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MORPHOLOGICAL AND ELECTRICAL CHARACTERIZATION OF HYBRID THIN-FILM COMPOSED OF TITANIA NANOCRYSTALS, POLY (3-HEXYLTHIOPHENE) AND PIPER BETLE LINN

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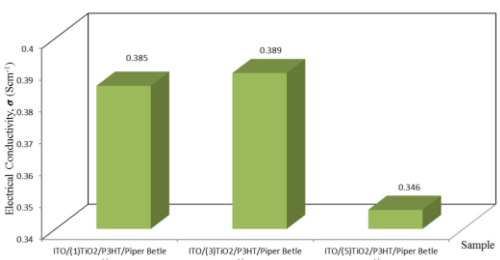
Graphical abstract



Abstract

In this research, the effect of scan numbers of titania nanocrystals (TiO_2 NCs) on the morphological and electrical characteristics of hybrid thin-films is investigated. These hybrid thin-films consist of a combination of organic (*Piper Betle Linn* extraction and Poly (3-hexytlthiophene) (P3HT)) and inorganic TiO_2 NCs (anatase structure) materials. These hybrid thin-films are fabricated in bilayer heterojunction of ITO/TiO_2 NCs/P3HT/*Piper Betle Linn* via electrochemistry method using Electrochemical Impedance Spectroscopy (EIS). The scan numbers of TiO_2 NCs are varied by 1, 3 and 5 number of scans. The morphological characterization is carried out via Field Emission Scanning Electron Microscopy (FESEM) meanwhile the electrical characteristic of the hybrid thin-film is measured by using four point probes. FESEM image indicates the particle size was found to be around 17-34 nm. The increment of scan number of TiO_2 NCs from one to five scan numbers of TiO_2 NCs in bilayers thin films showed that the atomic percentage of titanium decrease from 5.23% to 2.20%. This result indicates that as the thickness of thin films increases, the electrons required more energy to excite into conduction band of TiO_2. Meanwhile, the electrical conductivities of hybrid solar cell increase from 0.385 Scm^{-1} to 0.389 Scm^{-1} as the scan numbers of TiO_2 increase from one to three, however the electrical conductivity decrease to 0.346 Scm^{-1} at five scan numbers. As a conclusion, this study shows that the morphological and electrical properties of hybrid thin-films can be significantly affected by the scan number of TiO_2 NCs.

Keywords: Electrical conductivity, Field Emission Scanning Electron Microscopy, Piper Betle Linn, Poly (3-hexylthiophene), Titania nanocrystals

Abstrak

Dalam kajian ini, kesan jumlah bilangan imbasan nanohablur titanium dioksida, TiO_2 ke atas pencirian sifat morfologi dan sifat kekonduksian elektrik filem nipis hibrid telah dijalankan. Sel-sel suria hibrid ini terdiri daripada gabungan bahan organik (ekstrak *Piper betle Linn* dan poli (3-heksiltiofena), P3HT) dan bahan bukan organik (nanohablur TiO_2 dalam bentuk struktur anatase). Sel-sel hibrid suria difabrikasi mengikut lapisan demi lapisan iaitu ITO/TiO_2/P3HT/*Piper betle Linn* melalui kaedah elektrokimia dengan menggunakan spektroskopi impedans elektrokimia. Bilangan imbasan nanohablur TiO_2 divariasikan kepada 1, 3 dan 5 bilangan imbasan. Pencirian morfologi dilakukan menggunakan mikroskop elektron imbasan medan pancaran (FESEM) manakala pencirian sifat kekonduksian elektrik filem diukur dengan menggunakan alat penduga empat titik. Imej mikroskop elektron imbasan medan pancaran menunjukkan bahawa saiz zarah TiO_2 berada dalam julat 17-34 nm. Nilai peratusan atom titanium menurun dari 5.23% kepada 2.20% apabila jumlah imbasan nanoablur TiO_2 meningkat dari satu kepada lima imbasan. Keputusan ini menunjukkan bahawa semakin bertambah ketebalan filem TiO_2, elektron memerlukan lebih banyak tenaga untuk bergerak ke jalur konduksi TiO_2. Sementara itu, nilai kekonduksian elektrik meningkat dari 0.385 Scm^{-1} kepada 0.389 Scm^{-1} apabila bilangan imbasan nanohablur TiO_2 meningkat dari satu imbasan kepada tiga imbasan dan menurun kepada 0.346 Scm^{-1} bagi lima imbasan nanohablur TiO_2. Kesimpulannya, kajian ini menunjukkan sifat-sifat morfologi dan elektrik filem nipis hybrid

