The Effect of Spin Coating Rotation on the Optoelectronic Properties of PANI/TiO$_2$/FTO-Glass Photoanode

S W Himmah$^1$, U Sa’adah$^1$, A D Iswatin$^1$, M Diantoro$^{1,2,*}$, Arif Hidayat$^1$, Z A Imam Supardi$^3$

$^1$Department of Physics, Faculty of Mathematics and Natural Science, Universitas Negeri Malang, Jl. Semarang 5 Malang 65145, Indonesia
$^2$Center of Advanced Materials for Renewable Energy (CAMRY), Universitas Negeri Malang, Jl. Semarang 5, Malang 65145, Indonesia
$^3$Department of Physics, Universitas Negeri Surabaya, Indonesia

*Corresponding author’s email: markus.diantoro.fmipa@um.ac.id

Abstract. Today, solar cells have become one of the promising renewable energy alternatives to provide a clean and environmentally friendly energy. One of the solar cell technologies, which has been widely developed and studied intensively, is dye-sensitized solar cells (DSSC). DSSC optimization component is performed to produce a high conversion efficiency. One part of DSSC which plays an essential role in energy conversion is photoanode, and TiO$_2$ nanocrystals have been proven to be high-efficiency DSSC photoanode components. The metal oxide TiO$_2$ exhibits a high mesoporous surface area which can be used for dye absorption. The most widely developed organic material in DSSC is PANI. It is a conducting polymer that has a wide range of absorbance, porous morphology, excellent electrical properties, and ease of bond with metal ions. The PANI-TiO$_2$ composite system forms a bilayer structure that is expected to improve the efficiency of DSSC conversion. So far, no comprehensive study of DSSC-based PANI/TiO$_2$/FTO-Glass bilayer thin film structure as a photoanode component has been done. In this work, we report the effect of photoanode thickness represented by spin rotation on the optoelectronic properties is needed.

Keywords: Spin coating rotation, optoelectronic properties, PANI/TiO$_2$/FTO-glass, DSSC

1. Introduction
Currently, solar cells become one of the promising renewable energy alternatives to provide a clean and environmentally friendly energy. A dye-sensitized solar cell (DSSC) is a solar cell technology which has been widely developed and intensively studied recently. One component that has a vital role in energy conversion is the semiconductor in the photoanode system. Among all types of inorganic semiconductors, TiO$_2$ (type-n) is a semiconductor material which has been widely developed as a photoanode component [1,2]. TiO$_2$ has the most potent oxidizing power and has been successfully used as an electron acceptor in solar cell devices. TiO$_2$ shows a wide band gap, low electron mobility, high recombination rate, and short diffusion hole length (10-100 nm) [3–5]. Metal oxide-conductive polymer hybrids have attracted much attention because the combined absorption bands of the two materials can
harvest sunlight better [6]. The composites material shows the synergy performance of optoelectrical properties from the supporting materials [7].

Conducting polymers which have been extensively developed in DSSC component was polyaniline (PANI). The conductive polymer can function as a transport hole layer in DSSC system [8]. PANI has many advantages such as good environmental stability, wide absorbance range, porous morphology, good optical, and electrical properties, and ease of bonding with metal ions [9,10]. PANI is known as a polymer with a mixed oxidation state consisting of a reduced benzoic unit and an oxidized quinoid unit [11]. PANI can also be used as a stable photosensitizer to generate absorption of visible light and can extend the spectral response of TiO$_2$ to the range of visible light. The heterojunction of PANI/TiO$_2$ facilitates the separation of charge photogeneration so that it causes the performance of photovoltaic to increase [12].

Several studies on heterojunction of PANI/TiO$_2$ as DSSC photoanode component have been conducted. However, it still generates a relatively low-efficiency. DSSC device based on aniline/TiO$_2$ plasma polymerization reach the efficiency of 0.005% [13]. The recent report state that the PANI/TiO$_2$ heterojunction system using spin coating method produces an efficiency of 0.0004% under the illumination of 50 mW/cm$^2$ [14]. So far, PANI/TiO$_2$ heterojunction hybrid coating method has not been carried out as a DSSC photoanode component using screen printing and spin coating as well as the study of optical and electrical properties of PANI/TiO$_2$ composite layers. We report the study of PANI layer thickness of PANI/TiO$_2$/FTO-Glass on their optoelectronic properties.

