Physical Science International Journal
10(2): 1-7, 2016, Article no.PSIJ.25295
ISSN: 2348-0130

SCIENCEDOMAIN *international*
www.sciencedomain.org

Photoelectrochemical Performance of Dye-sensitized Organic Photovoltaic Cells Based on Natural Pigments and Wide-bandgap Nanostructured Semiconductor

Eli Danladi[1*], Ezeoke Jonathan[1], M. S. Ahmad[2], Danladi Ezra[3], S. H. Sarki[4], Ishaya Iliyasu[4] and P. M. Gyuk[2]

[1]Department of Physics, Nigerian Defence Academy, Kaduna, Nigeria.
[2]Department of Physics, Kaduna State University, Kaduna, Nigeria.
[3]Department of Agricultural Science, Kaduna State University, Kaduna, Nigeria.
[4]Department of Science Laboratory Technology, Nuhu Bamali Polytechnic, Zaria, Nigeria.

Authors' contributions

This work was carried out in collaboration between all authors. Author ED designed the study, undertook the experimental work, performed the statistical analysis, wrote the protocol, wrote the first draft of the manuscript and managed part of literature searches. Authors EJ, MSA, DE, SHS, II and PMG managed the analyses of the study and literature searches. All authors read and approved the final manuscript.

Article Information

DOI: 10.9734/PSIJ/2016/25295
Editor(s):
(1) Preeti Singh, Department of Physics, DIT, Greater Noida (U.P.), India.
(2) Stefano Moretti, School of Physics & Astronomy, University of Southampton, UK.
Reviewers:
(1) Anonymous, Technical University of Cluj Napoca, Romania.
(2) A. Ayeshamariam, Khadir Mohideen College, India.
(3) Mohamed Nazar Ibrahim, Benghazi University, Libya.
Complete Peer review History: http://sciencedomain.org/review-history/14100

Original Research Article

Received 26th February 2016
Accepted 1st April 2016
Published 9th April 2016

ABSTRACT

Four natural dyes, extracted from natural materials such as flowers, and leaves, were used as sensitizers to fabricate dye-sensitized solar cells (DSSCs). The photoelectrochemical performances of the DSSCs based on these dyes show that the open circuit voltages (V_{OC}) varies from 0.433 to 0.470 V, and the short circuit photocurrent densities (J_{SC}) ranges from 0.044 to 0.138 mAcm^{-2}, the fill factors (*FF*) and the cell efficiencies (η) also vary from 0.400 to 0.570 and 0.021 to 0.065%,

**Corresponding author: E-mail: danladielibako@gmail.com;*

respectively. The DSSC sensitized with *Hibiscus sabdariffa* flowers extract was found to be superior to those obtained from other dyes. The DSSC gave a J_{SC} of 0.138 mAcm^{-2}, V_{OC} of 0.470 V, *FF* of 0.504, and η of 0.065%. The sensitization performance related to interaction between the dye and TiO_2 surface is discussed.

Keywords: Natural pigments; DSSCs; photoelectrochemical performance; TiO_2.

1. INTRODUCTION

At present, the main method of utilization of solar energy is the conversion of solar energy into other energy sources. In 1954 the silicon solar cell developed by Bell marks that human can make solar energy converts into electrical energy for use, is epoch-making significance [1]. However, it is not suitable for large-scale usage, since this type of cell has the more stringent requirements for raw materials and production process. Although the subsequent development of polysilicon and amorphous silicon solar cells is relatively simple in production process, high prices still can't meet the large-scale use.

In 1991, Professor Grätzel reported a new low-cost chemical solar cell by the successful combination of nanostructured electrodes and efficient charge injection dyes, known as Grätzel cells or dye-sensitized solar cells which gave a photoelectric conversion efficiency of 7% under simulated sunlight irradiation [2]. It was designed to imitate photosynthesis; the natural processes plants convert sunlight into energy by sensitizing a nanocrystalline TiO_2 film using novel ruthenium (Ru) bipyridl complex. In dye sensitized solar cell, charge separation is accomplished by kinetics competition like in photosynthesis leading to photovoltaic action. The organic dye monolayer in the photoelectrochemical or dye sensitized solar cell replaces light absorbing pigments (chlorophylls), the wide bandgap nanostructured semiconductor layer replaces oxidized dihydro-nicotinamideadenine-dinucleotide phosphate (NADPH), and carbon dioxide acts as the electron acceptor. Moreover, the electrolyte replaces the water while oxygen as the electron donor and oxidation product, respectively [3,4]. It has been shown that DSSCs are promising class of low cost and moderate efficiency solar cells based on organic materials [5,6,7]. The DSSC promises extremely cheap photovoltaic energy production by combining the advantages of none vacuum processing, extremely low costs components, low embodied energy of production, potentially high efficiencies and superior performance compared to silicon solar cells under diffuse light conditions.