Kata kunci: Kekonduksian elektrik, Mikroskop elektron imbasan medan pancaran, Piper Betle Linn, Poli (3-heksiltiofena), Nanohablur titanium dioksida

1.0 INTRODUCTION

Green technology application is seen as one of the sensible solutions which are being adopted by many countries around the world to address the issues of energy [1-2] and environment [3-4] simultaneously. Green technology is a technology that allows us to progress more rapidly but at the same time minimizes the negative impact to the environment [5]. However, the world needs to find more efficient and effective ways to adopt green technology against other technologies which have been widely used and though cheaper, not necessarily benevolent. Every hour the sun shining onto earth is more than enough energy to satisfy global energy needs for an entire year [6-7]. One of the green energy, solar energy is the technology used to harness the sun's energy and make it usable [8]. The main device that converts the solar energy into the electrical energy is known as solar cell [9].Solar electricity in this era is no longer an imaginary, fringe idea. With photoelectric cells and a solar electric panel system, a household can easily reduce its electricity consumption [10] and realistically reverse its cost by generating more energy than the energy being consumed. The latest generation of solar cell can be classified into organic solar cell (OSC), dye-sensitized solar cell (DSSC) [11-12] and hybrid solar cell (HSC) [13]. Among these three types of latest generation of solar cell, hybrid solar cell has gained much more interest by the researchers due to combination of unique properties between an inorganic and an organic material [14].

In this study, the effect of scan numbers of titania nanocrystals (TiO_2 NCs) on morphological and electrical characteristics is studied. An inorganic materials (TiO_2 NCs) and organic materials (Poly (3-hexylthiophene) (P3HT) and *Piper Betle Linn's* leaves) are employed for hybrid thin-films application. These hybrid thin films are fabricated in bilayer heterojunction of ITO/TiO_2 NCs/P3HT/ *Piper Betle Linn*/Au by using electrochemistry method. TiO_2 NCs-anatase is selected because it possesses high absorption coefficient [15], low cost, high electron mobility, physical and chemical stability, and environmentally friendly materials [16] and often used in photocatalytic application. Moreover, [17] had stressed out that the photocatalytic properties of TiO_2 nanoparticles are strongly depend on the surface area, the exposed surface and the crystallinity of the particles. According to Lira-Cantu *et al.* [18], semiconductor oxide such as TiO_2 is employed as an active support for trapping S-containing impurities. The study also shown that thiophene can be bond to TiO_2 via the aromatic ring, but also by the S-end atom. Meanwhile, the conjugated polymer P3HT is one of the promising conducting polymers which have high charge carrier mobility, low cost and good environmental stability [19]. *Piper Betle Linn* leaves are selected due to the ability to capture or to absorb over a wide range of light spectrum, low cost, environmentally friendliness as reported by Salmah *et* *al.* [20]. According to Wu *et al.* [3], the lowest unoccupied molecular orbital (LUMO)/highest occupied molecular orbital (HOMO) energy levels of P3HT and TiO_2 are about -3.53/-5.20 and -4.2/-7.2 (eV vs Vacuum); respectively. Under ultraviolet photoexcitation, electron-hole pairs are created in the TiO_2 semiconductor and then are dissociated into free charge carriers (electrons and holes). The electrons are transferred to the conducting Indium glass substrate via TiO_2 grid; the holes are reduced by electron donation from the valence band of P3HT and then from the platinum-plate (Pt) counter electrode, with the circuit being completed via electron migration through the external load.