2. Methods

2.1. Materials
Spinach leaves, dragon fruit, aniline (C$_6$H$_5$NH$_2$) Merck (99%, PA), ammonium peroxydisulfate (NH$_4$)$_2$S$_2$O$_8$ Merck (99%, PA), hydrochloric acid (HCl), TiCl$_3$ Merck (99%, PA), ethanol 97%, conductive substrate FTO, NH$_3$ Merck (99%, PA), sodium dodecyl sulfate (SDS), polyethylene glycol (PEG), acetylacetone, m-cresol.

2.2. Natural Photosensitizer Extraction
The natural photosensitizer used originated from the extraction of spinach leaves and dragon fruit, which produces chlorophyll and anthocyanin dyestuffs. 5 g and spinach and 10 g of dragon fruit were washed thoroughly, then mashed using mortar, added 50 mL of ethanol and stirred until homogeneous, then filtered using Whatman filter paper, respectively. Both solutions are then mixed and stirred until homogeneous.

2.3. Preparation of PANI/TiO$_2$/FTO-Glass
PANI Emeraldine Salt (ES) was synthesized using a chemical polymerization method followed our previous works [15-17], and TiO$_2$ nanoparticles were synthesized using a coprecipitation method. TiO$_2$ paste was prepared by adding 0.5 g TiO$_2$ which was dissolved into 2 mL paste solution consisting of 0.9 g PEG, 0.9 g SDS, 2 mL distilled water, and 0.03 mL acetylacetone, then subsequently stirred. On the other hands, the PANI solution was prepared by adding 0.2 g PANI ES into 8 mL m-cresol, followed by stirring at 450 rpm for 2 hours. Furthermore, TiO$_2$ paste was deposited on the FTO conductive surface (active area of 0.5 x 0.5 cm$^2$), then heated at 90 °C for 30 minutes and sintered at the temperature of 450 °C for 60 minutes. The next step, PANI solution was deposited on TiO$_2$/FTO-Glass film using a spin coating with variations in speeds of 1500, 2000, and 2500 rpm, then heated at the temperature of 100 °C for 10 minutes. On each PANI/TiO$_2$/FTO-Glass film variant was dripped with natural photosensitizer.

2.4. Assembly of DSSC
The used counter electrode component was carbon nanotube / FTO-Glass films, and KI solutions were used as liquid electrolytes. Fabricated DSSCs form sandwich arrangements as shown in Figure 1.
3. Results and Discussion

3.1. Data analysis of Functional Group Bounds of TiO$_2$ and PANI/TiO$_2$ Film films

Figure 2 is the characteristics of the FTIR spectrum of TiO$_2$ and PANI/TiO$_2$ films with the range of wavelength of 4000-400 cm$^{-1}$. In Figure 2, (a) there are absorption peaks around 1630 cm$^{-1}$ which is the bending of Ti-OH [18,19], the absorbance characteristics at 758 cm$^{-1}$ are O-Ti-O [20], at the wavenumber of 558 cm$^{-1}$ showed the existence of stretching vibration of Ti-O bond [21]. In Figure 2. (b), (c), and (d) there was a stretching vibration of Quinoid ring C (C = N) at the wavenumber of 1511 cm$^{-1}$ and benzenoid ring (NBN) at 1404 cm$^{-1}$ which were PANI backbone [14,22]. In the range of wavenumbers of 1316 cm$^{-1}$ occurred C - N stretching, while the strongest vibration wave was found at the wavenumber of 1158 cm$^{-1}$ which was the stretching vibration of C = N from the protonation of the Quinoid ring [23]. The C-Cl bond was at the wavenumber of 974 cm$^{-1}$ [24]. Peak absorption in PANI/TiO$_2$ film FTIR spectrum shows a shift around the higher wavenumbers compared to the PANI conductive polymer spectrum. This shift represents the interactions between particles TiO$_2$ and polymer chain of PANI [14].
Figure 2. Characteristics of FTIR spectrum (a) TiO\(_2\) film, (b) 1500PANI/TiO\(_2\), (c) 2000PANI/TiO\(_2\), and (d) 2500PANI/TiO\(_2\).

