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

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/cm^2). The dye-sensitized solar cell was assembled as a sandwich scheme, where the photoelectrode 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 its 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

Manuscript received August 3, 2019; revised October 30, 2019. This work was supported in part by Consejo Nacional de Ciencia y Tecnología through grants # PN-2016/4320 and INFR294694.

A. Orona-Navar, I. Aguilar-Hernández, Adriana Pacheco, and N. Ornelas-Soto are with Escuela de Ingeniería y Ciencias of Tecnológico de Monterrey, Ave. Eugenio Garza Sada 2501, Monterrey, N.L., 64849, Mexico (e-mail: angelica_orona@hotmail.com, iaguilarh@itesm.mx, adrianap@itesm.mx, ornel@itesm.mx)

T. López-Luke is with Centro de Investigaciones en Óptica, León, Gto., 37150, Mexico (e-mail: tzarara@cio.mx)

doi: 10.18178/ijcea.2020.11.1.772

Culture Collection of Algae at The University of Texas at Austin (UTEX). TiO_2 paste WER2-O reflector and TiO_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 ℃. 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_2 photoelectrode was carried out by depositing a layer of titanium isopropoxide solution and two layers of TiO_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 in ethanol and acetylacetone solution was deposited at 450 ℃ by the spray pyrolysis technique. Then the FTO was calcined at 500 ℃ for 30 min. After that, two TiO_2 pastes were deposited on the substrate in the following way: the transparent layer of TiO_2 (TiO_2 paste WER2-0 reflector from DYESOL) was deposited by screen printing. Next the TiO_2 dispersing layer (TiO_2 paste DSL 18NR-T from DYESOL) was deposited in the same manner. Finally, the substrate was calcined at 500 ℃ 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 ℃. The electrolyte used was a redox couple containing I^-/I_3^-. The solution consisted of 1-methyl-3-propylimidazodio iodide 0.6M, I_2 0.05M, LiI 0.05M dissolved in Acetronitrile: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_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^2 were placed under a solar simulator (Oriel Sol 3A) with power of 100 mW cm^{-2}. A Reference 600 potentiostat (Gamry) was also used. The photoelectric conversion efficiency was determined as indicates equation (1):

$$\eta\ (\%) = \frac{FF\ x\ J_{sc}\ x\ V_{oc}}{P_{inc}} \tag{1}$$

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

$$FF\ (\%) = \frac{J_{max}\ x\ V_{max}}{J_{sc}\ x\ V_{oc}}\ x\ 100 \tag{2}$$

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):

$$Ca\left(\frac{\mu g}{ml}\right) = 16.72A_{665.2} - 9.16A_{656.4} \tag{3}$$

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.

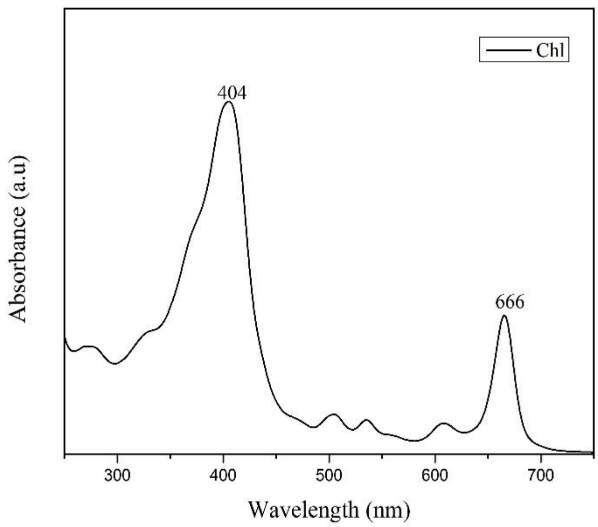

Fig. 1. Absorption spectrum Uv-vis of Chlorophyll (Chl) solution.

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.

