The Effect of Light Irradiation on Performance of Photo-Supercapacitor of FTO/TiO₂-ZnO-β Carotene-Quercetin /Carbon/Al/PVDF-BaTiO₃/Al

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Abstract. We performed a study to obtain the effect of duration of light irradiation on the performance of photo supercapacitor system based on TiO₂-ZnO and TiO₂/ BaTiO₃/ PVDF materials. Dye-Sensitized Solar Cells (DSSC) based on the TiO₂ material are potential because of several advantages such as high photostability, high thermal stability and are very effective for dye absorption. However, TiO₂ has limitations regarding electron mobility. It needs to be composited with other materials for electron mobility. The material preferred is ZnO. ZnO also has similar band gap range as TiO₂. In this process, TiO₂-ZnO composite system becomes more potential used as DSSC electrodes. In the Photo-Supercapacitor with the presence of a high electrical energy source from the DSSC, a supercapacitor unit with sufficient capacitance is needed. In this case, selection of capacitor electrodes is a crucial exercise. In this study, electrodes based on PVDF /BaTiO₃ composite systems were used. PVDF polymer-based electrodes have advantages regarding their flexible nature, high thermal stability, and easy in synthesis. However, the polymer material-based supercapacitor electrodes have limitations such as low dielectric constant. This problem is to overcome with ceramic-polymer composite systems. Among ceramic materials, the BaTiO₃ is the best choice because it has the highest dielectric constant compared to other ceramic materials. Thus, PVDF-BaTiO₃ composite system can function well because of dielectric constants and excellent mechanical properties. As a result, this composite system has the potential to be used as a supercapacitor electrode.

Keywords: DSSC-photo-supercapacitor, TiO₂, ZnO, PVDF, BaTiO₃, capacitance

1. Introduction
It has been 10 years since the concept of Photo-Supercapacitor (PS) was discovered to start the development of Dye-sensitized solar cells (DSSC) and supercapacitors in an integrated system [1]. Light energy absorbed by DSSC dye molecules is transferred into electrical energy and stored in supercapacitor units [2]. These days, many Photo-Supercapacitor systems have been developed to produce optimal energy conversion efficiently [3].

Several factors affect the performance of Photo-Supercapacitor. Among of them are the oxide layer, electrolyte, and electrode use [2]. Of these factors, the selection of oxide material in DSSC units is a
critical factor. The oxide materials that are often used are TiO$_2$, Nb$_2$O$_5$, and SnO$_2$ [4]. TiO$_2$ is the best of all the oxides [5,6]. TiO$_2$ is the best because it has high photostability, it is non-toxic and inexpensive [4]. Above all, TiO$_2$ is mesoporous making it suitable during the dye absorption process [7]. Nano TiO$_2$ has limitations in when it comes to electron mobility which impacts DSSC efficiency negatively [8]. One way to assure this problem is with the use of a composite system with other materials. Other materials that can be used in this process include ZnO, WO$_3$, CdS, SnO$_2$ and Nb$_2$O$_5$ [8]. ZnO is the best material oxide compared to other materials. It shows a high electron mobility, with a band gap range is similar to TiO$_2$. The preparation for nanosize powder is also quick [9,10].

The selection of supercapacitor electrodes is crucial [2]. This electrode can be carbon-based, metal oxides or conductive polymers [11]. In this study, the type of electrodes used are based on PVDF-BaTiO$_3$ composite system. PVDF polymer-based electrodes have advantages because of their flexibility properties, high thermal stability and easy synthesis process [12]. PVDF also exhibits a dielectric constant of 12, the highest compared to other types of polymers such as Polystyrene, Polyethylene (PE) and Polypropylene (PP) [13,14]. However, the electrode made of polymer supercapacitors show a significantly low dielectric constant. Thus it may affect to negatively impacts on supercapacitor capacitance. This problem can be overcome with a ceramic-polymer composite system [15]. Among ceramic materials, the BaTiO$_3$ material is the most preferred one because it has a dielectric constant of 1700 [13], the highest compared to other ceramic materials [16]. Thus, PVDF-BaTiO$_3$ performs effectively. Besides, this composite system could improve the nature of BaTiO$_3$ such as brittle, inflexible, and has low processability [16].