2.0 EXPERIMENTAL DETAILS

2.1 Materials and Dyes

All the solvents and the other chemicals employed for the research were reagent and were used as received without any further purification. The conductive glass plate (ITO, Indium doped SnO_2, sheet resistance 7 Ω/sq) and TiO_2 NCs were purchased from Magna Value Sdn. Bhd. and Sigma Aldrich Sdn. Bhd.; respectively. Meanwhile, P3HT was synthesized accordingly as reported by Nik Aziz *et al.* [21]. The ITO glass substrates were cut into 2 cm × 2 cm for this research purposes.

2.2 Preparation of Titanium Dioxide Nanocrystals, TiO_2 NCS Solution

The TiO_2 solutions were made using 100 ml 0.5 M TiO_2 nanoparticles anatase structures and were prepared by dissolved 3.994 g of TiO_2 in deionized water under magnetic stirring. Then, the solutions were treated with 0.035 M acetic acid for better surface morphology of TiO_2. A macroscopic phase separation or aggregation of the inorganic nanoparticles and a bad interfacial contact between inorganic and organic materials will occurred if both materials were incompatible, which leads in low efficiency of the charge transfer from organic to inorganic materials and easy interfacial charge recombination as reported by Zhong *et al.* [14]. Thus, modification of TiO_2 with acetic acid was expected to improve the surface morphology and reduce the aggregation of TiO_2 nanoparticles.

2.3 Preparation of *Piper Betle Linn* Dyes Solution

Samples of *Piper Betle Linn*'s leaves were collected in Kuala Kangsar, Perak, Malaysia. The *Piper Betle Linn*'s leaves were washed with water and dried in the oven at 60 ° C to remove water. After that, these dried leaves were crushed in a mortar and pestle and prepared as a powder form. Then, these fine powders were immersed in absolute ethanol at room temperature in the dark for a week. After a week, the solid were filtered out and the filtrates were used as sensitizers. This extraction method was carried out as recommended by Zhou *et al.* [22]. The dye solution was also characterized by UV-Visible spectroscopy and Fourier Transform Infrared (FTIR) spectroscopy. The dyes can absorbed the visible light spectrum and the presence of carbonyl and hydroxyl groups were reported and further discussed in [20].

2.4 Fabrication of Thin Film

The hybrid thin-films were fabricated in bilayer heterojunction via electrochemistry method. The ITO coated glass substrate must be clean from dust and dirt to avoid any contamination. Ultrasonic water bath was used to clean the ITO coated glass substrates. The first step to clean the ITO coated glass substrates were by using detergent solution where the ITO coated glass substrates should be immersed in this solution for 10 minutes at 30 ^{0}C. Then, the ITO coated glasses were immersed with distilled water at the same temperature condition for 5 minutes and repeated for three times. After that, the ITO coated glass substrates were immersed in acetone at the same time and temperature conditions as the previous step. Finally, the ITO coated glass substrates were dried by using a dryer and place in a clean petri dish [23].

Electrochemical Impedance Spectroscopy (EIS) PGSTAT302 was employed to deposit TiO_2 NCs, P3HT and also natural dyes on ITO coated glass substrates. The scan numbers of TiO_2 NCs is varied by 1, 3 and 5 and the scan numbers of P3HT and natural dyes are fixed to 5 scan numbers. The scan number also known as number of complete cyclic and the number of cyclic determine the difference in thickness [10]. The electrodeposited thin films of TiO_2 NCs then were annealed at 450 °C for two hours. The fabrication of hybrid thin film is shown in Figure 1.

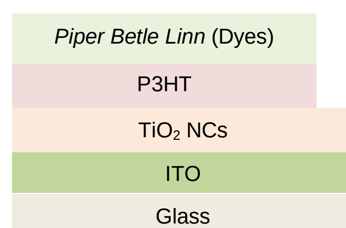


Figure 1 The schematic diagram of hybrid thin film

2.5 Measurements

The morphological characteristics of TiO_2 NCs thin films with different scan numbers was observed using Field Emission Scanning Electron Microscope (FESEM) model JEOL SEM or LEO 1455 Variable Pressure SEM attached with Oxford Inca Energy Dispersive X-Ray (EDX) at 20 kV. The X-ray diffraction (XRD) patterns of TiO_2 NCs thin films with different scan numbers was recorded by using an X-ray diffractometer (Model Rigaku MiniFlex II Desktop) with CuKa radiation (λ=1.5405 Å). The 2θ angle of the XRD spectra will be recorded at a scanning rate of 0.3° min^{-1}. The ultraviolet-visible (UV-

