Dye Sensitized Solar Cell (DSSC) by Using a Natural Pigment from Microalga

A. Orona-Navar, I. Aguilar-Hernández, T. López-Luke, Adriana Pacheco, and N. Ornelas-Soto

Abstract—Photovoltaic devices such as dye sensitized solar cells (DSSC), are an interesting alternative source of renewable energy because they convert solar radiation into electric current. In these solar cells, the use of natural pigments as sensitizers represents complete biodegradation, simple preparation technique, low cost, non-toxic pigments, high reduction of use of noble metals and cost of chemical synthesis. A natural pigment obtained from the microalga Scenedesmus obliquus was tested as sensitizer of a DSSC. The absorption characteristics and the photoelectrochemical parameters were studied to determine the photoconversion efficiency of the cell sensitized with this pigment. The sensitization was carried out by the pipetting technique and the photovoltaic efficiency was obtained under standard conditions under 1 sun illumination (AM 1.5G at 100mW/cm²). The dye-sensitized solar cell was assembled as a sandwich scheme, where the photodeode faced the platinum counter electrode and an iodide electrolyte solution was between them. The energy conversion efficiency reached was 0.064%, the fill factor 69.3%, open circuit voltage 0.502 V and short-circuit photocurrent density 0.185 mA cm⁻². According to these results, the extract obtained from the microalga Scenedesmus obliquus shows promise as a sensitizer for solar cells.

Index Terms—Dye-sensitized solar cells, natural pigments, photoelectrochemical parameters, energy conversion efficiency.

I. INTRODUCTION

It is known that the sun can potentially provide energy to satisfy a percentage of the global energetic needs. Solar energy is considered clean and free, making it a suitable form of achieving a sustainable development. Photovoltaic technology allows the conversion of sunlight into electricity. In photovoltaic devices, the electrons are excited by photons from their valence band to the higher energy conduction band to finally be collected and transported to an external circuit [1]. Derived from this technology, the first-generation solar cells are based on mono crystalline silicon. This requires complicated fabrication process and is not environmentally convenient due to the generation of significant amounts of toxic by-products [2], [3]. However, these cells have the highest conversion efficiency reaching up to 24% [4]. The second generation of photovoltaic cells are based on thin films of amorphous semiconductors such as amorphous silicon (a-Si), cadmium telluride (CdTe), copper indium gallium selenite (CIGS) and recently crystalline silicon [5]. The efficiency in these cells is increased due to thin layers of semiconductors deposited, but the methods and process involved in the manufacturing increase the cost as well. Despite this, the efficiency in silicon-based solar cells is greater [1]. On the other hand, third generation photovoltaic cells are focused in optimizing the efficiency and decreasing the production cost. Dye sensitized solar cells (DSSC), heterojunctions cell, polymer solar cells, quantum dot cells and hot carrier cells belong to this generation of photovoltaic technology [6]. DSSC have attracted a lot of interest since Grätzel and his coworkers developed a low-cost solar cell based on crystalline semiconductor sensitized by synthetic or natural dyes. These cells have the potential to simplify fabrication processes and high conversion efficiency [7]-[9]. The main natural pigments used in solar cells are chlorophylls, carotenoids, betalains and anthocyanins [10] which are obtained from flowers, leaves, roots and recently from some microorganism such as micro and macroalgae and some bacteria [11], [12]. The extraction process is relatively simple and less expensive compared to synthetic dyes. Natural dyes as photosensitizers in DSSC also present strong advantages like a relative abundance, complete biodegradation and environmental friendliness [13].

Microalgae have received great attention because of their capability to produce photosynthetic pigments like chlorophylls and carotenoids with higher efficiency than terrestrial plants [7]. Also, they can be produced at large scale. Using all bioproducts produced by microalgae, these are considered as a source of renewable energy production. Besides pigments, microalgae also synthesize carbohydrates and lipids that can be used to produce bioethanol, biohydrogen and biodiesel [14]. On the other hand, the use photosynthetic pigments extracted from microalgae as sensitizers in solar cells could be effective and an interesting research topic. There is a wide range of efficiencies obtained with algae extracts, but the use of extracts from microalgae has not been comprehensively studied. The aim of this work was to test chlorophyll pigment as sensitizer in a dye sensitized solar cell. The use of chlorophylls extracted from the microalga Scenedesmus obliquus to the extent of our knowledge were tested for the first time as sensitizers in DSSC. The photoconversion data of the sensitization of the cell was analyzed.

