Journal of Applied Science and Agriculture, 10(5) Special 2015, Pages: 196-200

AENSI Journals

JOURNAL OF APPLIED SCIENCE AND AGRICULTURE

ISSN 1816-9112

Journal home page: www.aensiweb.com/JASA

Nanocrystals Titania/Poly(3-Hexylthiophene) Combined with Piper Betle Linn as a Dye Source for Hybrid Solar Cells

[1]Salmah Mohd Ghazali, [2]Hasiah Salleh, [3]Mohd Sabri Mohd Ghazali, [1]Ahmad Nazri Dagang, [1]Muhammad Aimy Mahfuzzan Mohd Zaini, [3]Zakiyah Ahmad

[1]*Universiti Malaysia Terengganu, School of Ocean Engineering, 21030 Kuala Terengganu, Terengganu*
[2]*Universiti Malaysia Terengganu, School of Fundamental and Liberal Education, 21030 Kuala Terengganu, Terengganu*
[3]*Universiti Malaysia Terengganu, School of Fundamental Science, 21030 Kuala Terengganu, Terengganu*

A R T I C L E   I N F O

Article history:
Received 11 October 2014
Received in revised form 21 November 2014 Accepted 25 December 2014
Available online 14 January 2015

Keywords:
Electrochemical method
Hybrid solar cells
Nanocrystals Titania
Piper Betle Linn
Poly (3-hexylthiophene)

A B S T R A C T

Background: Harnessing energy from sun rays is so far considered as one of effective solution in generating green energy because the current energy such as fossil fuels are damage to our environment. Thus, the device to harness solar energy and convert solar energy into electrical energy which is known as solar cells are invented. **Objective:** In this research, hybrid solar cells are produced by a combination of organic (*Piper Betle Linn* and Poly (3-hexylthiophene) (P3HT) and inorganic (nanocrystals Titania, NCs TiO_2 in anatase phase structure) materials. These hybrid solar cells are fabricated accordingly bi-layer of ITO/TiO_2/P3HT/*Piper Betle Linn*/Au via electrochemical method. The absorption spectrum and functional group of *Piper Betle Linn* extraction in ethanol solution was analyzed by using UV-Vis spectrophotometer and FTIR spectrometer; respectively. Meanwhile, the efficiency of the hybrid solar cells was measured by using two point probes. **Results:** The UV-vis absorption spectra show that the *Piper Betle Linn* extraction was absorbed light spectrum in the range of 258-311 nm, 362-521 nm and 641-702 nm. According to this research, the highest power conversion efficiency obtained was 0.00963 % for ITO/ (3) TiO_2/P3HT/*Piper Betle Linn* hybrid solar cell. **Conclusion:** This paper briefly discusses the simple extraction techniques of natural dyes, fabrication of hybrid solar cells and the performance of the hybrid solar cells.

To Cite This Article: Salmah Mohd Ghazali, Hasiah Salleh, Mohd Sabri Mohd Ghazali, Ahmad Nazri Dagang, Muhammad Aimy Mahfuzzan Mohd Zaini, Zakiyah Ahmad. Nanocrystals Titania/Poly(3-Hexylthiophene) Combined with *Piper Betle Linn* as a Dye Source for Hybrid Solar Cells. ***J. Appl. Sci. & Agric.**, 10(5): 196-200, 2015*

INTRODUCTION

Energy is a very crucial for human to maintain their life. The world currently relies heavily on fossil fuels for its energy. The combustion of fossil fuels will released the carbon monoxide (CO), carbon dioxide (CO_2), and then will caused acid rain and climate change (Docampo *et al*., 2014). Furthermore, fossil fuels are non-renewable energy, that is they will eventually depleted and becoming too expensive and too environmentally damaging to retrieve. Hence, a renewable energy resource such as solar energy is needed to replace the depleted fossil fuels (Wu *et al*., 2013). Solar energy can be used directly for heating and lighting homes and other buildings, for generating electricity, and for hot water heating, solar cooling, and a variety of commercial and industrial uses.