Vis) absorption spectra of hybrid thin films were measured using ultraviolet-visible spectrophotometer model Perkin Elmer, Lambda 25. Then, the optical energy gaps of the thin films are calculated by using Equation 1, where, *h* is Planck's constant, *c* is the velocity of light and λ is the emitted wavelength in photoluminescence spectrum. Meanwhile, the electrical conductivities of the hybrid thin films of ITO/TiO_2 NCs/P3HT/*Piper Betle Linn* were measured by using four points probes model Jandel RM3 under light intensity of 100 Wm^{-2}. Equation 2 is used to measure the sheet resistivity, R_s of the thin film, where *V* is voltage supplied, *I* is current and 4.532 is the correction factor.

$$E_g = \frac{hc}{\lambda} \quad \text{(Eq. 1)}$$

$$R_S = 4.532 \times \frac{V}{I} \quad \text{(Eq. 2)}$$

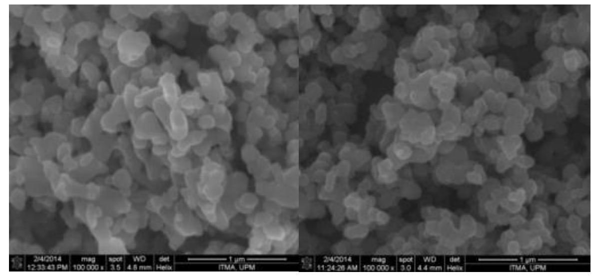
$$\sigma = \frac{1}{R_S} \quad \text{(Eq. 3)}$$

3.0 RESULTS AND DISCUSSIONS

3.1 Surface Morphology

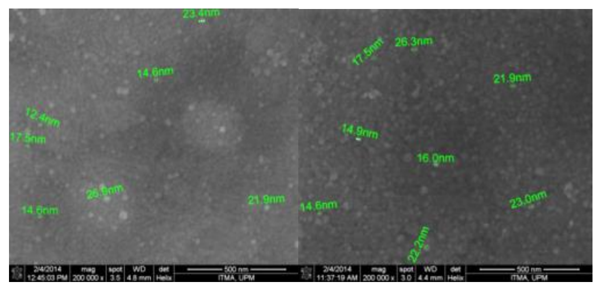
FESEM images of TiO_2 NCs for 1 and 5 scan numbers of TiO_2 NCs are shown in Figure 2 and Figure 3; respectively. The cluster formations of TiO_2 particles are due to the tiny water molecules and hydroxyl group are unavoidable on nanoparticles. Because of the small size of the cluster, they have a high surface energy, which leads to aggregation or oxidation. Thus, it is easy for nano-TiO_2 particles to heavily agglomerate in organic solvent or resin. To overcome this disadvantage, the agglomerate nanoparticles are loosened by being modified with acetic acid and Kamalan Kirubaharan *et al.* [24] had employed trifluoroacetic acid as capping agent to prevent the agglomeration of the titanium dioxide nanoparticles. The dark region was observed in Figure 2 (b) as compared to the bright region in Figure 2 (a) which indicates the difference in thickness of TiO_2 NCs deposited. Meanwhile, FESEM images as shown in Figure 3 indicates that the particles size was found to be around 17-34 nm, corroborating the crystallite size calculated from the XRD data. These particles have well-ordered tetragonal structure, which is in good agreement with the result of XRD in section 3.2.

The atomic percentage of titanium deposited on ITO glass substrates for different scan number of TiO_2 NCS are shown in Table 1. As shown in Table 1, the atomic percentage of titanium deposited on ITO glass substrates before annealed at 450 °C was 0.74% and increase to 2.20% after annealed at 450 °C (2 hours) for 5 scan numbers of TiO_2 NCs. However, the atomic percentage of titanium was 5.23% for 1 scan number of TiO_2 NCs after annealed at 450 °C (2 hours) which is larger than the atomic percentage of titanium for 5 scan numbers. This result indicates that heat treatment temperature and its duration can influence the rate of photodegradation. The long heating in air may results in decreasing of specific surface area, which also limits the photocatalytic activity of TiO_2 films [25].



