Fabrication and Characterization of Dye Sensitized Solar Cell Using Nanostructured TiO_2 Photoelectrode

Abel. F. Ole, Gil Nonato C. Santos, Reuben V. Quiroga

Abstract- Dye Sensitized Solar Cells (DSSCs) with photoelectrodes synthesized via Horizontal Vapor Phase Crystal (HVPC) Growth Technique were fabricated and characterized in the present study. Nanostructured TiO_2 was first synthesized on glass substrates at growth temperatures of 1000 °C, 1100 °C, and 1200 °C with varying substrate distance from the bulk powder. Flourine-doped Tin Oxide (FTO) was used to deposit nanostructured TiO_2 for the photoelectrodes of the DSSCs employing the optimum substrate distance identified by SEM analysis. Bixin dye extracted from Annatto was utilized as a low-cost sensitizer and a graphite coated FTO as counter-electrode. All the DSSCs with photoelectrode fabricated by HVPC growth technique achieved a relatively large open-circuit voltage (V_{oc}) of 387 mV, 427 mV, and 412 mV for growth temperature of 1000 °C, 1100 °C, and 1200 °C respectively.

Keywords- Nanostructured Titanium oxide (TiO_2), Dye Sensitized Solar Cell (DSSC), Photoelectrode, Annatto

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1 INTRODUCTION

One of the most promising types of solar cell that has attracted much of attention in the scientific community already belongs to the third generation of photovoltaics (PVs). Unlike the common solid state solar cells based on crystalline silicon, the dye-sensitized solar cell (DSSC) does not depend on the principle of a p-n junction for its basic operation (Aydil 2007) [1]. The DSSC can be classified as a photoelectrochemical (PEC) solar cell due to its utilization of photons, charges, and electrolyte for its basic operation (Yu & Chen 2009) [34]. Since its invention by O'Regan and Grätzel in 1991, it has attracted widespread academic and industrial interest because it offers some advantages over the traditional photovoltaic cells. Based on the reports in the literature, the group of Y. Zhang et al. (2009) [35] said that DSSCs are easily fabricated, low-cost, environmentally benign, and have relatively high energy conversion efficiency. Another advantage of DSSCs over competing technologies is that temperature changes do not degrade their performance in contrast with conventional silicon solar cells (Gratzel 2004) [9]. This photovoltaic cell is one of the leading candidates as a substitute for the traditional and expensive silicon solar cell because of its comparable conversion efficiency using low-cost fabrication techniques and the other advantages mentioned above (Gratzel 2003) [10].

Another interesting characteristic of DSSCs is the incorporation of nanomaterials among its components. So far, among all the emerging PVs that employ nanotechnology, DSSCs are the most efficient (Aydil 2007) [1]. Based on the original design of Gratzel, the cell is basically composed of a working electrode made up of nanocrystalline TiO_2 typically 5-10 nm in diameter deposited on a transparent conducting oxide (TCO), a dye sensitizer usually Ruthenium based, an Iodide/Triiodide redox couple electrolyte, and a Platinum or Carbon coated counter-electrode (Gratzel 2003) [10]. For almost two decades, many investigators have tried various combinations of nanocrystalline TiO_2, dye sensitizers, electrolytes, and assembly methods to optimize the solar cell performance (Aydil 2007) [1].

The most common aspect of the DSSC that has been extensively studied to improve its efficiency is the design and fabrication of the photoelectrode using TiO_2 nanomaterials (Y. Zhang et al. 2009) [35]. The unique characteristics of nanomaterials such as their very large surface areas per unit volume or per unit mass (Aydil 2007) [1] can potentially improve the solar cell's efficiency. The large surface and interfacial areas found in nanostructured materials is also said to present significant advantages on the two critical steps in solar-to-electric energy conversion such as light absorption and charge separation (Aydil 2007) [1]. Hence, the

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present work will mainly concentrate on trying to fabricate nanostructured TiO_2 as working electrode of a standard DSSC and study whether the novel method of synthesis can be effectively employed in the process of DSSC assembly. In this paper, nanostructured TiO_2 synthesized via Horizontal Vapor Phase Crystal (HVPC) Growth Technique [6] will be introduced as the photoelectrode of Dye-Sensitized Solar Cells (DSSCs).