Never the less, the technology still suffers from a number of technical challenges that has hindered large-scale deployment, notably, difficulty in scale-up, low efficiencies and stability. Advances in the synthesis of materials and experimental tools have led to an improvement of more than 12% [8]. Because of the simple production process, much lower cost relative to silicon cells, this type of cells provides a feasible approach for large-scale utilization of solar energy [9].

Natural dyes have become a viable alternative to expensive and rare organic sensitizers because of its low cost, easy attainability and abundance in supply in the environment. Various components of a plant such as the flower petals, leaves and bark have been tested as sensitizers. The nature of these pigments together with other parameters has resulted in varying performances.

In this study pigments from *Bougainvillea spectabilis (B S)* flowers*, mangifera indica* leaves known as mango *(M L), Hibiscus sabdariffa (H S)* flowers commonly known as Roselle*,* and *Ocimum gratissimum* commonly known as Scent Leaves *(S L),* were extracted and used as sensitizers. The results from the sensitization performance shows that, the DSSC sensitized with the extract of H S outperformed the other DSSCs sensitized with other natural dyes in this paper. All the photoelectrochemical performances were measured and characterized for all the above sensitizers.

1.1 Principles and Operation of DSSCs

Dye-sensitized solar cells are prepared in a sandwich arrangement and are comprised of two electrodes: the photoanode and the counter-electrode, Fig. 1 [10]. The photoanode is a conducting glass covered by a mesoporous and nanocrystalline TiO_2 film, sensitized by the dye-sensitizers. The counter electrode is a conducting glass covered by a thin film of catalyst, such as platinum or graphite. Between these electrodes is placed a mediator layer, usually a solution of I^{3-}/I^- in nitriles.

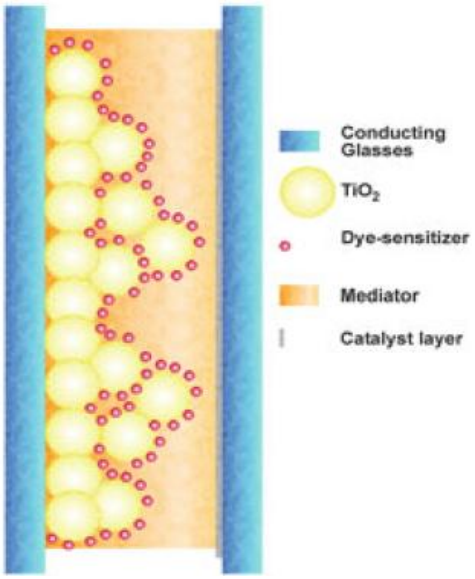

Fig. 1. Schematic arrangement of a dyesensitized solar cell

In order to promote the energy conversion, the sunlight is harvested by the dye-sensitizers leading to an excited-state capable of injecting an electron into the semiconductor conducting band. The oxidized dye is immediately regenerated by the mediator and the injected electron percolates through the semiconductor film, reaches the conducting glass and flows by the external circuit to the counter electrode. The counter electrode is responsible for regenerating the oxidized specie of the mediator, reducing it by a catalyzed reaction using electrons from the external circuit. Since there is not a permanent chemical change for dye-sensitized solar cells, the estimated lifetime of these devices is 20 years [11].