The research on Photo-Supercapacitors with active ingredients TiO$_2$-ZnO and PVDF-BaTiO$_3$ is rarely informed [17,18]. Further research is needed in regards to the perform of Photo-Supercapacitors of FTO / TiO$_2$-ZnO-β-Carotene-Quercetin / Carbon / Al / PVDF-BaTiO$_3$ / Al. In this study, the effect of duration light exposure on the performance of photosuper capacitors is based on TiO$_2$-ZnO and PVDF-BaTiO$_3$ materials.

2. Methods

2.1. Fabrication of FTO / TiO$_2$-ZnO-β Carotene-Quercetin-KI DSSC-based device

The first step is synthesizing the TiO$_2$-ZnO composite paste. The TiO$_2$ powder was obtained from Sigma Aldrich. On the other hand, ZnO nanoparticles were synthesized through sol-gel method. The producing of TiO$_2$-ZnO composite paste (0.06 g - 0.012 g) was carried out using distilled water, acetylacetone, PEG 6000 and SDS. TiO$_2$-ZnO paste was deposited onto a 0.5 x 0.5 cm$^2$ FTO substrate using the screen-printing method. The layer was heated on a hotplate at 100 ºC for one hour.

The second step is to cover DSSC devices with FTO / TiO$_2$-ZnO material. About 0.025 mL of β-carotene-queretin solution was dripped on a layer of TiO$_2$-ZnO, followed by dripped 0.025 mL of KI solution onto the FTO / TiO$_2$-ZnO-β Carotene-Quercetin film. On the other hand, the counterpart of the DSSC electrode we also prepare carbon tape followed a heating on an aluminum foil substrate. DSSC devices are made by merging of the two layers.

2.2. Fabrication of supercapacitor devices based on PVDF-BaTiO$_3$ composites

The initial stages carried out were the PVDF-BaTiO$_3$-Al Film Synthesis. BaTiO$_3$ and PVDF materials are obtained from Sigma Aldrich. The PVDF-BaTiO$_3$ film produced has an active surface area of 0.5×0.5 cm$^2$ 0.25 grams of PVDF and 0.5 grams of BaTiO$_3$ are dissolved in 3 ml of DMF. The PVDF-BaTiO$_3$ film is fabricated using Dip Coating method. The next stage was to fabricate supercapacitor devices with PVDF-BaTiO$_3$ composites. The electrodes used were dipped in the PVDF-BaTiO$_3$-Al film, between the two supercapacitor electrodes which were separated by PTFE (Polytetrafluoroethylene). Among the Separators are H$_3$PO$_4$ electrolytes.
2.3. Photo Fabrication of FTO / TiO$_2$-ZnO-β Carotene-Quercetin / Carbon / Al / PVDF-BaTiO$_3$ / Al Photo Supercapacitors

Fabrication of photo space capacitors was done to form sandwiches with KI electrolytes in the DSSC section and on the supercapacitor part using H$_3$PO$_4$ electrolyte gel.

2.4. Sample Characterization

The samples were categorized according to the structural features, absorbance, DSSC efficiency, and capacitance. Structure characterization includes XRD, SEM-EDAX, and FTIR. The efficiency was obtained from Solar Simulator measurement. For the characterization of I-V in the DSSC section, cables A and B was connected to the operating test of the device as shown in Figure 1. Supercapacitor capacitance measurements were performed by using LCR meter, Cable B and C were connected. Measurement of Photoelectric flow of Solar Cells as a function of the time of LED irradiation, was done by connecting cables A and B to the Solar Simulator. Measurement of Photo-Charging Supercapacitor was carried out when the FTO substrate was illuminated by light. When the cables A and C are connected to the diode and B and C cables connected to the LCR meter, the resulting capacitance was measured against time.