3.2. Analysis of Surface Morphology and PANI/TiO\(_2\) Film Thickness

The surface morphology of PANI/TiO\(_2\) films was explored through the SEM characterization as shown in Figure 3. Based on Figure 3, it can be seen that the PANI/TiO\(_2\) layer composites are round, porous, and form agglomerations. Rpm speed increase in PANI coating process using spin coating can increase TiO\(_2\) nanoparticle size. Film 1500PANI/TiO\(_2\) has a smaller particle size compared to 2500PANI/TiO\(_2\) film with the same magnification (100,000x). The porous morphology and particle size reduction can provide a better light absorption pathway, thereby increasing the catalytic properties of DSSC [25]. EDAX analysis data also shows the composite layer of PANI/TiO\(_2\) was formed well. The appearance of TiO\(_2\) nanoparticles in PANI/TiO\(_2\) film was 83.7 wt.%, and the result was supported by the FTIR functional group bond of PANI/TiO\(_2\) film.

The thickness of PANI/TiO\(_2\) layer on FTO conductive substrates measured using SEM with a cross section position so that micrographs can be obtained as shown by Figure 4. Rpm speed increase in spin coating process affects the thickness of the PANI/TiO\(_2\) layer on the conductive substrate of FTO.

Figure 3. Micrographs of (a) 1500PANI/TiO\(_2\) and (b) 2500PANI/TiO\(_2\) films
Figure 4. Cross section film (a) 1500PANI/TiO$_2$, (b) 2000PANI/TiO$_2$, (c) 2500PANI/TiO$_2$

SEM micrographs were analyzed using ImageJ software to measure layer thickness. In each film, 8 measurement points were taken, and the average thickness of the layer was 104.14, 91.90, and 65.14 nm respectively for 1500PANI/TiO$_2$, 2000PANI/TiO$_2$, and 2500PANI/TiO$_2$.

3.3. Absorbance Data Analysis

Figure 5 shows that the maximum absorbance value occurs in the wavelength region of 300-400 nm which is an ultraviolet wavelength area. The absorption of TiO$_2$ of anatase phase was at the wavelength around 328 nm. Meanwhile, the peak at 389 nm indicated the transition of $\pi-\pi^*$ from PANI benzenoid ring. The appearance of PANI/TiO$_2$ film has successfully reduced TiO$_2$ band gap from the ultraviolet range to the visible light region [26]. Also, as happened in the FTIR spectra, there is also a shift around the higher wavenumbers [14].
Figure 5. Absorbance spectra of TiO$_2$ and PANI/TiO$_2$ films.

The semiconductor used in the Photocatalytic process has a band gap that is proportional to the energy of visible or ultraviolet photons (for example <3.5 eV). Anatase TiO$_2$ band gap was obtained as much as 3.2 eV [27]. In this study, to determine the energy band value, the plotting was carried out in this research to determine the band gap value, a plotting was conducted $(a h \nu)^2$ vs. $h \nu$ by assuming that the transition occurs directly. Figure 6 shows the linear fitting $(a h \nu)^2$ vs. $h \nu$ TiO$_2$/FTO-Glass film and PANI/TiO$_2$/FTO-Glass. The rpm speed when the PANI ES layer deposition process affects the composite film’s energy band value, the more rpm speed increases, the film energy band value of PANI/TiO$_2$/FTO-Glass increases. PANI-TiO$_2$ nanocomposite film has band energy of $\sim$2.10 eV [26] as presented in Table 1.

Figure 6. Linear fitting $(a h \nu)^2$ vs. $h \nu$ TiO$_2$/FTO-Glass and PANI/TiO$_2$/FTO-Glass films.
Table 1. Energy band Pita results of linear fitting \((\alpha h\nu)^2\) vs. \(h\nu\) TiO\(_2\)/FTO-Glass film and PANI/TiO\(_2\)/FTO-Glass.

| Film             | Eg (eV) |
|------------------|---------|
| TiO\(_2\)        | 3.22    |
| 1500PANI/TiO\(_2\)| 2.87    |
| 2000PANI/TiO\(_2\)| 2.93    |
| 2500PANI/TiO\(_2\)| 3.06    |