II. EXPERIMENTAL SECTION

A. Reagents

Scenedesmus obliquus strain was obtained from the...
Culture Collection of Algae at The University of Texas at Austin (UTEX). TiO\textsubscript{2} paste WER2-O reflector and TiO\textsubscript{2} paste DSL 18NR-T were obtained from DYESOL (Queanbeyan, Australia). Fluorine doped Tin Oxide (FTO) glass (TEC 15) (3×3×2.2 mm) was obtained from MTI Corporation. Methanol, lithium iodide, iodine, 1-methyl-3-propylimidazodium iodide, acetonitrile anhydrous, valeronitrile, isopropanol and chloroplatinic acid hexahydrate were purchased from Sigma Aldrich.

B. Photosynthetic Pigment Extraction

The chlorophyll extract (Chl) was obtained from Scenedesmus obliquus microalgae. For extraction, 4 mg of lyophilized microalgae biomass was sucked in 10 ml of methanol. Then the lyophilized microalgae biomass in methanol was centrifuged at 4500 rpm for 10 min at 4°C. This was repeated three times. It was then sonicated for 2 h and left overnight with gentle shaking in the dark. Finally, the biomass without color was removed and the methanol with green color is recovered. The concentration of chlorophylls was determined using the UV-Vis spectroscopy method reported by H. Lichtenthaler and Buschmann [15]. Also, the UV-Vis absorption spectrum (250-750nm) of the extract solution was measured using an Agilent Technologies spectrophotometer (Cary 5000).

C. Preparation of Photoelectrode, Counter Electrode and Electrolyte

The preparation of the TiO\textsubscript{2} photoelectrode was carried out by depositing a layer of titanium isopropoxide solution and two layers of TiO\textsubscript{2} pastes as indicated in previous works [12] with some modifications. The substrate used for the fabrication of the photoelectrodes was tin oxide doped with fluoride (FTO) which was forst washed with a large amount of water and soap and then with a solution of isopropanol:acetylacetone 1:1 (v/v) for 30 min in an ultrasonic bath. Then it was exposed 15 min to UV light. On the FTO, first a compact layer of titanium (IV) isopropoxide was deposited in the same manner. Finally, the substrate was calcined at 500°C for 30 min.

On the other hand, a solution of hexachloroplatinic acid in isopropanol 10mM was deposited on a FTO glass to fabricate the counter electrode. It was calcined 30 min at 500°C. The electrolyte used was a redox couple containing I\textsubscript{3}I\textsubscript{-}. The solution consisted of 1-methyl-3-propylimidazodium iodide 0.6M, I\textsubscript{2} 0.05M, LiI 0.05M dissolved in Acetonitrile:Valeronitrile 85:15 (v/v).

D. Dye Sensitized Solar Cell Sensitization

Sensitization of the photoelectrodes was carried out by means of the pipetting technique depositing 200μl of the chlorophyll solution on TiO\textsubscript{2} semiconductor at room temperature. This method was similar as mentioned in Esparza et al. methodology [16]. The UV-Vis absorption spectrum (350-800nm) of the sensitized cell and of a cell without sensitizer (untreated) were measured using an Agilent Technologies spectrophotometer (Cary 5000).

E. Photoelectric Characterization of DSSC

To measure the photoelectric conversion efficiency, the cells with an active area of 0.19 cm\textsuperscript{2} were placed under a solar simulator (Oriel Sol 3A) with power of 100 mW cm\textsuperscript{-2}. A Reference 600 potentiostat (Gamry) was also used. The photoelectric conversion efficiency was determined as indicates equation (1):

\[
\eta \, (\%) = \frac{FF \times J_{sc} \times V_{oc}}{P_{inc}}
\]  

where \(J_{sc}\) is the short-circuit photocurrent density (mA cm\textsuperscript{-2}), \(V_{oc}\) is the open circuit voltage (V), \(P_{inc}\) is the intensity of the incident light (W cm\textsuperscript{-2}), and FF is the fill factor calculated as follows in equation (2):

\[
FF \, (\%) = \frac{J_{max} \times V_{max}}{J_{sc} \times V_{oc}} \times 100
\]  

\(J_{max}\) and \(V_{max}\) were extracted from maximum current and voltage of J-V curve data.