2. EXPERIMENTAL SECTION

2.1 Natural Dyes Extraction

Fresh leaves of (*Mangifera Indica* and *Ocimum gratissimum*), and flowers of (*Bougamvillea spectabillis,* and *Hibiscus sabdariffa*) were collected. The collected leaves of *Mangifera Indica, Ocimum gratissimum* and the flower of *Bougamvillea* were grinded to small particles using a blender with 100 ml deionized water each as extracting solvent. The solution was filtered to separate the solid from the pure liquid. Also the collected flowers of the *Hibiscus sabdariffa* were air dried in a shade to prevent pigment degradation till they became invariant in weight. The dried flowers of *Hibiscus sabdariffa* were left uncrushed because previous attempts proved failure to extract the dye from crushed samples [12]. The method of heating in water was used to extract the dye. Distilled water was the solvent for aqueous extraction. 5 g of the *Hibiscus sabdariffa* sample was measured using analytical scale balance and dipped in 50 ml of the solvent heated to 100ºC for 30 min after which solid residues were filtered out to obtain clear dye solutions.

2.2 Preparation of TiO_2 Paste

The TiO_2 films was prepared using a modified sol–gel method, in which 2 g of P25 TiO_2 powder was dissolved in 10 ml of deionized water mixed with 0.2 mol of Triton-X 100 and 0.4 g of acetaldehyde, then vibrated ultrasonically for 24 hours.

2.3 DSSCs Assembly

All the materials were first cleaned and rinsed with distilled water and dried. The photoanode was prepared by first depositing a blocking layer on the FTO glass (solaronix), followed by the nanocrystalline TiO_2. The blocking layer was deposited from a 2.5 wt % TiO_2 precursor and was applied to the FTO glass substrate by spin coating and subsequently sintered at 400ºC for 30 mins. The nanocrystalline TiO_2 layer was deposited by screen printing. It was then sintered in air for 30 mins at 500ºC. The counter electrode was prepared by screen printing a platinum catalyst gel coating onto the FTO glass. It was then dried at 100ºC and fired at 400ºC for 30 mins. The sintered photoanode was sensitized by immersion in the sensitizer solution at room temperature overnight. Sensitization was achieved by immersing the photoanode in the extracts. The cells were assembled by pressing the photoanode against the platinum-coated counter electrodes slightly offset to each other to enable electrical connection to the conductive side of the electrodes. Between the electrodes, a 50 μ m space was retained using two layers of a thermostat hot melt sealing foil. Sealing was done by keeping the structure in a hot-pressed at 100ºC for 1 min. the liquid electrolyte constituted by 50 mmol of tri-iodide/iodide in acetonitrile was introduced by capillary action into the cell gap through a channel previously fabricated at opposite sides of the hot melt adhesive, the channel was then sealed.

2.4 Characterization

The current-voltage (*J-V*) data was obtained using a keithley 2400 source meter under AM1.5 (100 mw/cm^2) illumination from a Newport A solar simulator. The film morphology was obtained by scanning electron microscope (Phenom Pro X model, Eindhoven de Netherlands). The absorption spectrum of the dyes were recorded on Ava-spec-2048 spectrophotometer in the region of 350–700 nm. The cell active area was 0.5 cm^2. Thickness measurement was obtained with a Dektac 150 surface profiler. X-ray microanalysis was carried out with INCA EDX analyzer.

3. RESULTS AND DISCUSSION

Fig. 2 shows the representative UV–vis absorption spectra for the aqueous extracts of H S, B S, S L, and M L. The extracts of H S exhibits an absorption peak of 550 nm. This absorption is attributed to the presence of anthocyanins. The chemical adsorption of these dyes is accepted to occur because of the formation of bond with the surface of nanostructured TiO_2. In the extract of *Bougainvillea spectabilis* [Fig. 2 (B S)] the absorption peak was found around 370 nm, which can be associated to the presence of indicaxanthin, and betacyanin pigment.

The extract of *Mangifera indica* leaves and *Ocimum gratissimum* [Fig. 2 (M L) and (S L)] shows absorption peaks at 360 nm and 390 nm.

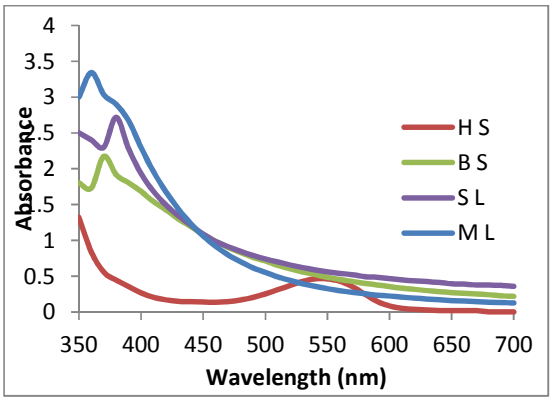

Fig. 2. Shows the UV–vis spectra of H S, B S, S L, and M L extracts

Fig. 5 presents the Energy Dispersive X-ray Image of TiO_2. The elements present in the TiO_2 are Titania, Oxygen and Nitrogen. Nitrogen is present due to the blower that was used to dry the TiO_2 semiconductor.

