GRÄTZEL TYPE-SOLAR CELLS SENSITIZED WITH SOME COLOMBIAN'S DYES.

CELDAS SOLARES TIPO GRÄTZEL SENSIBILIZADAS CON COLORANTES COLOMBIANOS

Eduardo Perez*, Kiara Montalvo*, María Acuña*, Tomás Rada* , Florian Buchholz**

ABSTRACT

Perez, E., K. Montalvo, M. Acuña, T. Rada, F Buchholz. Grätzel type-solar cells sensitized with some Colombian's dyes. Rev. Acad. Colomb. Cienc., 37 (1): 36-39, 2013. ISSN 0370-3908.

In the present work we want to show some progress related to the effects of two colombian´s natural dyes in the sensitized solar cells (Grätzel type). The dyes used are achiote and blackberry, which are used to develop a photochemical process that mimics photosynthesis. The use of sensitizers in conjunction with nanocrystalline oxide semiconductor films (TiO_2) permits to increase the absorption of sunlight. Raman spectroscopy technique has been used to characterize the achiote. They show that the samples have a strong fluorescence in the range between 640 and 800 nm, and this fluorescence is very sensitive to the laser power. After the construction of the solar cells, the efficiencies determined are around 0.13%, in the best of our cases.

Key words: Dye-sensitized solar cells; Nanocrystalline oxide semiconductor films; titanium dioxide TiO_2. Bixa Arellana

RESUMEN

En el presente trabajo se muestran algunos logros relacionados con los efectos de dos colorantes naturales colombiano en las celdas solares tipo Grätzel. Los colorantes usados son achiote y mora de castilla, los cuales son usados para desarrollar un proceso fotoquímico que asemeja la fotosíntesis. El uso de estos sensibilizadores en unión con películas nanocristalinas de un óxido semiconductor (TiO_2) permite incrementar la absorción de luz solar. La técnica de espectroscopía Raman se ha usado para caracterizar el achiote. En los espectros se observa que las muestras tienen una fuerte fluorescencia en el rango entre 640 y 800 nm, la cual es muy sensible a la potencia del laser. Después de construidas las celdas solares, la eficiencia obtenida está alrededor de 0,13% en el mejor de nuestros casos hasta ahora.

Palabras claves: Celdas solares Sensibilizadas por colorantes; Películas de óxido semiconductor nanocristalinas; TiO_2. Achiote

* Grupo de Investigación en Física Aplicada, Universidad del Norte, Barranquilla, Colombia. Email: trada@uninorte.edu.co

* Technische Universität Berlin, Berlin, Germany

1. Introduction

Chemists and physicists have been interested for long time in the harnessing of sunlight to convert the light directly into electrical energy. A seminal work driven by **B. O'Reagan** and **M. Graetzel,** 1991 [1] showed that the application of dye molecules harvest the sunlight, with an additional interesting feature which is the low-cost. The study of this type of solar cells in Colombia has an important role because of two main aspects; one is Colombia's location near the equator with a high solar radiation throughout the entire year and second for the diversity of fruits and plants that we have here.

Typically, Dye Sensitized Solar Cell (DSSC) devices consist of two substrates of glass that are coated with a thin conductive layer (in this investigation it was used glass with fluorine-doped tin oxide (FTO)) that serve as basis for the electrodes. On the anode a layer of the mesoporous semiconductor is applied (nanoparticles of titania-oxide, TiO_2) and on the cathode (or counter electrode) a layer of a catalytic conductor (in this case carbon). In between the electrodes the sensitizing dye and a solution with a redox couple (in this case iodide/triiodide) is positioned. Two dyes were used: Achiote (*Bixa orellana*) and Blackberry (*Rubus glaucus or mora de castilla*) with several concentrations in ethanol and water.

For maximal power output a solar cell is operated at the so called maximum power point (P_{MPP}). The efficiency η of the solar cell is defined by the following equation (1):

$$\eta=P_{MPP}/P_{in}=(U_{MPP}*I_{MPP})/P_{in} \qquad (1)$$

Where P_{in} is the solar power input into the solar cell (SC) and U_{MPP} and I_{MPP} are voltage and current at maximum power point. For detecting the MPP (maximum power point) it is necessary to measure a so called IV-curve that is the graph of current as a function of voltage and calculate the product of both values. In order to have a main idea of the quality of the cells and also for deeper knowledge about other parameters of a cell, the open-circuit voltage and short-circuit current are important parameters. They are connected with P_{MMP} through the following equation (2):.

$$P_{MPP}=U_{MPP}*I_{MPP}=U_{OC}*I_{SC}*FF \qquad (2)$$

Where FF is the so called fill factor, which is defined as the ratio of $U_{MPP}*I_{MPP} / U_{OC}*I_{SC}$.