A device used to convert light energy into electrical energy without produce noise, toxic substance and greenhouse gas emission is known as solar cell (Saunders, 2011, Wu *et al*., 2013). However, solar cell technology comprises of silicon based materials are very expensive to be used as the main energy source for our normal life (Pudaisani and Ayon, 2013). Meanwhile, Lira-Cantu *et al*. (2011) have reported that the power conversion efficiency (PCE) obtained from polymer solar cells is only reached 8% at laboratory scale. Thus, research to find new structures and materials which have to be cheaper, easily processable and with a low environmental impact should be studied. Therefore, third generation of solar cells comprises of organic solar cell (OSC), dye-sensitized solar cell (DSSC) and hybrid solar cell (HSC) have been studied in order to realizing efficient and low cost photovoltaic devices. Lo *et al*. (2013) have reported that organic solar cells based on conjugated polymer-fullerene composites with the PCE up to 9 % have been achieved. Meanwhile, Nik Aziz *et al*. (2014) have reported that dye-sensitized solar cell (DSSC) has achieved up to 10 % of PCE and has an interesting

Corresponding Author: Salmah binti Mohd Ghazali, Universiti Malaysia Terengganu, School of Ocean Engineering, 21030 Kuala Terengganu.
Tel: 6017-9166023; E-mail: salma_3011@yahoo.com

low cost alternative to conventional solar cell (Snaith *et al*., 2007). However, due to low carrier mobilities and poor stability (Hardien *et al*., 2012) of the active layers in OSC and DSSC, HSC has attracted a great deal of attention towards the next generation of solar cells. HSC combine the advantages of both organic and inorganic semiconductors (Nik Aziz *et al*., 2014). According to Saunders (2011), hybrid polymer/nanoparticle solar cells are solar cells that have a light harvesting layer composed of semiconducting inorganic nanoparticles and a semiconducting conjugated polymer.

In this paper, hybrid solar cell composed of Nanocrystals anatase Titanium dioxide, NCs TiO_2 and poly (3-hexylthiophene) (P3HT) and natural dyes have been studied. Typically, nanocrystalline titanium dioxide (TiO_2), is the most promising material due to its chemical stability, easy control of size and shape, proper band gap, and low cost. According to Hossain *et al*. (2011), TiO_2 is an important material in the construction of DSSC, because of its suitable energy band position, and high photoelectric response as a porous photoelectrode material of DSSC. Moreover, TiO_2 is highly attractive as a photovoltaic material because it has been used as a photocatalyst (Ou and Lo, 2007, Rego *et al*., 2009) and is an n-type electrode in DSSC (Diebold, 2003, Kwon *et al*., 2004). Meanwhile, P3HT is a p-type semiconductor polymer and has high hole mobility (10^{-4}~10^{-2} $cm^2V^{-1}s^{-1}$) (Balis *et al*., 2010). P3HT is one of the most promising conducting polymers, easy synthesis through chemical or electrochemical processes, low cost, good environmental stability (Seyler *et al*., 2013), soluble polythiophene derivatives and better electroconductivity than other conducting polymer (Basel *et al*., 2014). It is usually used as an electron donor in polymer solar cells (Wu *et al*., 2008) and the application of P3HT is to modify the TiO_2 substrate by bonding through the S-end atom (Lira-Cantu *et al*., 2011). Instead of developing an efficient and low cost photovoltaic device, the objective of solar cell development also is to harvest as much as possible of the solar spectrum (Saunders, 2011). Hence, sensitizers from natural dyes were used to absorb over a broad range of light spectrum. Recently, research has focused on the easily available dyes extracted from natural sources and as a photosensitizer because of its large absorption coefficient, low cost, easy preparation and environment friendliness (Kim *et al*., 2013). Thus, *Piper Betle Linn*'s leaves were used as natural dyes in this research. The molecular structure of anatase stucture of NCs TiO_2, poly (3-hexylthiophene) and chlorophyll from natural dyes are shown in Fig. 1.

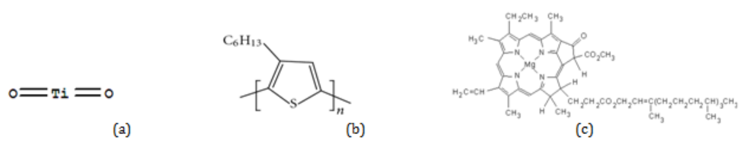

Fig. 1: The Molecular Structure of (a) Anatase Structure of NCs TiO_2 (b) Repeating Unit of Poly (3-hexylthiophene) (c) Chlorophyll.

1. *Methodology:*

1.1 *Preparation of Natural Dye Sensitizers:*

Samples of *Piper Betle Linn*'s leaves were collected in Perak, Malaysia. The *Piper Betle Linn*'s leaves were washed with water and vacuum dried at temperature of 60 °C. After that, the leaves were crushed into fine powder by using a mortar. 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*. (2011).

