

Photoanode Thickness and Sensitization Time Effects on Overall Performance of Nanocrystalline TiO₂ Based Solar Cell Sensitized with Roselle Flower Extracts

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Abstract: Semiconducting anode layer thickness and anode sensitization time are two major factors that can affect the overall responses of dye sensitized solar cells. By setting these fabrication parameters at different levels, different DSSCs were fabricated at different experimental conditions. FTO conductive glasses were used as substrates and counter electrode fabrication and Roselle flower extract was the chosen as sensitizer. Each cell was illuminated with constant light intensity of 1 Sun (100mW/cm²) A.M 1.5 to determine the photovoltaic responses. A maximum conversion efficiency and fill factor obtained are 0.3220% and 0.7501 respectively. Hence, optimum values of the two parameters investigated favour performance of dye-sensitized solar cells.

Keywords: Solar cell, photoanode thickness, sensitization time, natural dye, efficiency,

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Introduction

The conversion of solar energy to electricity has become more and more important, because solar radiation coming from sun is a clean and abundant energy source compared to the fossil fuel source (Gratzel, 2013). Solar energy technologies such as solar cells have been recorded significant progress. Solar cells are categorized into three generations based on their performance and cost effectiveness. The first generation of solar cells has a relatively higher efficiency but plagued with expensive production cost. Photo-generated electron-hole pair is separated and collected through the p-n junction of a doped semiconductor, mainly

silicon¹. The commercial market is dominated by this generation. Thin film solar cells based on CdTe or Cu(InGa)Se₂ make up the 2nd generation cells. They have a lower efficiency, but are much cheaper to produce and employ a less extensive fabrication process. The 3rd generation solar cells consist of any cells that aren't grouped into the 1st and 2nd generations. Most of the 3rd generation technologies are not yet commercially implemented, but there is a lot of research going on with a promising future. Dye sensitized solar cell is an organic solar cell of the 3rd generation⁴. The highest reported efficiency for DSCs with conventional Ru-based dyes is around 11.5%^{5,6}. Recently, a Zn-based dye and Co-based electrolyte pair have

been developed and their efficiency has exceeded 12%.⁷

The most efficient dyes so far for DSSC applications are Ru(II)^{11,12} and Os(II)¹³ because of their good absorption, long excited lifetime and highly efficient metal-to-ligand charge transfer. The disadvantages of these complexes are high cost and sophisticated preparation techniques. Therefore, alternative organic dyes such as natural dyes have been studied intensively to explore their availability, environmental friendliness and low cost. Efforts have been concentrated on organic dyes and organic metal complexes. On the other hand, natural dyes extracted from fruits, leaves, roots and flowers have been proven to be efficient dyes as photo-sensitizers in DSSCs^{[14], [15]}. An efficient DSSC with high shunt resistance is desirable because high shunt resistance provides the DSSC with no alternative path for current flow apart from the electrical contacts for current collection.

Designing a photo-anode with an efficient charge transport pathway from the photo injects carriers to the collector will enhance the performance of DSSCs. Film thickness and sensitization time are two key factors that must be taken into consideration during fabrication of photo-anode. Raising the thickness of film increases the total interfacial surface area of the porous film thereby boosts the amount of dye absorbed and the light absorption. Hence, raising the film thickness can increase the current

density (Lee, et al. 2010). However, when thickness exceeds an optimum value, current begins to decrease with increasing thickness because of increased recombination. This happens because the path for photo-generated electrons becomes longer with the increasing thickness beyond optimum value⁸. The thickness dependence is also a function of particle size and surface structure. For example, optimal thickness for 20nm particles is half of that obtained for the 42nm particles⁹. Another important factor is the sensitization time, which determines the quantities and the nature of the absorbed dye molecule. The dye sensitization time should be sufficiently long in order for the interfacial surface of the oxide film to be completely covered with a monolayer of dye molecules. Because the molecules of dyes must cover the oxide of the film before attaching to the interfacial surface of the film, therefore, the sensitization time of the film with the dye much likely depends on the thickness of the film. Though the two factors have been individually studied before, but a detailed and systemic study of the efforts of both factors together for TiO₂ based DSSCs is lacking using fresh roselle flower as a dye. Thus, the present study investigates the photoanode thickness and sensitization time effects on overall performance of nanocrystalline TiO₂ based solar cell sensitized with roselle flower extracts.

2.0 Experimental Procedure

2.1 Preparation of Anode

2.1.1 Fabrication Condition

Cell	Guide Layers (Thickness)	Sensitization Time (minutes)
C ₁	1	15
C ₂	1	30
C ₃	2	15
C ₄	2	30

2.1.2 Deposition of TiO₂ Layer

FTO glasses with sheet resistance $7\Omega/\square$ and average transmittance of 85% cut to $4\text{cm} \times 4\text{cm}$ were weighed and subjected to cleaning procedure involving rinsing with alkali free detergent solution for 5 minutes then rinsing with copious deionized (DI) water, stepwise sonication in 0.1M HCl, Acetone, Isopropanol each for 5 minute and finally boiling in isopropanol at 80°C for 5 minutes. This is done to remove all residual contaminants from the surface of the glasses.

Ethanol was added to Titanium (IV) Oxide (Anatase) powder in drops and stirred with plastic spatula until a slightly runny paste is obtained. The paste was deposited on the tape guided conductive sides of clean conductive glasses by doctor blading technique with the aid of clean glass rod, preheated at 60°C for 5 minutes then annealed at 450°C . The film area was measured and the thickness determined by mass difference technique.