2. Samples preparation

Two native dyes were used: Achiote and Blackberry. The dye of Achiote needs to be extracted from the shell of the seeds, thus it is not possible to just crush them. We did it in two different ways without noticeable differences in the results. First we took 10 g of fresh seeds in 10 ml of ethanol and stirred for about 20 min until an homogenous color was observed. Then it was heated up until powder was extracted and ethanol evaporated. Next we mixed 1g of Achiote powder with 10 ml of ethanol. The second way was to mix 10 g of Achiote with 10 ml (1:1 proportion or 50% for us) or 10 g of Achiote with 20 ml of ethanol (1:2 proportion or 25% for us), then we stirred for 20 min and finally we filtered the mixture to get rid of many solid particles. The fresh blackberries were smashed without water (100%) and 20 g mixed with 20 ml of water (1:1 proportion or 50%). We explore other proportions but good results came only from the previously mentioned.

As support for electrical contact in the SC, glass with a tin film of FTO was used both at the photoanode and the counter electrode. The glasses pieces are of approximately 2 x 2 cm^2, the counter electrodes had to be drilled two times for the injection of electrolyte. All pieces were cleaned through the following procedure: Primary each piece was wiped carefully with a soft sponge using tapped water, then rinsed with deionzed water and stored in a bath of deionzed water until the fat-free glasses were put in an ultrasonic bath of ethanol for some minutes to get rid of the last contaminating particles.

For the photoanode, a ready to use paste of semiconducting nanocrystalline TiO_2 from Solaronix (Ti-Nanoxide D) was used in conjunction with Dr Blade technique for layers depositions. Working areas were of 1x1 cm^2 or 0.5 x 0.5 cm^2 for smaller active areas. It is important to mention that the deposition of titania on the transparent conducting oxide (TCO) glasses is the most important part of the production process because the homogeneity of the layer is crucial for cell efficiencies. Primary masks of 1x1 cm^2 (or 0.5x0.5 cm^2 for smaller active areas) were cut into a stripe of adhesive tape (Scotch 3M Magic # 810) with a stencil. The area of the mask remained uncovered on the conductive layer and the paste was spread across the plate. For multilayers of Titania two or more layers of tape were applied (one layer of tape for up to two layers of Titania). Sintering of every layer occur in a programmable oven up to 450°C and leaving there for 20 to 30 min.

The sensitization of titanium dioxide by natural dyes consists of soaking the titania electrode in mashed fruits or Achiote solution. Complete staining can take from several minutes, for Achiote solution, to several hours for blackberries mixture, while the dye molecules naturally adsorb onto the titania particles. The longer the electrode soaks in the dye, the better dyed the titania will be. To remove the stained electrode we rinse it carefully with water (for Blackberries) or ethanol (for Achiote) and wait a few minutes for the ethanol to evaporate until the resulting stained titania looked homogeneously dyed almost all over its surface. If not, put it back in to the solution for further dyeing.

Properties of solar cell can be determined when it is under homemade 10.9 mW/cm^2 (for most of the cases) halogen illumination and tested using the standard silicon solar cell, as published by **Ali,** 2010 [2].