3.4. Photoresponse Characteristics of DSSC

Figure 7 shows the Photoresponse curve of DSSC based on TiO\(_2\) and 2500PANI/TiO\(_2\) under the dark condition and the lighting of 10.5408 mW cm\(^{-2}\) with the switching cycle on/off for 20 minutes each. DSSC with TiO\(_2\) film as a photoanode has the average current of 80.24 µA. Meanwhile, 2500PANI/TiO\(_2\) film produces an average current of 95.63 µA. The current increases to a stable value when in lighting conditions, and then drops dramatically to the initial value when the lamp is turned off. Irradiation of DSSC causes the formation of electron-hole pairs because of the internal photoelectric effect. Under the electric field, the electron-hole pairs are separated into the appropriate electrodes, the electrons to the photodiode PANI/TiO\(_2\) and the hole leads to the carbon nanotube counter electrode component. The current generated by the DSSC will increase with increasing light intensity because a photon absorption occurs and electron-hole pairs in DSSC will also increase. However, when the light intensity was decreased, there will be a recombination process between electron and hole, so the current declined [28].

![Figure 7](image_url)

Figure 7. Current curve vs DSSC time based on (a) TiO\(_2\) and (b) 2500PANI/TiO\(_2\).

3.5. Characteristics of Current and Voltage DSSC

Optimization of photoanode using PANI/TiO\(_2\) composites has been performed. The characteristics of the PANI/TiO\(_2\) composite showed that it reached the short-circuit current density of 3.15 mA/cm\(^2\), the open-circuit voltage of 0.656 V, and efficiency of 0.0004% [14]. Other studies using photoanode based on aniline/ TiO\(_2\) polymerization with short-circuit current density 0.036 mA/cm\(^2\), open-circuit voltage 0.33 V, and generated a higher efficiency which was 0.005% [13]. The efficiency of solar cells produced is quite low due to the increase in resistance which in turn decrease the voltage in the open circuit [14].
Figure 8. Characteristics of I-V DSSC based on TiO$_2$ and PANI/TiO$_2$.

Figure 8. is the characteristics of I-V DSSC based on TiO$_2$ and PANI/TiO$_2$ photoanode. The measurement was conducted under lighting conditions using LED with an intensity of 10.5408 mW/cm$^2$ as a light source.

Table 2. Parameters obtained from I-V curves.

| Film          | $J_{sc}$ (mA cm$^{-2}$) | $V_{oc}$ (V) | FF  | $\eta$ (%) |
|---------------|-------------------------|--------------|-----|------------|
| TiO$_2$       | 0.20                    | 0.08         | 0.25| 0.04       |
| 1500PANI/TiO$_2$ | 0.11                  | 0.32         | 0.50| 0.17       |
| 2000PANI/TiO$_2$ | 0.14                   | 0.30         | 0.34| 0.14       |
| 2500PANI/TiO$_2$ | 0.06                   | 0.26         | 0.71| 0.10       |

The parameters of the DSSC analyzed from the I-V curve is shown in Table 2. The efficiency was much higher than the previous work. DSSC produces the highest efficiency based on 1500PANI/TiO$_2$ reach up to 0.17%.

4. Conclusion
PANI/TiO$_2$/FTO-Glass composites have been successfully synthesized as shown by the analysis of the FTIR bond group and EDAX. SEM micrograph showed that PANI/TiO$_2$ fall to spherical, porous, and agglomerate. The 2500PANI/TiO$_2$ sample shows the lowest thickness of the coating (65.14 nm). The absorbance of PANI/TiO$_2$/FTO-Glass composites occurs in the range of visible light wavelength region which is a potential to be used as a photodiode of DSSC. The energy band of PANI/TiO$_2$/FTO-Glass increases with increasing spin-coating speed. The band gap energy reached 3.06 eV. We further found that the DSSC of PANI/TiO$_2$/FTO-glass generated an average current of 95.63 $\mu$A which is higher than without PANI. In general, it is shown that the efficiency decreases with an increase of coating speed. The highest efficiency of 0.17% was obtained by 1500PANI/TiO$_2$/FTO-glass sample.
References

[1] Hegazy A, Kinadjian N, Sadeghimakki B, Sivoththaman S, Allam NK, Prouzet E. TiO$_2$ nanoparticles optimized for photoanodes tested in large area Dye-sensitized solar cells (DSSC). Sol Energy Mater Sol Cells 2016;153:108–16. doi:10.1016/j.solmat.2016.04.004.

