ZnO Photoanode Effect on the Efficiency Performance of Organic Based Dye Sensitized Solar Cell

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Abstract. Dye sensitized solar cell has been emerged as one of the most promising candidates for photovoltaics applications in good quality of their low manufacturing cost and impressive conversion energy. Titanium dioxide (TiO\textsubscript{2}) which is used as photoanode in the market has the advantage of wide bandgap energy but low in electron mobility (~10 cm\textsuperscript{2}/(V.s)). Ruthenium in the other hand, as the dye sensitizer is a rare noble metal and harmful to human health. Thus, this article reveals the performance of photo-to-electric conversion efficiency with the usage of Zinc Oxide as photoanode with higher electron mobility (155 cm\textsuperscript{2}/(V.s)) compared to TiO\textsubscript{2} utilizing three natural fruit dyes of Prunus domestica, Magnifera indica and Citrus limon. ZnO and TiO\textsubscript{2} photoanodes were fabricated using sol gel and dr blade method respectively. The morphology of the photoanodes were characterized using Scanning Electron Microscope and the efficiency of the complete DSSC with all different fruit dyes were characterized using Semiconductor Parametric Analyzer. The different property of electron mobility photoanodes effect in DSSC proved to give better performance with the photoconversion efficiency of 3.082\% using ZnO with Prunus domestica dye. This article also reveals that pH indicator does not affect the selection and the performance of DSSC.

1. Introduction
Dye sensitized nanocrystalline solar cell (DSSC) is the third generation of solar cell invented by O’Reagan and Grätzel [1-3] is a cheap and versatile alternative to silicon based solar cells and has already achieved solar-to-electricity conversion efficiency as high as 11.5\% [4,5]. Major advantages of DSSCs are the large flexibility in shape, colour, transparency, and performance also under diffuse light [6,7]. DSSCs can be integrated into large varieties of products, e.g. handbags or clothing, indoor applications, and building-integrated photovoltaics such as roll-able devices for walls of buildings or windows [8,9]. The main stream of the research has been focusing on the development of materials which would enhance the conversion efficiency, simplify the production of DSSC and assure their long-lifetime [2].
Figure 1 shows the structure of DSSC which consists of titanium dioxide (TiO$_2$) photoanode semiconductor, synthetic dye (Ruthenium N79) as a photosensitizer, carbon counter electrode and iodine as the redox electrolyte mediator. The monolayer of the photosensitizer is attached to TiO$_2$ inside the cell and electrocatalyst material is separated from photoanode by the electrolyte redox mediator. The sensitizer becomes excited after absorbing sunlight and injects electrons to the conduction band of the semiconductor. The electrolyte then regenerates the sensitizer by donating electrons and diffuses towards the counter electrode, where the reduction reaction occurs. Instead of these forward charges transport processes, some back-electron transport processes also occur which drastically reduce the power conversion efficiency of solar devices [10].

![Image of DSSC structure](image_url)

Figure 1. The DSSC structure and graphical working operation.

Among these components, the photoanode directly determines the photo-current density because it not only transports photo-induced electrons but also adsorbs dyes [11]. Accordingly, the semiconductor material used in photoanode play an important role in the working process of DSSCs. Among various semiconductors, nanocrystalline anatase TiO$_2$ is a promising photoanode material in DSSCs and has been widely investigated in recent years [12-19]. However, the large band gap of TiO$_2$ (3.2 eV) limits its utilization of visible light and many dyes failed to inject electrons from excited dyes into the conduction band of TiO$_2$ owing to insufficient electron injection driving force [20]. In this study, Zinc Oxide of having a band gap similar to the TiO$_2$ with 3.37 eV is proposed to enhance the performance of DSSC due to its advantage of higher excitonic electron mobility ~115 cm$^2$/V.s compared to anatase TiO$_2$ which is reported to be only ~10 cm$^2$/V.s [21-24].