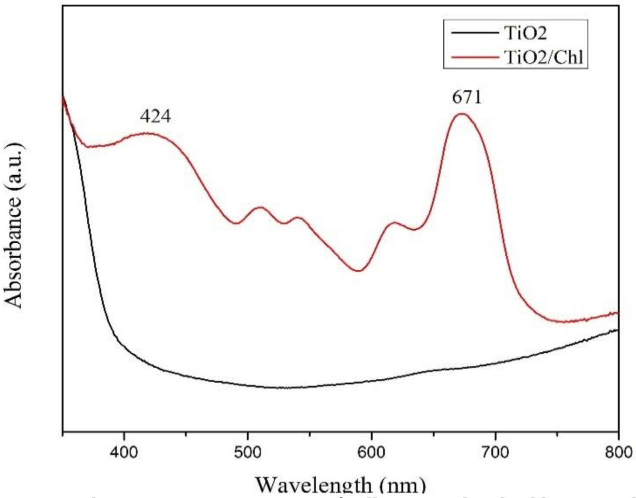

Fig. 2. Absorption spectrum Uv-vis of cell sensitized with Chl compared with an untreated cell (TiO_2).

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_{max}) and photocurrent densities (J_{max}) 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.

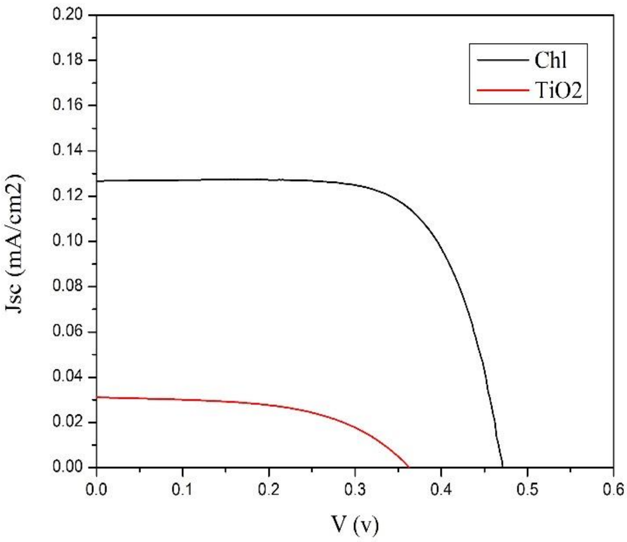

Fig. 3. Curve I-V of cell sensitized with Chlorophyll (Chl) compared with an untreated cell (TiO_2).

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

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/µc-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. Bonaccorso, "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.

[6] N. T. R. N. Kumara, A. Lim, C. Ming, and M. Iskandar, "Recent progress and utilization of natural pigments in dye sensitized solar cells: A review," *Renew. Sustain. Energy Rev.*, vol. 78, pp. 301-317, April 2017.
[7] 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," *Bioresour. Technol.*, vol. 163, pp. 1-5, Jul. 2014.
[8] S. A. Taya, T. El-Agez, H. El-Ghamri, and M. Abdel-Larif, "Dye-sensitized solar cells using fresh and dried natural dyes," *Int. J. Mater. Sci. Appl.*, vol. 2, no. 2, pp. 37-42, March 2013.
[9] 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.
[10] 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.
[11] 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.
[12] 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.
[13] 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.
[14] A. Bahadar and M. B. Khan, "Progress in energy from microalgae: A review," *Renew. Sustain. Energy Rev.*, vol. 27, pp. 128-148, Jul. 2013.
[15] H. K. Lichtenthaler and C. Buschmann, "Chlorophylls and carotenoids: Measurement and characterization by UV-VIS spectroscopy," *Curr. Protoc. Food Anal. Chemestry*, p. F4.3.1-F4.3.8, 2001.
[16] D. Esparza *et al.*, "Effect of different sensitization technique on the photoconversion efficiency of CdS quantum dot and CdSe quantum rod sensitized TiO_2 solar cells," *J. Phys. Chem. C*, vol. 119, no. 24, pp. 13394-13403, Jun. 2015.
[17] 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.