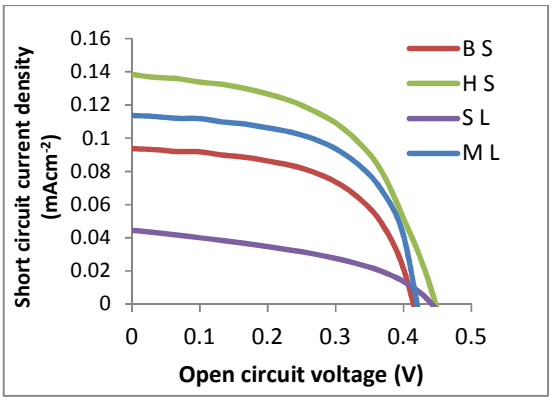

Fig. 3. The photocurrent density–voltage (*J –V*) curves with different natural pigment

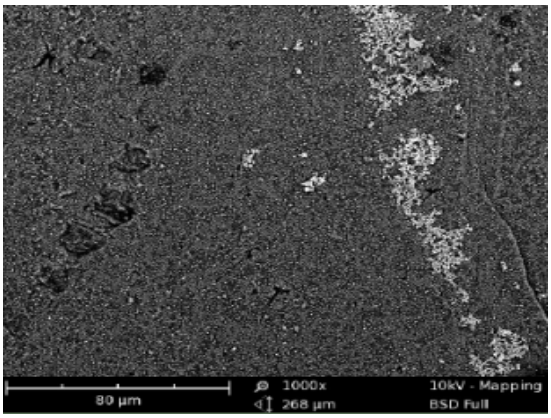

Fig. 4. The scanning electron microscope surface morphology of TiO_2 sample

Fig. 4 shows the SEM micrograph morphology of TiO_2 film. From the figure, it shows that the TiO_2 nanoparticles produced have a mean particle size of about 15 nm. It also reveals that the surface of the TiO_2 is porous

The typical *J–V* curves of the DSSCs using the sensitizers extracted from mango leaves, *Bougainvillea* flowers, scent leaves and *Hibiscus sabdariffa* flowers are shown in Fig. 3.

Based on the *J-V* curve, the *fill factor* (*FF*) which measures the ideality of the device, and the *solar cell efficiency* (η) were determined using equations (1) and (2) [13] respectively.

$$FF = \frac{P_{\max}}{P_{in}} = \frac{J_{\max} \times V_{\max}}{J_{SC} \times V_{OC}} \quad (1)$$

$$\eta = \frac{FF \times J_{SC} \times V_{OC}}{P_{IRRADIANCE}} .100\,\% \quad (2)$$

Where

V_{max} = maximum voltage (V);
J_{max} = maximum current density (mA/cm^2);
J_{sc} = short circuit current density (mA/cm^2);
V_{oc} = open circuit voltage (V) and
$P_{IRRADIANCE}$ = light intensity (mW/cm^2)

Photovoltaic test of DSSCs using these natural dyes as sensitizers are summarized in Table 1. From the effective area of 0.5 cm^2 the performance of the natural dyes as sensitizers in DSSCs were evaluated by short circuit current density (J_{SC}), open circuit voltage (V_{OC}), fill factor (*FF*), and energy conversion efficiency (η).

As displayed in Table 1 and Fig. 3, the fill factors of these DSSCs varies from 0.400 to 0.570. The V_{OC} varies from 0.433 to 0.470 V, and the *Jsc* changes from 0.044 to 0.138 mAcm^{-2}. Specifically, a high V_{OC} (0.470 V) and J_{SC} (0.138 mAcm^{-2}) were obtained from the DSSC sensitized by the *Hibiscus sabdariffa* extract; the efficiency of the DSSC reached 0.065 %. These data are significantly higher than those of the DSSCs sensitized by other natural dyes in this work. This is due to broader absorption range of the sensitizers, higher interaction between TiO_2 nanocrystaline film and the pigment extracted from *Hibiscus sabdariffa* which leads to a better charge transfer [14].