2 EXPERIMENTAL DETAILS

2.1 Synthesis of Nanostructured TiO_2

First, an amorphous silica tube with an inner diameter of 8.5 mm, outer diameter of 11 mm, and length of 290 mm was sealed at one end using the flame torch which is an approximate mixture of LPG and oxygen. Three different tubes was dented at about 50 mm, 80 mm, and 110 mm, respectively from the sealed end to prevent the substrate from reaching the region where the TiO_2 powder will be located. The sealed amorphous silica tubes were cleaned using an ultrasonic cleanser for 30 minutes and were washed and dried. Approximately 0.035 g of high purity (99.99%) P25 Degussa TiO_2 powder was loaded into the tube sealed at one end. The glass, with approximate dimensions of 25 mm by 7 mm, was placed inside each tube to serve as a substrate. Finally, the quartz tube with the TiO_2 powder and the substrate was connected to the Thermionic High Vacuum System until it reached the desired pressure of around 10^{-5} to 10^{-6} Torr. Once it acquired the right pressure range, the tube was sealed and detached carefully at approximately 140 mm from the sealed end using the flame torch.

The as-prepared amorphous silica tube containing the TiO_2 powder and the substrate was placed inside the Thermolyne Horizontal Tube Furnace to facilitate the synthesis of the TiO_2 nanomaterial via the Vapor-Solid (VS) growth or evaporation-condensation technique. The furnace was set at varying growth temperature from 1000 °C to 1200 °C in increments of 100 °C and fixed dwell time of 6 h for three separate sets of vacuum-sealed tubes. A constant ramp rate of 10^{o} C per minute was used for the furnace to go from the ambient to the desired temperature. In order to create a thermal gradient that will serve as the transport mechanism for the vapor during the deposition process, the completely sealed tubes were inserted halfway through the furnace. Before retrieving the synthesized TiO_2, the whole system, including the amorphous silica tube must be allowed to cool down naturally to room temperature. The nanostructured TiO_2 were retrieved by breaking the amorphous silica tube carefully without damaging the substrate.

2.2 Characterization of Nanostructured TiO_2

Nanostructured TiO_2 grown on the glass substrate was subjected to a series of characterization. Surface and morphological characteristics were examined with the aid of JEOL JSM-5310 scanning electron microscope (SEM). The elemental composition of the TiO_2 nanomaterial was also analyzed using the same instrument but under the Energy Dispersive X-ray (EDX) mode.

Two empty or blank glass substrates, one baked without TiO_2 powder while the other unbaked, was also characterized so that the researcher had an idea about the morphology and composition of the substrate that served as a background.

2.3 *DSSC Fabrication*

After determining the optimum substrate distance for each growth temperatures, FTO was used as substrate instead of ordinary glass in growing TiO_2 nanomaterials to serve as photoelectrode of the DSSC.

The nanostructured TiO_2 grown on the FTO substrate was soaked in a dye solution of *Bixin*, extracted from *Annatto* by boiling water, for a period of 24 h to adsorb enough amount of dye as sensitizer. Twenty-four hours later, the FTO with the TiO_2 nanomaterial and the sensitizer was rinsed with water to remove the excess dyes that were not completely adsorbed to the nanostructured TiO_2 [2], [9], [10].

Once the working electrode has totally dried, two small drops of an electrolyte containing an Iodide/Triiodide redox couple was applied on the side with the TiO_2 nanomaterials and dye. Finally, a graphite-coated FTO was placed on top of the working electrode which served as its counter-electrode [2], [9], [10].

The two electrodes were fixed one on top of the other using a pair of alligator clips. An offset of about 2.5 mm on opposite electrodes was included to serve as electrical contacts. The fabricated DSSC was sealed on all its sides to prevent the leakage of the electrolyte.

2.4 Assessment of the DSSCs' Photovoltaic Performance

The photovoltaic performance of the DSSC based on nanostructured TiO_2 produced via HVPC growth technique was evaluated. The DSSC was connected to a series of potentiometers with resistance ranging from very low (70 Ω) to very high (2.93 MΩ) resistance values.

Using a very sensitive digital voltmeter (Fluke, 0.1 mV), the open-circuit voltage (V_{oc}) was determined by setting the resistance high enough. Next is the measurement of the short-circuit current (I_{sc}) which was accomplished with the aid of a very sensitive ammeter (Newstar UT33D, 1 μA) and the resistance set at a very low value. The artificial light source in the set-up is a 120 W OMNI lamp available in the laboratory. An *I-V* curve was obtained by varying the resistance from very low to a very high value while measuring the particular current and voltage for each amount of load. The maximum power point was identified from the *I-V* curve and the maximum power point voltage (V_{mp}) and current (I_{mp}) was consequently determined. From the values obtained for V_{oc}, I_{sc}, V_{mp}, and I_{mp}; the fill factor (*FF*) and therefore the overall energy conversion efficiency (η) were calculated using the equations presented below [2].

$$\eta = \frac{P_{\max}}{P_{in}} \times 100 = \frac{(I_{sc} V_{oc} FF)}{P_{in}} \times 100$$

$$where:$$

$$FF = \frac{I_{mp} V_{mp}}{I_{sc} V_{oc}}$$

3 RESULTS AND DISCUSSION

3.1 Nanomaterial Characterization

3.1.1 Surface Morphology

The following figures are the representative SEM micrographs for each sample utilized in the fabrication of DSSC photoelectrodes.

