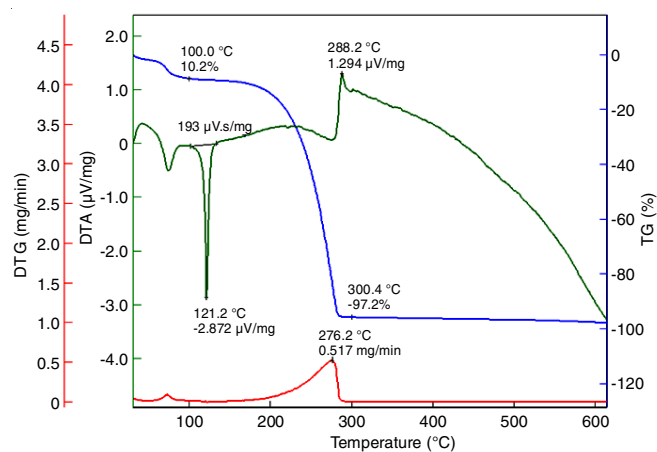


Fig. 3. DTA-TGA Thermogram of synthesized Schiff base

Fabrication of dye-sensitized solar cell (DSSC): The use of TiO_2 and ZnO with a dye from Schiff base produced a yellow paste, which was coated uniformly on the conductive side of six ITO glasses. When applying sensitizers to DSSC, the efficiency of the dyes mixed with TiO_2 and ZnO pastes was higher than that of immersion [17]. This is because the dye molecules stick strongly to TiO_2 thereby making the electron injection process into the TiO_2 conduction band more efficient.

The DSSC current and voltage were measured by connecting a digital multimeter cable with a crocodile clip to the circuit. The light source used was the sunlight with bright irradiation and intensity of approximately 1000 W/m^2 or 0.1 W/cm^2 . The amount of DSSC efficiency was calculated using eqn. 1:

$$\eta (\%) = \frac{P_{\max}}{P_{\text{in}}} \times 100 \quad (1)$$

where P_{\max} is the maximum power generated by the DSSC, while P_{in} is the light source power used. The P_{in} s in this study were sourced from sunlight, while the maximum power was calculated using the following relationship:

$$P_{\max} = V_{\max} \times I_{\max} \quad (2)$$

where V_{\max} is the maximum power generated and I_{\max} is the maximum current generated from the DSSC. The results of current, voltage and efficiency (η) of DSSC with electrolyte variations are shown in Table-1.

| Conc. of PEG electrolyte (M) | V _{max} (mV) | | I _{max} (mA) | | η (%) | |
|------------------------------|-----------------------|-----|-----------------------|-----|------------------|------|
| | TiO ₂ | ZnO | TiO ₂ | ZnO | TiO ₂ | ZnO |
| 0.05 | 62 | 214 | 0.7 | 0.3 | 0.04 | 0.06 |
| 0.10 | 98 | 234 | 0.8 | 0.5 | 0.08 | 0.11 |
| 0.15 | 170 | 247 | 1.1 | 0.6 | 0.18 | 0.15 |

Table-1 shows the efficiency obtained from DSSC with 0.15 M PEG electrolyte solution using TiO₂ and ZnO semiconductors. The DSSC circuit with TiO₂ semiconductor exhibited the highest efficiency of 0.18% at the maximum voltage of 170 mV and a maximum current of 1.1 mA. Whereas, ZnO semi-conductor based DSSC circuit generate an efficiency of 0.15% with a maximum voltage of 247 mV and a maximum current of 0.6 mA.

The performance of DSSC was also influenced by altering the concentration of the PEG semi-solid electrolyte solution on the TiO₂ and ZnO semiconductors. Semi-solid electrolytes containing PEG have been utilized in this study due to their several excellent characteristics, such as their high ionic conductivity at constant temperature, higher shelf life and resistance to evaporation. Similarly, modifications were made to the use of semiconductors to establish the impact on DSSC performance efficiency.

As TiO₂ has a larger bandgap energy than ZnO, its use in an electrolyte concentration of 0.15 M PEG results in the superior performance. The photocatalyst surface and the dye adsorption are both improved in semiconductors with a wide bandgap since electrons can more easily move from the conduction to the valence band. Consequently, TiO₂ semiconductors in 0.15 M PEG electrolytes with a variety of reference electrodes were used to create DSSCs.

Table-2 shows that the highest efficiency (η) namely 0.29% with a maximum voltage (V_{\max}) of 370 mV and a current (I_{\max}) of 0.8 mA was produced using the candle flame carbon soot comparison electrode. It has been known that amorphous carbon has a more porous surface layer than graphite. Meanwhile, a porous surface structure is highly efficient in the comparison electrode layer as it causes more electrons to be captured from the external circuit and also facilitates a quicker uptake by the electrolyte solution [18]. As a result, the solar current accelerates the electron transfer process and the redox cycle in the electrolyte solution. Consistent with the findings

TABLE-2
CURRENT, VOLTAGE AND EFFICIENCY MEASUREMENT DATA FROM TiO₂ PASTE-BASED DSSC WITH A VARIETY OF COMPARISON ELECTRODES

| Variation of comparison electrode preparation | V _{max} (mV) | I _{max} (mA) | η (%) |
|--|-----------------------|-----------------------|-------|
| ITO glass scratched pencil 8B | 172 | 0.4 | 0.06 |
| ITO glass is burned by candle flame | 370 | 0.8 | 0.29 |
| ITO glass was scratched by an 8B pencil and burned by a candle flame | 182 | 0.5 | 0.09 |

of previous research [19], the modification of the carbon source comparison electrode found that candle flame carbon soot was the most effective carbon source, followed by a combination of pencil graphite and candle flame soot.

Conclusion

Schiff base synthesized from salicylaldehyde and ethylenediamine has great potential to be used as a sensitizer in DSSC. After experimenting with various electrolyte concentrations, it was found that 0.15 M PEG TiO₂-based semiconductor exhibited the highest efficiency (η) of 0.18% at a voltage of 170 mV and a current of 1.1 mA. However, a comparative electrode made from wax carbon soot achieved the maximum efficiency (η) of 0.29% with a voltage of 370 mV and a current of 0.8 mA.

ACKNOWLEDGEMENTS

The authors are grateful to the Head of Indonesia National Agency of Food and Drug Control, (BP POM) Bandar Lampung, for providing the research laboratory, in order to develop the analysis method, through the use of MP-AES.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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