Ruthenium in the other hand is widely used in the industry as the synthetic dye sensitizer which functions to absorb energy from the sunlight and excite its electron from the lower band to higher band energy for the electrical conversion. However, according to chemical properties report from Lenntech, besides of being one of the rarest material on earth, Ruthenium is a harmful chemical to human health even though it is not harmful to the environment. All Ruthenium compounds are regarded as highly toxic and as carcinogenic which may lead to cancer [25,26]. Thus, many researches have been done in exploring the possible alternative solutions for the sensitizer in DSSC using natural pigment dyes such as cyanin [27-38], carotene [39-40], tannin [41] and chlorophyll [42]. Calogero and Marco reported that a conversion efficiency of 0.66% was obtained using red Sicilian orange juice dye as sensitizer [34]. Wongcharee et al. employed rosella as a sensitizer in their DSC, which achieved a conversion efficiency of 0.70% [29]. Thus, in this study, three different fruit dyes of prunus domestica, magnifera indica and citrus limon is used in DSSC fabrication and the photo-to-electric conversion efficiency is compared.
2. Materials and methods

2.1. Materials
The conductive glass substrates (ITO, 25 mm x 25 mm, 10 Ω/sq, thickness 180 nm), ZnO powder (Sigma Aldrich, 205532), TiO₂ (Sigma Aldrich, 14027), prunus domestica (dark prune) fruit (pH 4.8), Magnifera indica (mango) fruit (pH 5.9), Citrus limon (lemon) fruit (pH 2.3), iodine, I₃ (Sigma Aldrich) and candle.

2.2. Fabrication of photoanodes
The process started with cleaning the ITO glasses by sonicating the glasses inside acetone solution for 10 minutes in the first stage. Next, the glasses were rinsed with DI water before sonicating it again in the acetone for 5 minutes. The glasses were blown dry using air dryer. Two photoanodes were prepared in this research which were ZnO and TiO₂. ZnO photoanode was prepared by mixing 16.93 g ZnO powder in 15.49 ml diethanolamine (DEA). This solution was stirred on a hot plate until the solution was homogeneous at 60°C for one hour. The solution was applied on the conducting side of the ITO glass using the sol-gel method. The process was done on a spin coater by dropping 3 drops of ZnO solution on the ITO at 250 RPM for 30 seconds.

![Figure 2. Doctor Blade Technique.](image)

TiO₂ photoanode was prepared by mixing 6 g of TiO₂ powder with 9 ml acetic acid solution. This combination was grinded using mortar and pestle. A drop of Triton X was added to the mixture which act as a surfactant to facilitate spherical TiO₂ nanoparticles. Using Dr Blade method as in figure 2, the conductive side of the ITO glass was taped with cellophane tape as to reserve a conductive part for conduction and to secure the thickness of the TiO₂ on the surface of the photoanode. Both ZnO and TiO₂ photoanodes were placed on a hot plate for soft bake at 150°C for 10 minutes. Next the samples were going through hard bake in the furnace at 450°C for 1 hour. The active cell area for both photoanodes are 4 cm².

2.3. Synthesis of organic dyes
Prunus domestica (dark prune) fruit (pH 4.8), Magnifera indica (mango) fruit (pH 5.9), Citrus limon (lemon) fruit (pH 2.3) chosen as the organic dyes in this research. The fruits are placed in the mortar
with a ratio of 10–20 g and 3–5 ml of DI water. Then by using a pestle, the fruits were crushed until it became a soupy mixture as shown in figure 3 (a). Next, the ZnO and TiO\textsubscript{2} photoanodes were immersed in the dye solution as shown in figure 3 (b) for 24 hours to allow the dye molecules attached to the photoanodes. After this process, the dye coated photoanodes were rinsed with DI water and were dried.

![Figure 3. (a) Dye preparation (b) Coating process of the dye to the photoanodes and (c) Deposition of soot of candle carbon.](image)

2.4. Fabrication of counter electrode

The counter electrode is prepared using the deposition of soot from a burning candle. A candle was lit and then the conductive side of ITO glass was placed facing down about 10 cm above the candle as shown in figure 3 (c). The carbon from combustion of wax from the candle will produce smoke and cause the black carbon deposition on the conductive side of the glass.

2.5. DSSC assembly

Coated ZnO and TiO\textsubscript{2} photoanodes were combined with the carbon coated counter electrode using the clip. Iodine was injected in between the two electrodes.