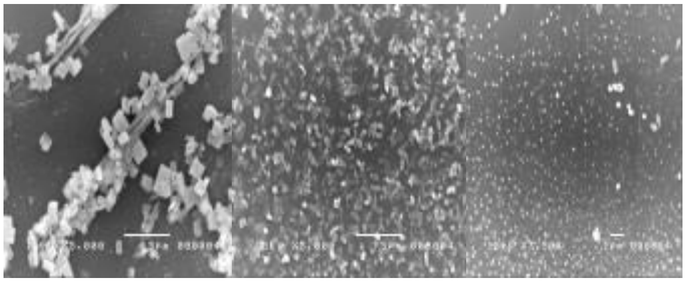

Figure 1: SEM micrographs of S1000-80

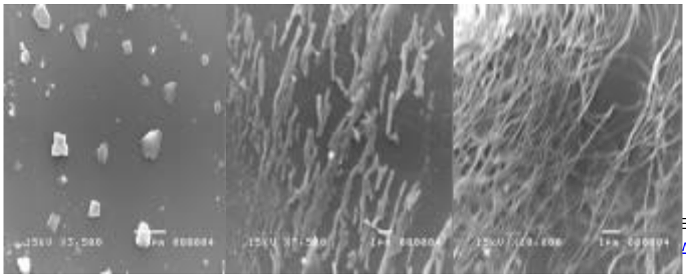

Figure 2: SEM micrographs of S1100-80

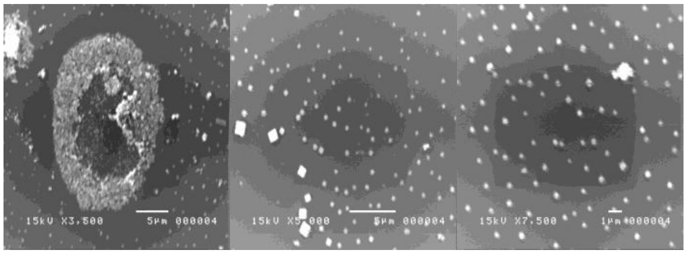

Figure 3: SEM micrographs of S1200-80

Based on the SEM micrographs and the summary of the grown TiO_2 nanostructures and microstructures, the researcher chose the substrate distance that will more likely produce a greater amount of nanostructured TiO_2 suitable for DSSC application. The first consideration was the size of the synthesized TiO_2, the smaller the size the better. Therefore, substrate distance of 50 mm was immediately excluded from the options because majority of the deposited TiO_2 were microstructures. Another deciding factor considered by the author was the amount as well as the distribution of the nanomaterials. Since monodispersed nanomaterials promote an increase in the interfacial surface area compared to agglomerated ones, the substrate distance with the greatest amount of monodispersed nanostructures was chosen to be used in the synthesis of the photoelectrodes for the DSSCs [30]. Large interfacial surface area of nanomaterials favor greater dye loading ability for the TiO_2 which promotes a higher light absorption capability for the photoelectrode of DSSCs [2]. As illustrated by the SEM micrographs, the most favorable substrate distance to be used for all growth temperatures was 80 mm from the bulk powder.

3.1.2 Elemental Composition

The Energy Dispersive X-ray analysis results shown below strongly suggest that indeed, TiO_2 nanomaterials were successfully synthesized on the glass substrate at different growth temperatures. Other elements present in the X-ray spectra were attributed to the composition of the substrate that served as a background in the deposition of nanostructured TiO_2.

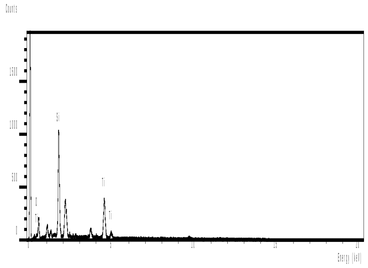

Figure 4: EDX result for nanostructured TiO_2 synthesized via HVPC growth technique

3.2 DSSC Characterization

The fabricated DSSCs were characterized inside the laboratory using a 120 W lamp that emits a mean intensity of 18 049 .82 lux. This light intensity was converted to the amount of W/cm^2 to serve as the input power density on the DSSC which was calculated to be 2.64 mW/cm^2. Actual sunlight characterization was also conducted for the fabricated DSSCs at approximately 11:00 am. From the measured average amount of light intensity (4396.48 lux), the power density input on the DSSC was computed to be 643.6μW/cm^2.