![Figure 1. Design of Photo-Supercapacitor](image)

3. Results and Discussion

3.1. Analysis of XRD, FTIR, SEM and UV Vis

The XRD of TiO$_2$-ZnO/FTO analysis results are shown in Figure 2(d). The pattern of Figure 2(b) shows the formation of anatase TiO$_2$ phase indicated by the appearance of 2θ peaks by the standard (COD-2310710) [19]. Figure 2(c) shows the formation of ZnO Zincite at 2θ peaks by the standard (AMCSD-0005203) [20]. Figure 2(d) shows the formation of a TiO$_2$-ZnO composite system, indicated by the formation of TiO$_2$ and ZnO without any shift in diffraction peaks. Other than that the peaks of other features appear at 2θ of 26.71, 33.82, 37.95, 51, 82, 61.87, 66.01 and 78.12° related to the FTO substrate. The obtained structural parameters of TiO$_2$ and ZnO is displayed in Table 1 and Table 2.
Figure 2. XRD Pattern of (a) FTO, (b) TiO$_2$, (c) ZnO, and (d) TiO$_2$-ZnO/FTO.

Figure 3. XRD Patterns of (a) Al, (b) PVDF, (c) BaTiO$_3$, and (d) PVDF-BaTiO$_3$. 
The results of XRD analysis of Al-PVDF-BaTiO$_3$ samples are shown in Figure 3. Experiment performed in 3(b) shows the formation of PVDF phase indicated $2\theta$ peaks is in line with the reference (CCDC-1207416) [21]. In details, the $\alpha$PVDF stage is indicated at $2\theta$ positions of 18.11, 26.34, 32.99 and 35.88° [22,23], while, the $\beta$PVDF phase is indicated by positions $2\theta = 20.01$ and 38.67° [24,25]. Figure 3 (c) shows the process of formation of the BaTiO$_3$ peaking at $2\theta$ in accordance with the standard (COD-1507756) [26]. Figure 3(d) shows the formation of PVDF-BaTiO$_3$ composite system, indicated by the constant peaks of PVDF and BaTiO$_3$ with no diffraction peaks. Other than the peaks of other characteristics at positions $2\theta = 44.38, 64.95$ and 78.24° as a result of Aluminum substrate used. The PVDF and BaTiO$_3$ structural parameters is presented in Table 3 and Table 4 respectively.
Table 1. TiO$_2$ parameters from refinement

| Parameter      | Database (COD-2310710) | TiO$_2$ | TiO$_2$ – ZnO |
|----------------|-------------------------|---------|---------------|
| Crystal system | Tetragonal              | Tetragonal | Tetragonal    |
| Space group    | I 41/A M D              | I 41/A M D | I 41/A M D |
| $a$            | 3.872                   | 3.784   | 3.877         |
| $b$            | 3.872                   | 3.784   | 3.877         |
| $c$            | 9.616                   | 9.488   | 9.520         |
| $R_p$          | -                       | 23.44   | 19.63         |
| $R_{wp}$       | -                       | 31.41   | 25.92         |
| $\chi^2$      | -                       | 1.737   | 1.272         |

Table 2. ZnO Parameters From Refinement

| Parameter      | Database (AMCSD-0005203) | ZnO | TiO$_2$ – ZnO |
|----------------|--------------------------|-----|---------------|
| Crystal system | Hexagonal                | Hexagonal | Hexagonal    |
| Space group    | P 6 3 M C                | P 6 3 M C | P 6 3 M C |
| $a$            | 3.249                    | 3.254   | 3.244         |
| $b$            | 3.249                    | 3.254   | 3.244         |
| $c$            | 5.203                    | 5.212   | 5.194         |
| $R_p$          | -                        | 14.09   | 19.63         |
| $R_{wp}$       | -                        | 20.91   | 25.92         |
| $\chi^2$      | -                        | 1.735   | 1.272         |