[2] Issar S, Poddar P, Mehra NC, Mahapatro AK. The growth of flower-like patterns of TiO$_2$ nanorods over FTO substrate. Integr Ferroelectr 2017;184:67–9. doi:10.1080/10584587.2017.1368640.

[3] Hwang YJ, Hahn C, Liu B, Yang P. Photoelectrochemical Properties of TiO$_2$ Nanowire Arrays: A Study of the Dependence on Length and Atomic Layer Deposition Coating. ACS Nano 2012;6:5060–9. doi:10.1021/nn300679d.

[4] Shakeel Ahmad M, Pandey AK, Abd Rahim N. Advancements in the development of TiO$_2$ photoanodes and its fabrication methods for dye-sensitized solar cell (DSSC) applications. A review. Renew Sustain Energy Rev 2017;77:89–108. doi:10.1016/j.rser.2017.03.129.

[5] Taleb A, Mesguich F, Hérissan A, Colbeau-Justin C, Yanpeng X, Dubot P. Optimized TiO$_2$ nanoparticle packing for DSSC photovoltaic applications. Sol Energy Mater Sol Cells 2016;148:52–9. doi:10.1016/j.solmat.2015.09.010.

[6] Liu R. Hybrid Organic/Inorganic Nanocomposites for Photovoltaic Cells. Materials (Basel) 2014;7:2747–71. doi:10.3390/ma7042747.

[7] Kawata K, Gan S-N, Ang DT-C, Sambasevam KP, Phang S-W, Kuramoto N. Preparation of polyaniline/TiO$_2$ nanocomposite film with good adhesion behavior for dye-sensitized solar cell application. Polym Compos 2013;34:1884–91. doi:10.1002/pc.22595.

[8] Rivnay J, Inal S, Collins BA, Sessolo M, Stavrinidou E, Strakosas X, et al. Structural control of mixed ionic and electronic transport in conducting polymers. Nat Commun 2016;7:11287. doi:10.1038/ncomms11287.

[9] Alam M, Ansari AA, Shaik MR, Alandis NM. Optical and electrical conducting properties of Polyaniline/Tin oxide nanocomposite. Arab J Chem 2013;6:341–5. doi:10.1016/j.arabjc.2012.04.021.

[10] Nemade K, Dudhe P, Tekade P. Enhancement of photovoltaic performance of polyaniline/graphene composite-based dye-sensitized solar cells by adding TiO$_2$ nanoparticles. Solid State Sci 2018;83:99–106. doi:10.1016/j.solidstatesciences.2018.07.009.

[11] Molapo KM, Ndangili PM, Ajayi RF, Mbambisa G, Mailu SM, Njomo N, et al. Electronics of Conjugated Polymers (I): Polyaniline. Int J Electrochem Sci 2012;7:17.

[12] Li H, Zhou J, Lu X, Wang J, Qu S, Weng J, et al. Camphorsulfonic acid-doped polyaniline/TiO$_2$ nanotube hybrids: synthesis strategy and enhanced visible photocatalytic activity. J Mater Sci Mater Electron 2015;26:7723–30. doi:10.1007/s10991-015-3416-2.

[13] Ameen S, Akhtar MS, Kim G-S, Kim YS, Yang O-B, Shin H-S. Plasma-enhanced polymerized aniline/TiO$_2$ dye-sensitized solar cells. J Alloys Compd 2009;487:382–6. doi:10.1016/j.jallcom.2009.07.126.

[14] Al-Daghman ANJ, Ibrahim K, Ahmed NM, Zaidan KM. Effect of TiO$_2$ Thin Film Morphology on Polyaniline/TiO$_2$ Solar Cell Efficiency. World J Nano Sci Eng 2015;5:41–8. doi:10.4236/wjNSE.2015.52006.

[15] Diantoro M, Purwaningtyas D, Muthoharoh N, Hidayat A, Taufiq A, Fuad A. The influence of iron- and copper-doped of PANi thin film on their structure and dielectric properties. AIP Conf Proc 2012;1454:268–71. doi:10.1063/1.4730737.