2.6. Characterization

The morphology of the ZnO and TiO\textsubscript{2} surfaces on the ITO glass was characterized by Scanning Electron Microscopy (SEM) (JOEL, JSM-6460LA). The current density (I-V) data are collected using Semiconductor Parametric Analyzer (SPA) (Keithley, 4200-SCS).

The incident light intensity was 100 W from the bulb used as the source power. Based on the I-V curve, the fill factor (FF) is defined as: \( FF = \frac{J_{\text{max}} \times V_{\text{max}}}{J_{\text{sc}} \times V_{\text{oc}}} \), where the \( J_{\text{max}} \) and \( V_{\text{max}} \) are the photocurrent density and photovoltage for maximum power output; \( J_{\text{sc}} \) and \( V_{\text{oc}} \) are the short circuit photocurrent density and open circuit photovoltage respectively. The overall energy conversion efficiency is defined as \( \eta = \frac{(FF \times J_{\text{sc}} \times V_{\text{oc}})}{P_{\text{in}}} \) where \( P_{\text{in}} \) is the power of the incident light.

3. Results and discussions

3.1. SEM Results

Figure 4 shows the SEM cluster images for TiO\textsubscript{2} and ZnO respectively. The clusters composed of these particles tended to fuse together to form large aggregates.

The ZnO spherical cluster has a uniform size and consist of well-defined, bigger surface area compared to TiO\textsubscript{2} cluster. Higher surface area of ZnO particle has the advantage of having more dye attached to it as compared to TiO\textsubscript{2}.
3.2. J-V Characteristics

The performance of the DSSC was evaluated through the efficiency calculation of the cells when it is illuminated. J-V characteristics of the ZnO and TiO\textsubscript{2} cells with all 3 dyes (Prunus domestica, Magnifera indica and Citrus limon) were evaluated using SPA tool and the parameters of $J_{sc}$, $V_{oc}$, FF and efficiency were calculated as in table 1. In this project, $P_{in}$ is equal to 100 W and the surface area is 4 cm\textsuperscript{2} for all samples.

| Sample                     | $J_{sc}$ (mA/cm\textsuperscript{2}) | $V_{oc}$ (mV) | FF  | η (%) |
|----------------------------|-------------------------------------|---------------|-----|-------|
| ZnO with Prunus domestica dye | 0.006                               | 124           | 3.95| 3.08  |
| TiO\textsubscript{2} with Prunus domestica dye | 0.008                               | 145           | 2.48| 2.88  |
| ZnO with Magnifera indica dye | 0.009                               | 175           | 1.26| 1.99  |
| TiO\textsubscript{2} with Magnifera indica dye | 0.012                               | 185           | 0.76| 1.72  |
| ZnO with Citrus limon dye  | 0.013                               | 201           | 0.51| 1.34  |
| TiO\textsubscript{2} with Citrus limon dye | 0.014                               | 224           | 0.31| 0.96  |

Figure 4. SEM images for (a) TiO\textsubscript{2} (b) ZnO.

Figure 5. J-V curves for ZnO and TiO\textsubscript{2} photoanodes with 3 different dyes.
Based on table 1, the ZnO photoanode trend of efficiency was higher compared to TiO$_2$ for all 3 different dyes tested. As for the dye factor comparison, Prunus domestica (pH 4.8) contributed the highest efficiency followed by Magnifera indica (pH 5.9) and Citrus limon (pH 2.3). The best performance of DSSC was given by the combination of ZnO photoanode and prunus domestica dye compared to other samples with 3.08% photoconversion efficiency. Based on these efficiency results, it is shown that pH indicator does not affect the performance of the DSSC. Figure 5 shows the J-V curve for all the samples of DSSCs tested, which clearly shows that the short circuit current density, open circuit voltage and fill factor of each sample.

4. Conclusions
Spherical clusters of ZnO photanode was obtained via SEM evaluation and it shows that it has a bigger surface area which helps in increasing the performance of DSSC as the more dye can be attached to the ZnO particle as compared to TiO$_2$. Prunus domestica dye with the darkest color of dye gave the highest efficiency compared to magnifera indica and citrus limon with the efficiency of 3.08% when fabricated with ZnO photoanode. This research also prove that pH indicator does not affect the efficiency of the DSSC.

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