Table 3. PVDF structural parameters from refinement

| Parameter      | Database (CCDC-1207416) | PVDF | PVDF-BaTiO$_3$ |
|----------------|--------------------------|------|----------------|
| Crystal system | Monoclinic               | Monoclinic | Monoclinic    |
| Space group    | P 21/C                   | P 21/C | P 21/C        |
| $a$            | 4.96                     | 5.02  | 4.95          |
| $b$            | 9.64                     | 9.72  | 9.71          |
| $c$            | 4.62                     | 4.69  | 4.76          |
| $R_p$          | -                        | 18.85 | 20.67         |
| $R_{wp}$       | -                        | 23.20 | 28.60         |
| $\chi^2$      | -                        | 3.345 | 1.602         |

Table 4. BaTiO$_3$ structural parameters from refinement

| Parameter      | Database (COD-1507756) | BaTiO$_3$ | PVDF-BaTiO$_3$ |
|----------------|-------------------------|-----------|----------------|
| Crystal system | Tetragonal              | Tetragonal | Tetragonal    |
| Space group    | P 4 m m                 | P 4 m m  | P 4 m m       |
| $a$            | 3.99                    | 4.02     | 4.02           |
| $b$            | 3.99                    | 4.02     | 4.02           |
| $c$            | 4.01                    | 4.03     | 4.01           |
| $R_p$          | -                       | 22.06    | 20.67          |
| $R_{wp}$       | -                       | 30.61    | 28.60          |
| $\chi^2$      | -                       | 1.838    | 1.602          |

The results of FTIR analysis of PVDF-BaTiO$_3$/Al samples are shown in Figure 4. The Spectra pattern in Figure 4 (a) shows the features of PVDF polymer chemical bonds. PVDF polymers have the characteristics of chemical bonds in the wave number range 1500 cm$^{-1}$ [26]. From the analysis, it shows the $\alpha$-PVDF phase of the chemical bond formed at wave 608.53, 672.15 and 754.18 cm$^{-1}$ [26]. The $\beta$-
PVDF phase is formed at wave 846.26, 900.66, 1279.01, 1428.01 and 1590.40 cm\(^{-1}\) [12,15]. The Spectra pattern in Figure 4 (b) shows the chemical bond characteristics of BaTiO\(_3\). BaTiO\(_3\) chemical bonds features occur in wave 453.68, 710.65, 1658.20 and 3524.83 cm\(^{-1}\) [27,28]. Figure 4 (c) shows the characteristics of PVDF-BaTiO\(_3\) composite system. This is indicated by the appearance of each bond characteristic of PVDF and BaTiO\(_3\) without showing the emergence of new peaks. Further analysis shows the PVDF phase which is formed only in the \(\beta\)-PVDF Phase. The FTIR analysis results can confirm XRD analysis which also shows the phases that appear in PVDF-BaTiO\(_3\) composite systems, but only in the \(\beta\)-PVDF phase.

SEM-EDX analysis results are shown in Figure 5. Figure 5 (a) shows the surface morphology formed from the FTO/TiO\(_2\)-ZnO film. The results show the morphology of the TiO\(_2\)-ZnO sample surface in the form of spheres, and there are several porosities. Besides that, it also shows the presence of accumulation on the surface of the sample [29,30]. Porous characteristics of the FTO/TiO\(_2\)-ZnO film sample will have a positive effect on the effectiveness of dye absorption, to increase the efficiency of solar cells [7]. Figure 5 (a) provides additional information regarding EDX characterization. The results of EDX analysis can confirm XRD analysis about the formation of TiO\(_2\)-ZnO composite systems. The composition of the elements formed is Zn, Ti and O. These elements represent the constituents of TiO\(_2\) and ZnO.

Figure 5 (b) shows the surface morphology formed from Al/PVDF-BaTiO\(_3\) film. Surface morphology shows PVDF-BaTiO\(_3\) samples have a spherical shape with some surrounding porosity. The presence of cluster is also shown in the sample surface morphology [31,32]. Figure 5 (b) provides additional information on EDX characterization. The results of EDX analysis indicates XRD and FTIR analysis about the formation of PVDF-BaTiO\(_3\) composite systems. The Compositions of the elements formed among them are elements of C, O, F, Ba, and Ti. Elements C, O, F related to the characteristics of the constituent elements of PVDF polymer. On the other hand, Ba and Ti elements show the characteristics of BaTiO\(_3\) constituent elements.