(a) (b)

Figure 2 The surface morphologies of TiO_2 NCs at different scan number (a) (1) TiO_2 NCs (b) (5) TiO_2 NCs



(a) (b)

Figure 3 The particle sizes of TiO_2 NCs at different scan number (a) (1) TiO_2 NCs (b) (5) TiO_2 NCs

3.2 X-Ray Diffraction Analysis

Figure 4 shows the XRD patterns of pure anatase TiO_2 and TiO_2 at different scan numbers of 1, 3 and 5 scan numbers. As can be seen in Figure 4, all samples show the same peaks characteristic of the anatase phase of TiO_2 NCs. Based on the XRD spectrum (PDF 71-1168, ICSD Number: 009854) report, the TiO_2 was in tetragonal structure. Besides that, the anatase structure of TiO_2 NCs was confirmed unchanged during the annealing process take places at 450 °C for 2 hours and it can be confirmed by comparing the peaks exhibit at 2θ of 25.1°, 37.6°, 47.9°, 53.8°, 54.9° and 62.6° with the *hkl* as stated in the pure TiO_2's graph and the intensity was tabulated in Table 2. As shown in Figure 4, the diffraction peak at 2θ ≈ 25.1° exhibits the highest intensity, which corresponds to the (101) plane of the TiO_2 anatase structure and it can be observed that the diffraction peak at plane (101) was shifted to the right as the scan numbers of TiO_2 increase. This shifting suggested that the linkage was made between TiO_2 NCs with the ITO coated glass substrate. Meanwhile, the optimum of scan number of TiO_2 NCS has significantly affected the crystallinity of TiO_2 films. As scan number of TiO_2 NCS is decreased to 1 scan number, the crystallinity of thin film is enhanced. However, the excess of TiO_2 content in film may destruct the interpenetrating pathways for hole transport and causing in decreasing of XRD intensity [15].

Table 1 The atomic percentage of titanium deposited on ITO glass substrates at different scan number of TiO_2 NCs

Sample	(5) TiO_2 NCs before annealed		(5) TiO_2 NCs annealed at 450 °C (2 hours)		(1) TiO_2 NCs after annealed at 450 °C (2 hours)	
Element	Weight (%)	Atomic (%)	Weight (%)	Atomic (%)	Weight (%)	Atomic (%)
O K	29.13	74.42	48.33	85.97	48.26	84.4
Ti K	0.87	0.74	3.70	2.20	8.96	5.23
In L	63.00	22.43	41.48	10.28	35.49	8.65
Sn L	7.00	2.41	6.49	1.56	7.29	1.72
Total	100		100		100	

Table 2 Two theta, peak list and intensity of TiO_2 NCs

2 theta, 2θ (°)	Peak List (hkl)	Intensity (a.u.)
25.1	(101)	999
37.6	(004)	180
47.9	(200)	224
53.8	(105)	139
54.9	(211)	135
62.6	(204)	97

Table 3 The energy band gap of titania, poly (3-hexylthiophene) and *Piper Betle Linn* dyes solution

Materials	Energy band gap, E_g (eV)
Titania	3.20
Poly(3-hexylthiophene)	1.70
Piper Betle Linn dyes solution	2.51