It was once reported that DSSCs based on anodes containing *Hibiscus sabdariffa* and *Bougainvillea spectabilis* extracts showed photoelectrochemical perfomances of (J_{SC}= 0.23 mAcm^{-2}, V_{OC}= 0.44 V, *FF*= 0.49 and η= 0.07 %) [12] and (J_{SC}= 0.088 mAcm^{-2}, V_{OC}= 0.2 V, *FF*= 0.374 and η = 0.0066 %) [14]. When compared to our results with H S extract sensitized DSSC, it is in agreement with Mphande and Pogrebnoi [12], and Eli et al. [15] and when compared to Yirga et al. [14], a 5.7% improvement in shortcircuit current density of the B S extract sensitized DSSC was observed. The differences in the *Hibiscus Sabdariffa* DSSC might be attributed to the differences in concentrations of phytoconstituents in different parts of the plant [16], and the differences in the *Bougainvillea Spectabillis* sensitized DSSC was due to the extracting solvent (water for our studies and ethanol in their research).

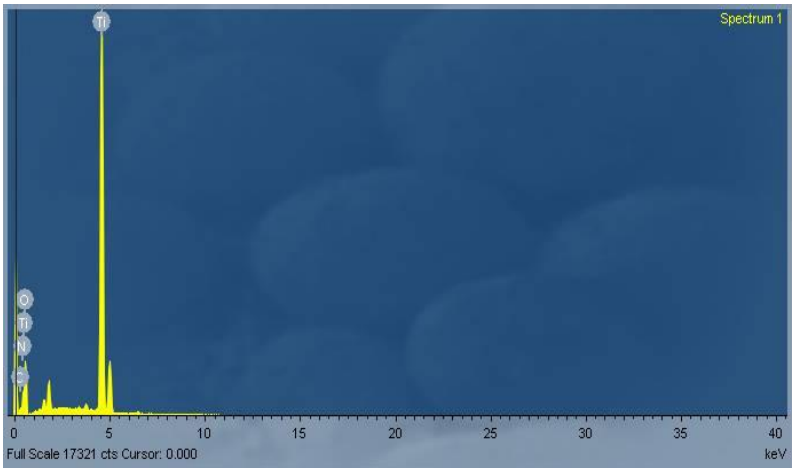

Fig. 5. EDX Image showing the elements present in the TiO_2 compound

Table 1. Photovoltaic performance of DSSCs with different sensitizers under 100 mWcm^{-2}

Sample	J_{sc}(mAcm^{-2})	V_{oc}(V)	FF	η (%)
H S	0.138	0.470	0.504	0.065
S L	0.044	0.466	0.400	0.021
M L	0.114	0.433	0.570	0.049
B S	0.093	0.433	0.550	0.040

The low conversion efficiency observed with DSSC sensitized with extract of *Ocimum gratissimum* was due to the presence of aggregated dyes or non-injecting dyes at the surface of the TiO_2 that leads to small solar to electricity conversion efficiency [17]. This is because there are no available bonds between the dye and TiO_2 molecules through which electrons can transport from the excited dye molecules to the TiO_2 film [18]. This result indicates that the interaction between the sensitizer and the TiO_2 film is significant in enhancing the energy conversion efficiency of DSSCs

4. CONCLUSIONS

Four dyes obtained from nature, including flowers, and leaves of plants were used as sensitizers in the formed DSSCs. The photoelectrochemical performances of the DSSCs based on these dyes show that the V_{OC} ranged from 0.433 to 0.470 V, and J_{SC} was in the range of 0.044 to 0.138 $mAcm^{-2}$. The DSSC sensitized by *Hibiscus sabdariffa* extract offered the highest conversion efficiency of 0.065 % among the four extracts. The results obtained are encouraging and should prompt more detailed studies to uncover the exact mechanism involved.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