Angelica Orona Navar received the B.S. degree in biochemical engineering from Instituto Tecnologico de Durango in 2015. She is student of the master's degree in engineering sciences at the Tecnologico de Monterrey. Her research activities include environmental chemistry and solar energy applications.

Iris Aguilar Hernandez received the B.S. degree in biotechnology engineering, the master's degree in environmental systems, with focus on sustainable water use and the PhD degree in engineering sciences all from Tecnologico de Monterrey, in 2001, 2013 and 2017, respectively. She worked with the synthesis of nanomaterials for environmental applications (water and energy), as well as the analysis of biological models. She has specialized in material characterization techniques such as: Raman spectroscopy, diffuse reflectance spectroscopy, microscopy and physisorption.

Tzarara Lopez Luke received the B.S. degree in physics and mathematics at UMSNH, Morelia, México, the master's degree in metallurgy and materials science at IIM-UMSNH and the PhD degree in metallurgy and materials science at IIM-UMSNH and CIO, in 1998, 2004 and 2008, respectively. From 2011 to 2012, she was visiting researcher in the Department of Chemistry and Biochemistry University of California Santa Cruz (UCSC), USA.

She is a member of the National Researchers Council of Mexico, currently as SNI Level 2. Her research activities include Synthesis of luminescent metal oxides and no luminescent, novel semiconductor and metals nanoparticles with special structures and morphologies, nanophotonics applications, solar energy conversion, hydrogen generation and storage; cancer biomarker detection and glucose detection.

Adriana Pacheco obtained her bachelor's degree in forestry from the Technological Institute of Costa Rica (Cartago, Costa Rica) in 1999. In 2001, she obtained a M.Sc. degree in biology at the University of Costa Rica (San José, Costa Rica), and in 2006 she completed her doctoral studies in environmental engineering sciences at the University of Florida (Gainesville, FL, USA), where she worked in bioremediation of chlorinated compounds by methanotrophic bacteria. In the latter, she did a one-year postdoctoral position at the Department of Microbiology and Cell Sciences (University of Florida), working with coenzyme biosynthesis in methanogenic archaea and methylotrophic bacteria.

In January 2008, Adriana Pacheco joined the Department of Biotechnology and Food Engineering at Tecnologico de Monterrey (Monterrey campus) as an assistant professor.

As a full-time research professor, Dr. Pacheco has conducted research in CO_2 capture by microalgae as a promising mitigation strategy for greenhouse gases. Her research group possesses a collection of environmental microalgae that have been acclimated to high CO_2 atmospheres and it is now studying their transcriptome to elucidate their adaptation strategy. She also works in metagenomic characterization of microbial consortia of environmental interest as for biogas production and plant-microbe beneficial interactions. In 2014 she was promoted to associate research professor. Dr. Pacheco is a member of the National Researchers Council of Mexico, currently as SNI Level 1.

Nancy Ornelas Soto received the B.S. degree in Chemistry and the PhD degree in chemical sciences both from Universidad de Guanajuato, in 2002 and 2008, respectively. From 2011 to 2012, she was visiting researcher in the research group of *Applied Biospectroscopy* of the Nofima Mat in Norway.

In 2013, Nancy Ornelas joined the Water Center for Latin America and Caribbean at Tecnologico de Monterrey, where she was appointed professor and researcher. Moreover, she is leader of the research group in environmental nanotechnology. She is member of the Mexican Research National System since 2010. Her research activities include (1) advanced spectroscopic characterization methods such as SERS, polarized raman spectroscopy and imaging spectroscopy; (2) synthesis of nanostructured photocatalysts/biocatalysts and their application in the transformation of persistent organic pollutants; and (3) development of surface plasmon resonance-based sensors for detection of emerging pollutants in the environment and biological materials. She has authored about 30 scientific JCR papers on environmental assessment and spectroscopy characterization in the last 5 years.