1.2 *Fabrication of Hybrid Solar Cells:*

The hybrid solar cells were fabricated accordingly bi-layer using electrochemical 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 hair dryer and place in a clean petri dish [Hasiah *et al*., 2014, Nik Aziz *et al*., 2014). Electrochemical Impedance Spectroscopy (EIS) was employed to deposit NCs TiO_2, P3HT and also natural dyes on ITO coated glass substrates. The scan numbers of NCs TiO_2 is varied by 1, 3 and 5 and the scan numbers of P3HT and natural dyes are fixed to 5 numbers of scans. The fabrication of thin film hybrid photovoltaic cell is shown in Fig. 2.

1.3 *Measurements:*

The absorption spectra of the photo-electrodes were recorded by a UV/VIS spectrophotometer (Perkin Elmer, Lambda 25) in a range 200 nm to 900

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nm. Meanwhile, the chemical structure of *Piper Betle Linn* dye solution was examined by FTIR technique (Model NICOLET 380 FT-IR). The two point probes (MU SCS-4200-Keithley) was used to measure the current, when voltage was applied from reverse to forward bias, then the efficiency percentage of the hybrid solar cell was calculated. The measurement of I-V curve was recorded under exposing with 100 Wm^{-2} of light intensity. The efficiency of the hybrid solar cell was calculated by using Eq. 1 and 2. Input power, P_{in} is defined as multiplication of incident ray intensity (100 Wm^{-2}) with effective surface area (4.0 x 10^4 m^2) of the hybrid solar cell. Effective surface area means the surface area of solar cell that exposed to the light radiation. Meanwhile, the fill factor, FF of the hybrid solar cells were calculated by using Eq. 3 as shown below. I_{sc} is the short circuit current and V_{oc} is the open circuit voltage calculated by referring to the I-V graph.

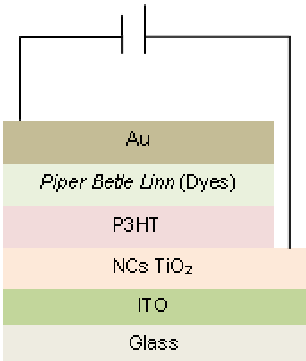

Fig. 2: The diagram of hybrid solar cell.

2. Results:

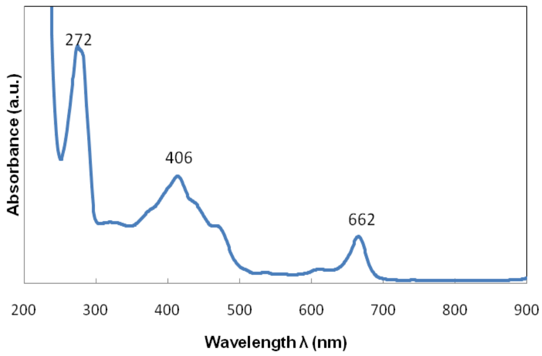

Fig. 3: UV-vis absorption spectrum of *Piper Betle Linn* in ethanol solution.

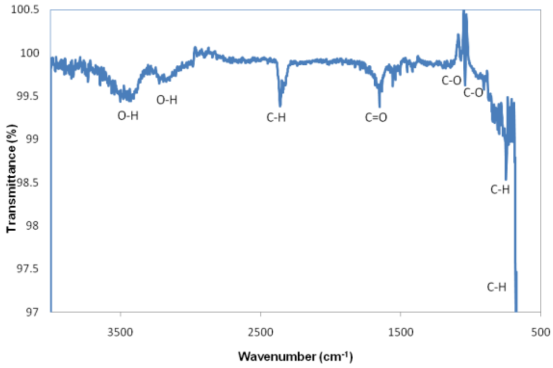

Fig. 4: FTIR spectra of *Piper Betle Linn* dye solution.

Table 1: The power conversion efficiencies of the hybrid solar cells.