REFERENCES

1. Chapin DM, Fuller CS, Pearson GL. A new silicon p-n junction photocell for converting solar radiation into electrical power. J. Appl. Phys. 1954;25:676.
2. O'Regan B, Grätzel M. A low-cost, high-efficiency solar cell based on dye-sensitized colloidal TiO2 films. Nature. 1991;353:737-740.
3. Lagref JJ, Nazeeruddin MK, Graetzel M. Artificial photosynthesis based on dyesensitized nanocrystalline TiO2 solar cells. Inorganica Chimica Acta. 2008; 361(3):735-745.
4. Smestad GP, Gratzel M. Demonstrating electron transfer and nanotechnology: A natural dye-sensitized nanocrystalline energy converter. Journal of Chemical Education. 1998;75(6):752-756.
5. Hara K, Arakawa H. Dye-sensitized Solar Cells, In: Handbook of photovoltaic science and engineering. Luque A, Hegedus S, (Ed.), John Wiley & Sons, Ltd, ISBN: 0-471-49196-9. 2003;Chapter 15:663-700.
6. Hagfeldt A, Gratzel M. Light-induced redox reactions in nanocrystalline systems Chem. Rev. 1995;95:49-68.
7. Haruna Isah, Danladi Eli, Gyuk PM. Development of organic dye sensitized solar cell incorporated with TiO_2 nanostructures with low conversion efficiency for exploring solar energy concepts. International Journal of Optoelectronic Engineering. 2015;5(1): 16-19.
   DOI: 10.5923/j.ijoe.20150501.03
8. Yella A, Lee HW, Tsao HN, Yi C, Chandiran AK, Nazeeruddin MK, Diau EWG, Yeh CY, Zakeeruddin SM, Grätzel M. Porphyrin-sensitized solar cells with cobalt (II/III)-based redox electrolyte exceed 12 percent efficiency. Science. 2011;334:629-634.
9. Hagfeldt A, Boschloo G, Sun L, Kloo L, Pettersson H. Dye sensitized solar cells. Chem. Rev. 2010;110:6595-6663.
10. Juliana dos Santos de Souza, Leilane Oliveira Martins de Andrade and André Sarto Polo. Nanomaterials for Solar Energy Conversion: Dye-Sensitized Solar Cells Based on Ruthenium (II) Tris-Heteroleptic Compounds or Natural Dyes. de Souza FL, Leite ER, (eds.). Nanoenergy. Springer-Verlag Berlin Heidelberg. 2013;49-80.
    DOI: 10.1007/978-3-642-31736-1_2
11. Grätzel M. Photoelectrochemical cells. Nature. 2001;414(6861):338–344.
12. Barness Chirazo Mphande, Alexander Pogrebnoi. Outdoor photoelectrochemical characterization of dyes from *Acalypha wilkesiana 'Haleakala'* and *Hibiscus sabdariffa* as dye solar cells sensitizers. British Journal of Applied Science & Technology. 2015;7(2):195-204.
13. Danladi Eli, Onimisi MY, Abdu SG, Gyuk PM, Ezeoke Jonathan. Enhanced performance of a dye sensitized solar cell using silver nanoparticles modified photoanode. Journal of Scientific Research & Reports. 2016;10(4):1-8.
14. Getachew Yirga, Sisay Tadesse, Teketel Yohannes. Photoelectrochmeical cell based on natural pigments and ZnO nanoparticles. Journal of Energy and Natural Resources. 2016;5(1):1-10.
    DOI: 10.11648/j.jenr.20160501.11

15. Danladi Eli, Onimisi MY, Abdu SG, Ezeoke Jonathan, Yakubu SO. Photoelectric characterization of a dye-sensitized solar cell based on natural pigment extracted from Roselle (*Hibiscus sabdariffa*) flower and TiO_2 nanoparticles. British Journal of Applied Science & Technology. 2016; 15(2):1-6.
16. Danladi Eli, Muhammad Ahmad, Idodo Maxwell, Danladi Ezra, Aungwa Francis, Sunday Sarki. Dye sensitized solar cells using natural dyes extracted from Roselle (*Hibiscus sabdariffa*) flowers and Pawpaw (*Carica papaya*) leaves as sensitizers. Journal of Energy and Natural Resources. 2016;5(1):11-15.
DOI: 10.11648/j.jenr.20160501.12
17. Qifeng Z, Christopher S, Xiaoyuan Z. ZnO nanostructures for dye-sensitized solar cells. Adv. Mater. 2009;21(41):4087–4108.
18. Hao S, Wu J, Huang Y, Lin J. Natural dyes as photosensitizers for dye-sensitized solar cell. Sol. Energy. 2006;80:209–214.

Peer-review history:
The peer review history for this paper can be accessed here:
http://sciencedomain.org/review-history/14100