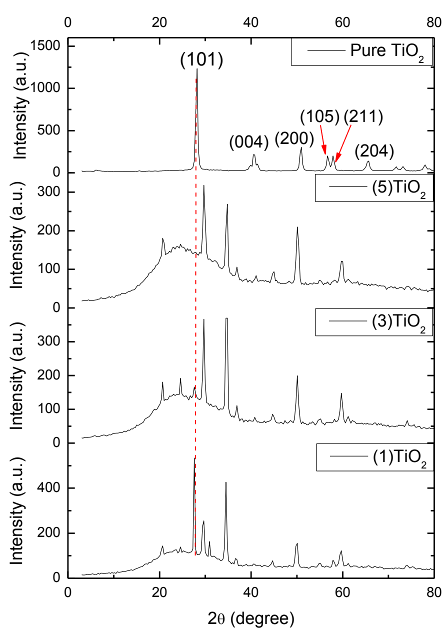


Figure 4 The XRD pattern of TiO_2 NCs at different scan numbers

3.3 Energy Gap

As mentioned in the [26], TiO_2 NCs was selected due to its behavior as photo-catalysts. Hence, the photo-catalysts reactions on TiO_2 surfaces take place through the generation of electron-hole pairs, known as excitons, by radiation exceeding energy band gap of the materials [27-28]. Moreover, Khalil [8] stated that the energy level of the polymer can be tuned by chemical modification of the backbone chain and the energy level of the nanoparticles can be tuned through the size-dependent quantum confinement effects. The optical energy band gap is defined as the energy difference between two bands or the amount of energy required to mobilize the electron in the system [29]. The optical energy band gap, E_g of each material was tabulated in Table 3.

3.4 Electrical Conductivity

The electrical properties of ITO/TiO_2 NCs/ P3HT/*Piper Betle Linn* hybrid thin film under 100 Wm^{-2} intensity of light are measured using four-point probe. The main function of four-point probe is used for measuring the resistivity of semiconductor samples. By passing a current through two outer probes and measuring the voltage through the inner probes allows the measurement of the resistivity. Electrical conductivity is the capacity of any object or substance to conduct an electric current. When an electrical potential difference is placed across a conductor its movable charges flow which giving rise to an electric current. The conductivity depends of the characteristics of the materials. A conductor such as a metal has a high conductivity and an isolator like glass, wood and vacuum has a low conductivity. The conductivity of a semiconductor is generally intermediate, but varies widely under different conditions. As can be seen in Figure 5, the electrical conductivities of thin films for different scan numbers of TiO_2 NCs lies in the semiconductor ranges (10^{-7}- 10^3 Scm^{-1}) [30]. This result indicates that the combination of these materials were suitable to applied in solar cell application. The electrical conductivities of thin films increase from 0.385 Scm^{-1} to 0.389 Scm^{-1} as the scan numbers of TiO_2 NCs increase from 1 scan number to 3 scan numbers of TiO_2 NCs. However, the electrical conductivity of thin film decreases to 0.346 Scm^{-1} when the scan numbers of TiO_2 NCs increase to 5 scan numbers. From the results, it observed that the scan numbers of TiO_2 NCs affected the conductivities of these hybrid solar cells. The result indicates that 3 scan numbers was the most effective thickness of TiO_2 for the electron to inject or promote to the conduction band of TiO_2 and dissociated at P3HT and the holes dissociated at ITO glass substrate (excitons phenomenon).

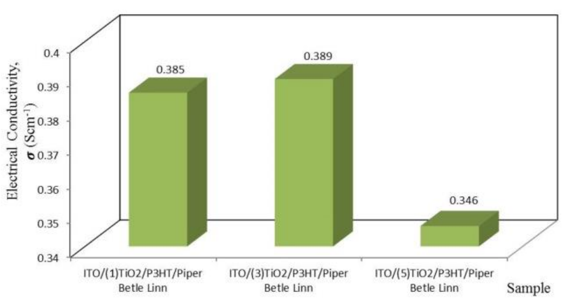


Figure 5 The electrical conductivity of hybrid solar cell at different scan numbers of TiO_2 NCs

4.0 CONCLUSIONS

It can be concluded that the morphological and electrical properties of ITO/ TiO_2 /P3HT/*Piper Betle Linn* hybrid thin films can be significantly affected by the scan numbers of TiO_2 NCs. The performances of the device are significantly dependent on the charge transport properties of the TiO_2. The incorporation of optimum amount of TiO_2 into polymer P3HT may aid in the enhancing the crystallinity and providing a more continuous, efficient pathway for charge transport. This works suggested that the optimum TiO_2 content is at 3 scan numbers with the electrical conductivity of 0.389 Scm^{-1} under 100 Wm^{-2} of light intensity. However, the excess amount of TiO_2 may destroy the interpenetrating pathway for charge transport properties of the P3HT that lead to the deterioration of hybrid solar cell performance.

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