III. RESULTS AND DISCUSSION

A. Preparation and Characterization of the Extract

Concentration of chlorophyll \(a\) in the microalgae extract was determined according to the protocol reported by H. Lichtenthaler and Buschmann [15] using the data of the UV-Vis absorption spectrum in the following equation (3):

\[
Ca \left( \frac{\mu g}{ml} \right) = 16.72A_{665.2} - 9.16A_{656.4}
\]  

The concentration obtained was 1.54 μg/ml.

Fig. 1 shows the UV-Vis absorption spectrum of chlorophyll extract (Chl) dissolved in methanol. The maximum absorption observed was at the wavelength of 404 and 666 nm.
**B. Dye Sensitized Solar Cell Characterization**

Fig. 2 shows the spectrum of the cell sensitized with the chlorophyll extract as well as the cell without sensitization (untreated). There are differences between the cell without sensitizing and the sensitized cells, which demonstrates the addition of molecules of pigments to the TiO$_2$ semiconductor. Also, when the extract interacts with TiO$_2$, some changes occur in the absorption spectrum of chlorophyll. Its absorption band becomes wider and red shifted.

![Absorption spectrum UV-vis](image)

Fig. 2. Absorption spectrum UV-vis of cell sensitized with Chl compared with an untreated cell (TiO$_2$).

**C. Photoelectrochemical Parameters**

Fig. 3 shows the J-V curves of the cells sensitized with Chl as well as the untreated cell. The measurements were made by assembling the cells as a sandwich with the platinum counter electrode and placing the electrolyte between the two electrodes. The incident power in the cells was a singlet sunlight (100mW cm$^{-2}$) over the active area (0.196 cm$^2$).

From the J-V curves the values of photovoltage ($V_{oc}$) and photocurrent densities ($J_{sc}$) were obtained. These values together with the maximum power output ($P_{max}$) determine the fill factor (FF) and the photoconversion efficiency (PCE). These values are shown in Table I.

![J-V curve](image)

Fig. 3. Curve I-V of cell sensitized with Chlorophyll (Chl) compared with an untreated cell (TiO$_2$).

The open circuit voltage ($V_{oc}$) results from the difference between the TiO$_2$ conduction band edge and the redox potential of the electrolyte, and the photocurrent generated by irradiation in the cell per unit area is represented by the short-circuit photocurrent density ($J_{sc}$) [4].

With the cell without sensitization, the following was obtained: $J_{sc}$ of 0.037mA cm$^{-2}$, $V_{oc}$ of 0.33 V, 48% of FF and 0.006% of photocurrent efficiency. The efficiency reached using the chlorophyll extract was 0.064%, a fill factor of 69.3%, open circuit voltage of 0.502 V and short circuit current density of 0.185 mA cm$^{-2}$. With the sensitized cell the values of these parameters increase, which indicates that the pigments used benefits the photoconversion efficiency. This efficiency falls within the range of reported efficiencies between 0.001% and 0.9% by other authors for microalgae chlorophyll extracts [7], [17].

**IV. Conclusions**

A novel pigment extracted from the microalgae Scenedesmus obliquus (Chl) was tested as individual sensitizer in solar cells. A photoconversion efficiency of 0.064% was obtained with this chlorophyll extract. This might be attributed to the broader absorption spectra in the visible range of 404 and 666 nm. This natural pigment extracted from a microalga strain resulted promising as sensitizer in dye sensitized solar since its present advantages over those extracted from higher plants such as large-scale production, and their intense photosynthetic properties, their low cost, simple extraction methods and eco-friendliness.

It is considered of great importance as future work to study the interaction effect between chlorophylls obtained from Scenedesmus obliquus mixed with natural dye systems as sensitizers with the aim to increase the photoconversion efficiency in the cell.

**REFERENCES**

[1] M. A. M. Al-alwani, A. Bakar, N. A. Ludin, A. Amir, H. Kadhum, and K. Sopian, “Dye-sensitised solar cells: Development, structure, operation principles, electron kinetics, characterisation, synthesis materials and natural photosensitisers,” Renew. Sustain. Energy Rev., vol. 65, pp. 183-213, Jul. 2016.

[2] A. Belfar and R. Mostefaoui, “Simulation of n1-p2 microcrystalline silicon tunnel junction with AMPS-1D a-Si/µ c-Si:H tandem solar cells,” J. Appl. Sci., vol. 11, no. 16, pp. 2932-2939, Jul. 2011.