2.2 Dye Preparation

Fresh Roselle flower were collected and air dried. The dried flowers were ground into powder. 10g of the powder was weighed and poured into a bottle. 100ml of concentrated ethanol was added and stirred with a glass rod until a uniform suspension was obtained. The solution is left for 24 hours to ensure complete extraction of Anthocyanin and filtered to remove solid fragments. The extracts were optically characterized using Jenway UV-VIS spectrophotometer. To ensure stability before use, the filtrates were kept in separate clean bottles, protected from direct sunlight and refrigerated at about 4°C .

2.3 Sensitization and Fabrication of the DSSCs

The deposited TiO₂ samples were sensitized with Roselle flower extract. The counter electrodes were made by shading the conductive sides of another set of clean conductive glasses with pencil to deposit a layer of graphite as catalyst for current collection. Each of the sensitized TiO₂ sample and each graphite coated counter electrode were assembled to form a solar cell by sandwiching a redox (I^-/I_3^-) electrolyte solution. The electrolyte contains 0.025g of Iodine, 0.025g of Potassium Iodide and excipients to 1ml.

2.4 I-V Characterization of Solar Cells

2 J-V Characterization of Solar Cells

The J-V characterization of the DSSCs was carried out with Keithley 2400 series source meter under constant illumination of 1 Sun (100mW/cm²) A.M 1.5 from a solar simulator to obtain the J-V characteristics curves. The overall conversion efficiencies and fill factors were calculated using equations (1)-(2):

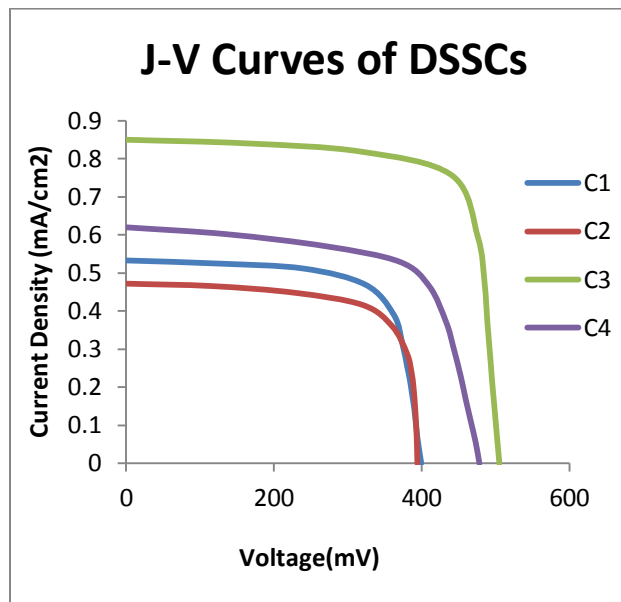
$$\text{Fill Factor } FF = \frac{I_m \times V_m}{I_{sc} \times V_{oc}} \quad (1)$$

$$\eta = J_{sc} (\text{mAcm}^{-2}) \times V_{oc} (V) \times FF \quad (2)$$

The shunt and series resistances were determined from I-V curves of the DSSCs. The shunt resistance is the inverse of the slope at I_{sc} while the inverse of the slope at V_{oc} is though not the exact value but proportional to the series resistance of a solar cell.

3.0 Results and Discussions

3.1 J-V Curves of DSSCs



Cell	C1	C2	C3	C4
R _s Ω	173.7	60.4	108.9	214.4
R _{sh} Ω	5529.8	1472.0	5017.6	747.7
V _{oc} (mV)	399.3	394.0	505.0	478.0
J _{sc} (mA/cm ²)	0.533	0.470	0.850	0.620
FF	0.7094	0.7452	0.7501	0.5709
η %	0.1510	0.1380	0.3220	0.1692

The J-V responses of the DSSCs range between 0.1380 % to 0.3220 %, 0.5701 to 0.7501, 747.7 Ω to 5529.8 Ω and 60.4 Ω to 214.4 Ω for IPCE, Fill Factor, shunt resistance and series resistance respectively. The relatively higher values of efficiencies in C₃ and C₄ than in C₁ and C₂ are attributed to the thick nature of the semiconducting TiO₂ anode layer giving room for more dye molecules to be absorbed during fabrication procedure. This results in increase in the number photo-generated electrons that constitute larger value of current. Hence, it is evident that the thickness effect on increased absorbed dye molecules outweighs its effect on the increased recombination due to longer path for photo-generated electrons. Comparing the conversion efficiency of C₃ and C₄, the lower efficiency in C₄ is as result of less dye molecules absorbed because of relatively shorter sensitization time than in C₃ even though the TiO₂ layer was yet to be saturated. Despite longer sensitization time during fabrication of C₂, its conversion efficiency is lower than that of C₁. This is attributed to the fact that the TiO₂ layer became saturated earlier because of its

smaller thickness compared to C_3 and C_4 . Sensitization after saturation does not improve performance of DSSC, rather, the unreacted dye molecules that are not completely removed can contribute to the series resistance of DSSC.

4.0. Conclusion

TiO_2 layers were prepared with varying thicknesses by "Doctor Balding" method and used as photoanodes to fabricate DSSCs. The highest conversion efficiency and fill factor of 0.3220 % and 0.7501 respectively were obtained for DSSC fabricated with double layer tape

Photoanode thickness and sensitization time are important factors that play interconnective roles in the DSSC performance. However an optimum sensitization time for known photoanode thickness is desirable which will likely vary with different dye types because of variation in chellativity to metallic oxide layers.

guide deposition of TiO_2 layer and sensitization time of 30 minutes. Thus, by selecting the optimum values of photoanode thickness and sensitization time during the fabrication process can favour performance of dye-sensitized solar cells.

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