[16] Diantoro M, Kholid, A. Mustikasari Y and Yudyanto. The Influence of SnO$_2$ Nanoparticles on Electrical Conductivity, and Transmittance of PANI-SnO$_2$ The Influence of SnO$_2$ Nanoparticles on Electrical Conductivity, and Transmittance of PANI-SnO$_2$ Films. IOP Conf Ser Mater Sci Eng 2018;367:012034. doi:10.1088/1757-899X/367/1/012034.

[17] Diantoro M, Z Masrul M and Taufiq A. Effect of TiO$_2$ Nanoparticles on Conductivity and Thermal Stability of PANI-TiO$_2$/Glass Composite Film Effect of TiO$_2$ Nanoparticles on Conductivity and Thermal Stability of PANI-TiO$_2$/Glass Composite Film. J Phys Conf Ser
[18] León A, Reuquen P, Garín C, Segura R, Vargas P, Zapata P, et al. FTIR and Raman Characterization of TiO$_2$ Nanoparticles Coated with Polyethylene Glycol as Carrier for 2-Methoxyestradiol. Appl Sci 2017;7:49. doi:10.3390/app7010049.

[19] Mugundan S, Rajamannan B, Viruthagiri G, Shanmugam N, Gobi R, Praveen P. Synthesis and characterization of undoped and cobalt-doped TiO$_2$ nanoparticles via sol-gel technique. Appl Nanosci 2015;5:449–56. doi:10.1007/s13204-014-0337-y.

[20] Bagheri S, Shameli K, Abd Hamid SB. Synthesis and Characterization of Anatase Titanium Dioxide Nanoparticles Using Egg White Solution via Sol-Gel Method. J Chem 2013;2013:1–5. doi:10.1155/2013/848205.

[21] Vinosel VM, Janifer MA, Anand S, Pauline S. Structural and Functional Group Characterization of Nanocomposite Fe$_2$O$_3$/TiO$_2$ and Its Magnetic Property. Mater Sci 2017:7.

[22] Ibrahim M, Bassil M, Demirci UB, Khoury T, El Haj Moussa G, El Tahchi M, et al. Polyaniline–titania solid electrolyte for new generation photovoltaic single-layer devices. Mater Chem Phys 2012;133:1040–9. doi:10.1016/j.matchemphys.2012.01.130.

[23] Manaf A, Bimantoro A, Hafizah MA. Synthesis and microwave characterization of conductive polyaniline prepared by continuous polymerization process. IOP Conf Ser Mater Sci Eng 2017;223:012051. doi:10.1088/1757-899X/223/1/012051.

[24] Diantoro M, Fitriana IN, Parasmayanti F, Taufiq A, Mufti N, Nur H. Crystallinity and Electrical Conductivity of PANI-Ag/Ni Film: The Role of Ultrasonic and Silver Doped. IOP Conf Ser Mater Sci Eng 2017;202:012005. doi:10.1088/1757-899X/202/1/012005.

[25] Pawar SG, Patil SL, Chougule MA, Mane AT, Jundale DM, Patil VB. Synthesis and Characterization of Polyaniline: TiO$_2$ Nanocomposites. Int J Polym Mater 2010;59:777–85. doi:10.1080/00914037.2010.483217.

[26] Jumat NA, Wai PS, Ching JJ, Basirun WJ. Synthesis of Polyaniline-TiO$_2$ Nanocomposites and Their Application in Photocatalytic Degradation. Polym Compos 2017;25:8.

[27] Dette C, Pérez-Osorio MA, Kley CS, Punke P, Patrick CE, Jacobson P, et al. TiO$_2$ Anatase with a Bandgap in the Visible Region. Nano Lett 2014;14:6533–8. doi:10.1021/nl503131s.

[28] Hong Q, Cao Y, Xu J, Lu H, He J, Sun J-L. Self-Powered Ultrafast Broadband Photodetector Based on p–n Heterojunctions of CuO/Si Nanowire Array. ACS Appl Mater Interfaces 2014;6:20887–94. doi:10.1021/am5054338.

**Acknowledgments**

We would like to thanks the Ministry of Research Technology and Higher Education through PUPT Grant.