[3] A. Yassin, F. Yebesi, and R. Tingle, “Occupational exposure to crystalline silica dust in the united states , 1988-2003,” Environ Health Perspect., vol. 113, no. 3, pp. 255-260, Dec. 2004.

[4] G. Calogero, A. Bartolotta, D. Marco, D. Carlo, and F. Bonacorso, “Vegetable-based dye-sensitized solar cells,” Chem. Soc. Rev., vol. 44, pp. 3244-3294, Sep. 2014.

[5] N. A. Ludin et al., “Review on the development of natural dye photosensitizer for dye-sensitized solar cells,” Renew. Sustain. Energy Rev., vol. 31, pp. 386-396, Jan. 2014.

**TABLE I: PHOTOELECTROCHEMICAL PARAMETERS OF DSSC AND NON-SENSITIZED CELL.**

| Cell configuration | Short circuit current density (mA cm$^{-2}$) | Open circuit voltage (V) | Fill factor (%) | Efficiency (%) |
|--------------------|---------------------------------------------|--------------------------|----------------|---------------|
| TiO$_2$ untreated   | 0.037                                       | 0.33                      | 48             | 0.006         |
| TiO$_2$/Chl         | 0.185                                       | 0.502                     | 69.3           | 0.064         |
Q. Fu, C. Zhao, S. Yang, and J. Wu, “The photoelectric performance of dye-sensitized solar cells,” Renew. Sustain. Energy Rev., vol. 78, pp. 301-317, April 2017.

R. Mohammadpour, S. Janfaza, and F. Abbaspour-Aghdam, “Light harvesting and photocurrent generation by nanostructured photoelectrodes sensitized with a photosynthetic pigment: A new application for microalgae,” Biosens. Bioelectron., vol. 163, pp. 1-5, Jul. 2014.

S. A. Taya, T. El-Agez, H. El-Ghamri, and M. Abdel-Latif, “Dye-sensitized solar cells using fresh and dried natural dyes,” Int. J. Mater. Sci. Appl., vol. 2, no. 2, pp. 37-42, March 2013.

H. Hug, M. Bader, P. Mair, and T. Glatzel, “Biophotovoltaics: Natural pigments in dye-sensitized solar cells,” Appl. Energy, vol. 115, pp. 216-225, Feb. 2014.

M. R. Narayan, “Review: Dye sensitized solar cells based on natural photosensitizers,” Renew. Sustain. Energy Rev., vol. 16, no. 1, pp. 208-215, Sep. 2011.

Q. Fu, C. Zhao, S. Yang, and J. Wu, “The photoelectric performance of dye-sensitized solar cells fabricated by assembling pigment – Protein complexes of purple bacteria on nanocrystalline photoelectrode,” Mater. Lett., vol. 129, pp. 195-197, May 2014.

A. Orona-navar, I. Aguilar-hernández, A. Cerdán-pasarán, and T. López-luke, “Astaxanthin from Haematococcus pluvialis as a natural photosensitizer for dye-sensitized solar cell,” Algal Res., vol. 26, pp. 15-24, Jul. 2017.

S. Shalini, R. B. Prabhu, S. Prasanna, T. K. Mallick, and S. Senthilarasu, “Review on natural dye sensitized solar cells: Operation, materials and methods,” Renew. Sustain. Energy Rev., vol. 51, pp. 1306-1325, Nov. 2015.

A. Bahadar and M. B. Khan, “Progress in energy from microalgae: A review,” Renew. Sustain. Energy Rev., vol. 27, pp. 128-148, Jul. 2013.

H. K. Lichtenthaler and C. Buschmann, “Chlorophylls and carotenoids: Measurement and characterization by UV-VIS spectroscopy,” Curr. Protoc. Food Anal. Chemistry, p. F4.3.1-F4.3.8, 2001.

D. Esparza et al., “Effect of different sensitization technique on the photoconversion efficiency of CdS quantum dot and CdSe quantum rod sensitized TiO2 solar cells,” J. Phys. Chem. C, vol. 119, no. 24, pp. 13394-13403, Jun. 2015.

Z. Nurachman et al., “Tropical marine Chlorella sp. PP1 as a source of photosynthetic pigments for dye-sensitized solar cells,” Algal Res., vol. 10, pp. 25-32, Jul. 2015.