Figure 6 shows the UV-Vis characterization. This graph provides information about the characteristics of light at certain wavelengths that are effectively absorbed by TiO\(_2\)-ZnO / FTO film samples [33]. The results of the analysis show that the maximum absorbance occurs at a wavelength of 323 nm. The wavelength at this point is in the range of visible light. Further analysis of the value of band gap energy is done by graphing the relationship between \(hv\) and \((ahv)^2\) [34,35]. Figure 7 represents the results of the analysis. Bandgap value is related to the energy needed by the electrons to be excited from the valence bond to the conduction band [36]. The results of the analysis showed that TiO\(_2\)-ZnO film had 3.0 eV band gap.
3.2. I-V, Time-dependent of Electric Current and Capacitance

The maximum of unilluminated capacitance reached a value of 4.9 nF. On the other hand, the efficiency of solar cells reached 0.068%. The results of the Solar Simulator measurement are shown in Figure 8. Figure 9 shows the graph of the relationship of photoelectrical flow as a function of the time of LED irradiation. When exposed under the LED light, photons with energy above the TiO$_2$-ZnO band gap may result in a hole to occur on the surface of the TiO$_2$-ZnO film, combining with adsorbed free electrons. Through this mechanism, an electron-hole pair will be produced. By increasing the photogeneration of electron-hole pairs, there will be an increase in the electrical current. After that at a specific point results to the current value to be constant, i.e., a saturation occurs [37,38].

![Figure 8. I-V Curve Characteristic Of TiO$_2$-ZnO Film](image)

![Figure 9. The relation between Photocurrent with time duration of light](image)

![Figure 10. The relation between Capacitance with time duration of light](image)
Figure 10 shows a graph of the capacitance relationship with the LED irradiation time. When the LED light is on the FTO photoanode, the DSSC unit converts the adsorbed photons into electric current or potential difference. This causes the supercapacitor charging process to occur; the capacitance of the capacitor increases with increasing time. After reaching a particular capacitance value, the saturation process also occurs [39,40].

4. Conclusion

Structural analysis including XRD, FTIR, and EDX showed the success of the synthesis of TiO$_2$-ZnO and PVDF-BaTiO$_3$ composites. UV-Vis analysis showed that the maximum adsorption of TiO$_2$-ZnO/FTO film occurred at a wavelength of 323 nm, while the other band gap owned by TiO$_2$-ZnO film was 3 eV. Analysis of photo-supercapacitor electric photo flow to the duration of the LED beam irradiation shows the formation of a linear curve then at a certain point there will be saturation of the generated photoelectric flow. The charging of electrical energy of the supercapacitor capacitance resulted from DSSC conversion of the LED beam irradiation shows the formation of linear curves, and then at a certain point, capacitance saturation occurs as a function of time duration.