Table 1: Summary of the DSSC Photovoltaic Performance under Artificial and Actual Sunlight Illumination

Sample DSSC	Voc (mV)		Isc (μA)		FF		η (%)	
	Lamp	Sunlight	Lamp	Sunlight	Lamp	Sunlight	Lamp	Sunlight
1000	387	414	40	6	0.19	0.26	0.08	0.07
1100	427	305	39	9	0.21	0.21	0.09	0.06
1200	412	276	45	19	0.24	0.23	0.12	0.13

Table 1, revealed that even under sunlight illumination, the performance of DSSC-1000 and DSSC-1100 were still comparable with each other while DSSC-1200 demonstrated a relatively larger efficiency as before. There were some variations in the values of the average FF and η of the first two DSSCs in actual sunlight characterization suggesting that their performance has a degree of instability affected by light intensity. On the other hand, DSSC-1200 exhibited a consistent performance in terms of both the quality and the efficiency of the cell as indicated by its unchanged FF and largest η both in artificial light and actual sunlight testing. Therefore, among the three DSSCs with photoelectrodes fabricated by HVPC growth technique, DSSC-1200 has the optimum performance and reliability. These positive results were attributed to the thicker deposition of TiO_2 nanostructures on its photoelectrode as a consequence of the higher growth temperature during fabrication via HVPC growth technique [6].

All the DSSCs with photoelectrode fabricated by HVPC growth technique achieved a relatively large open-circuit voltage (V_{oc}) of 387 mV, 427 mV, and 412 mV for growth temperature of 1000 °C, 1100 °C, and 1200 °C; respectively. Among the fabricated DSSCs with photoelectrodes grown at different temperatures, DSSC-1200 exhibited the largest short-circuit photocurrent (I_{sc}) of 45 μA compared to 40 μA for DSSC-1000 and 39 μA for DSSC 1100. As a consequence, DSSC-1200 demonstrated the largest recorded fill-factor of 0.24 and efficiency of 0.12 % among the three during artificial light characterization.

When the photoelectrode of a DSSC fabricated by solution-based method was first subjected to HVPC growth technique, a very large enhancement in open-circuit voltage (V_{oc}) was achieved. The DL-DSSC-1200 resulted to the following cell parameters; I_{sc} = 290 μA, V_{oc} = 488 mV, I_{mp} = 119 μA, V_{mp} = 269 mV, FF = 0.23, and η= 0.87 % making it the best performing DSSC in the present study.

4 CONCLUSION

From the research findings discussed in the previous section, it can be said that nanostructured TiO_2 was effectively grown on glass substrate via HVPC growth technique. Substrate distance from the bulk powder aside from the growth temperature also influenced the synthesis of TiO_2 nanomaterials. When the substrate distance was fixed, increase in growth temperature resulted to a thicker deposition of TiO_2 nanomaterials on the substrate [6]. Greater amount of nanostructured TiO_2 was deposited because the increase in growth temperature caused an increase in the amount of TiO_2 vapour producing a greater number of nucleation sites [6].

The presence of nanostructured TiO_2 was considered as the determining factor of the relatively large open-circuit voltage (V_{oc}) of the fabricated DSSCs due to the smaller particle size of the TiO_2 nanomaterials on the photoelectrode [30]. On the other hand, the photocurrent values were limited by the low-cost natural organic dye sensitizer [27] and the thickness of TiO_2 deposition utilized in the DSSC. Better performance of the DSSC could be achieved by maximizing both the V_{oc} and I_{sc} which was accomplished through an optimized deposition of nanostructured TiO_2 if availability of the best sensitizer was lacking. Therefore, the highest growth temperature should be employed in the fabrication of photoelectrode via HVPC growth technique for DSSC application.

In conclusion, HVPC growth technique could be incorporated in the fabrication of photoelectrode for DSSC either by itself or in conjunction with the solution based technique. Independently, it can be used to grow nanostructured TiO_2 on FTO to serve as photoelectrode but an efficient sensitizer should be used in order to enhance its light absorption ability When used in conjunction with solution based technique, a low-cost sensitizer like Bixin extract from *Annatto* used in the present study will be sufficient to demonstrate an enhancement in DSSC performance as a result of the relatively high open-circuit voltage (V_{oc}) when its photoelectrode was first subjected to HVPC growth technique.

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