	Power	Open	Short circuit	Fill factor, FF	Power

Sample	maximum, P_{max} (Watt)	Circuit Volatge, V_{oc} (V)	current, I_{sc} (A)		conversion efficiency (%)
ITO/TiO_2(1)/P3HT/Piper Betle Linn	3.51×10^{-6}	40×10^{-3}	211.2322×10^{-6}	415.4197×10^{-3}	8.78×10^{-3}
ITO/TiO_2(3)/P3HT/Piper Betle Linn	3.85×10^{-6}	40×10^{-3}	211.3711×10^{-6}	455.3603×10^{-3}	9.63×10^{-3}
ITO/TiO_2(5)/P3HT/Piper Betle Linn	3.12×10^{-6}	40×10^{-3}	211.0991×10^{-6}	369.4947×10^{-3}	7.80×10^{-3}

3. Discussion:

3.1 Absorption of Natural Dyes:

Fig. 3 shows the representative UV-vis absorption spectra for the ethanol extracts of *Piper betle Linn*'s leaves. The ethanol extracts of *Piper Betle Linn*'s leaves exhibit three absorption peak at 272 nm, 406 nm and 662 nm. These absorption ascribes to their identical components, namely as chlorophyll. The chlorophyll is used as the absorber of the light (Hasiah *et al.*, 2014). Furthermore, Calogero *et al.* (2014) stated that an efficient sensitizer should absorb light over a wide range from the visible to the near-infrared (400 nm-700 nm) and, the energy of its electronic excited state should lie energetically above the conduction band (CB) edge of the NCs TiO_2. These three parts of the absorption spectrum enhancing the absorption of energy thus increase the efficiency of hybrid solar cells.

3.2 Chemical Structure of Natural Dyes:

The chlorophyll extracted from the *Piper Betle Linn* leaves using ethanol was confirmed by FTIR spectroscopy. Fig. 4 shows the FTIR spectra of the chlorophyll. The peak at 678.9 cm^{-1} is assigned to the cis-disubtituted alkenes, C-H. The peak at a wavenumber of 751.4 cm^{-1} corresponding to C-H bend,ortho aromatic ring. The spectral region between 1043-1071.3 cm^{-1} corresponds to C-O alkoxy group. In addition, the peak at 1652 cm^{-1} can be correlated with the C=O stretching carbonyl group. Furthermore, the peak at 2361.4 cm^{-1} corresponds to the C-H, alkanes group. Moreover, at peak 3176.7 cm^{-1} show that the present of O-H stretching of alcohols group. Last but not least, the peak 3424.2 cm^{-1} of wavenumber corresponds to the O-H stretching vibration. The performance of hybrid solar cell is affected by many factors. Firstly, the dye structure must possess several carbonyl (C=O) or hydroxyl (-OH) group capable of complexion to the Ti (IV) sites on the TiO_2 surface. This in fact explains why dyes from grapes are not good sensitizer, while the California blackberries (*Rubus ursinus*) are excellent source of dye for sensitization (Khalil, 2012). Thus, the present of carbonyl and hydroxyl groups in *Piper Betle Linn* responsible for the good sensitizer of this hybrid solar cell. Besides that, the thickness of each layers of the hyrid solar cells also affected the efficiency of solar cell.

3.3 Efficiency of Hybrid Solar Cells:

The efficiencies of the hybrid solar cells are shown in Table 1. The highest efficiency of the ITO/TiO_2 /P3HT/*Piper Betle Linn/*Au hybrid solar cell was 0.00963 % obtained with the 3 numbers scans of TiO_2. As can be seen in Table 1, the efficiency is also affected by the number of scans of NCs TiO_2 where 3 number scans of NCs TiO_2 offer the highest efficiency meanwhile 1 and 5 number scans of NCs TiO_2 only give 0.00878 % and 0.0078 %. We noted that the performances of the device are significantly dependent on the charge transport properties of the nanocrystal 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. We found that the optimum TiO_2 content is at 3 number of scan with the power conversion efficiency of 0.00963 %. 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.

4. Conclusion:

Piper Betle Linn dye obtained from nature is used as sensitizer in this study. The dye extracted from this material contained chlorophyll which can absorbed light spectrum in the range of 258-311 nm, 362-521 nm and 641-702 nm. Furthermore, the combination of NCs TiO_2 anatase structure, P3HT and this nature dyes as well can increase the absorption over a wide range of light spectrum. Thus, increasing the efficiency of the hybrid solar cell. The efficiency of the hybrid solar cell in this study can be significantly affected by the number of scan of NCs TiO_2. We found out that the the power conversion efficiency of 0.00963 % was obtained for 3 number of scans of NCs TiO_2. The optical, morphological and electrical properties will be further study in the next work. Overall, the *Piper Betle Linn* leaves are promising because of their low cost, easy preparation and environmental friendliness.

ACKNOWLEDGEMENT

The authors would like to thank MyBrain15 for MyPhD scholarship and Fundamental Physics Laboratory UMT's staff for facilitating the fund and equipment for the research purposes.

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