References

[1] Xu J, Ku Z, Zhang Y, Chao D and Fan H J 2016 Integrated Photo-Supercapacitor Based on PEDOT Modified Printable Perovskite Solar Cell Adv. Mater. Technol. 1
[2] Ng C H, Lim H N, Hayase S, Harrison I, Pandikumar A and Huang N M 2015 Potential active materials for photo-supercapacitor: A review J. Power Sources 296 169–85
[3] Scalia A, Bella F, Lamberti A, Bianco S, Gerbaldi C, Tresso E and Pirri C F 2017 A flexible and portable powerpack by solid-state supercapacitor and dye-sensitized solar cell integration J. Power Sources 359 311–321
[4] Umale S V., Tambat S N, Sudhakar V, Sontakke S M and Krishnamoorthy K 2017 Fabrication, characterization and comparison of DSSC using anatase TiO$_2$ synthesized by various methods Adv. Powder Technol. 28 2859–64
[5] Sulaeman U and Zuhairi Abdullah A 2017 The way forward for the modification of dye-sensitized solar cell towards better power conversion efficiency Renew. Sustain. Energy Rev. 74 438–52
[6] Zama I, Martelli C and Gorni G 2017 Preparation of TiO$_2$ paste starting from organic colloidal suspension for semi-transparent DSSC photo-anode application Mater. Sci. Semicond. Process. 61 137–144
[7] Sengupta D, Das P, Mondal B and Mukherjee K 2016 Effects of doping, morphology and film-thickness of photo-anode materials for dye sensitized solar cell application – A review Renew. Sustain. Energy Rev. 60 356–76
[8] Chao C-H, Chang C-L, Chan C-H, Lien S-Y, Weng K-W and Yao K-S 2010 Rapid thermal melted TiO$_2$ nano-particles into ZnO nano-rod and its application for dye sensitized solar cells Thin Solid Films 518 7209–7212
[9] Liao J-Y, He J-W, Xu H, Kuang D-B and Su C-Y 2012 Effect of TiO$_2$ morphology on photovoltaic performance of dye-sensitized solar cells: nanoparticles, nanofibers, hierarchical spheres and ellipsoidal spheres J. Mater. Chem. 22 7910–7918
[10] Chandiran A K, Abdi-Jalebi M, Nazeeruddin M K and Grätzel M 2014 Analysis of electron transfer properties of ZnO and TiO$_2$ photoanodes for dye-sensitized solar cells ACS Nano 8 2261–2268
[11] Wang G, Zhang L and Zhang J 2012 A review of electrode materials for electrochemical supercapacitors Chem. Soc. Rev. 41 797–828
[12] Kulkarni S S, Belavi P B and Khadke U V. 2018 Synthesis, structural, characterization and dielectric spectroscopy of PVDF–BaTiO$_3$ polymer composite AIP Conference Proceedings vol 1953 (AIP Publishing) p 090046
[13] Barber P, Balasubramanian S, Anguchamy Y, Gong S, Wibowo A, Gao H, Ploehn H J and Zur
2015 UV/VIS Spectrophotometry: Fundamentals and Applications 1–52
[34] Divya K S, Xavier M M, Vandana P V, Reethu V N and Mathew S 2017 A quaternary TiO$_2$/ZnO/RGO/Ag nanocomposite with enhanced visible light photocatalytic performance New J. Chem. 41 6445–54

[35] Hussein A M, Mahoney L, Peng R, Kibombo H, Wu C-M, Koodali R T and Shende R 2013 Mesoporous coupled ZnO/TiO$_2$ photocatalyst nanocomposites for hydrogen generation J. Renew. Sustain. Energy 5 33118

[36] Patil P T, Anwane R S and Kondawar S B 2015 Development of electrospun polyaniline/ZnO composite nanofibers for LPG sensing Procedia Mater. Sci. 10 195–204

[37] Wang Z, Wang H, Liu B, Qiu W, Zhang J, Ran S, Huang H, Xu J, Han H and Chen D 2011 Transferable and flexible nanorod-assembled TiO$_2$ cloths for dye-sensitized solar cells, photodetectors, and photocatalysts ACS Nano 5 8412–9

[38] Jia C, Wang Q, Xin N, Zhou J, Gong Y, Li L, Sun Q and Guo X 2016 Logic Control of Interface-Induced Charge-Trapping Effect for Ultrasensitive Gas Detection with All-Mirror-Image Symmetry Adv. Mater. Technol. 1 1600067

[39] Kim B K, Sy S, Yu A and Zhang J 2015 Electrochemical Supercapacitors for Energy Storage and Conversion Handbook of Clean Energy Systems (Chichester, UK: John Wiley & Sons, Ltd) pp 1–25

[40] Cohn A P, Erwin W R, Share K, Oakes L, Westover A S, Carter R E, Bardhan R and Pint C L 2015 All silicon electrode photocapacitor for integrated energy storage and conversion Nano Lett. 15 2727–2731

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