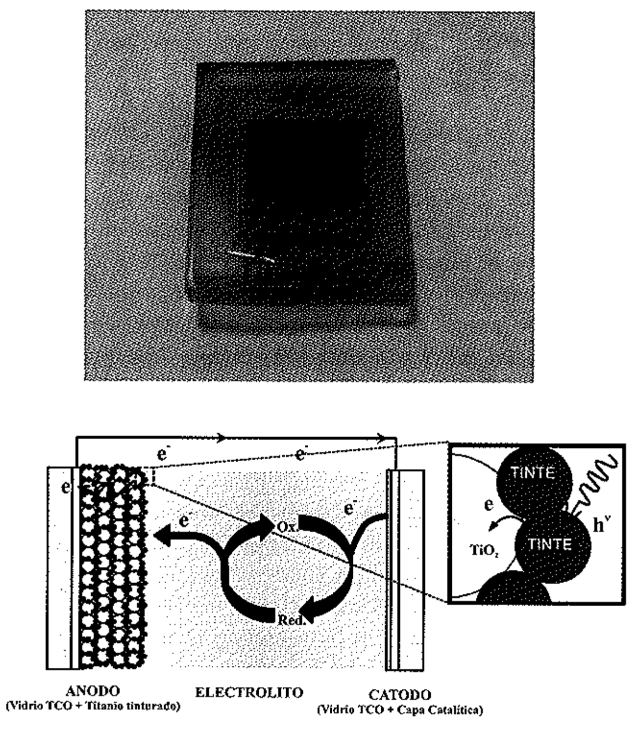

Figure 1. A picture of a full assembled SC in the left. In the right a schematic SC under illumination is showed.

3. Results and discussions

There is little information regarding the physical and chemical properties of Achiote, therefore some Raman measurements were made in order to identify the basic molecule. According to the results the Achiote contains mainly carotene molecule as shown in Fig 2. In addition, the Achiote showed a strong fluorescence in the range from 640 to 800 nm, however this fluorescence is very sensitive to the laser power.

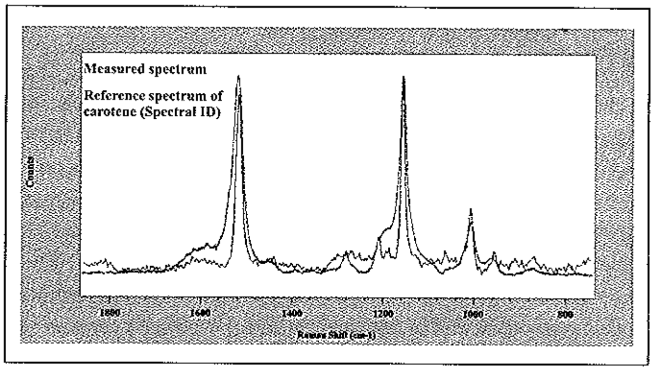

Figure 2. A Raman spectrum of Achiote match with a reference spectrum of carotene. Courtesy of Aphèlie Lancry from HORIBA Jobin Yvon SAS and S&S Ingeniería Colombia.

3.1 Current-voltage measurements

Several variables were explored in our approach to study their effects in the solar cells construction ranging from dye concentration, TiO_2 layer thickness and sizes of active areas. In the table No. 1 we show the effect of layers number on the I-V measurements of the SC using blackberry as sensitizing dye. We considered that good results for the current were obtained using either 4 or 6 layers with size of 1.0 x 1.0 cm^2. However the voltage seems similar regardless the thicknesses of titania layers: all measurements are above 400 mV.

Table 1: Parameters of SC with Blackberry.

Cell N°	Layers	A (cm^2)	UOC (mV)	ISC (μA)
89	2	1,0X1,0	450	47
73	3	0,5X0,5	419	39
84	4	1,0X1,0	440	74
82	5	1,0X1,0	440	14
79	6	1,0X1,0	427	64

For Achiote as sensitizing dye, in table No. 2, we observe that the best results for voltage and current occurs with 6 TiO_2 layers with active area of 1.0x1.0 cm^2. The voltage values are also around 400 mV for any number of layers in our range and the current is increased with layers.

Table 2: Parameters of SC with Achiote

Cell N°	Layers	A (cm^2)	UOC (mV)	ISC (μA)
50	2	1,0x1,0	391	24
88	4	1,0x1,0	454	39
71	6	1,0x1,0	427.1	103.6

3.2 Efficiency

The IV-characteristics curve and the performance values of some of the best cells are demonstrated in Fig. 3 and Tab. 3. The best efficiency of 0.130 % was obtained using Achiote and 6 layers of Titania, despite the very low fill factor of 32%. A calculation of the best cell with smaller area (No.74), with a fill factor of 49,8 % showed a very similar efficiency of 0.118%. These are close to the 0.22% reported by **Ali, R.A.M.& Nayan, N,** 2010.[2] for Dragon Fruit and 0.42% and 0.56% reported by **G. Galogero et al.,** 2012 [3] for Raw Blackberry and Giacchè Grape, respectively.

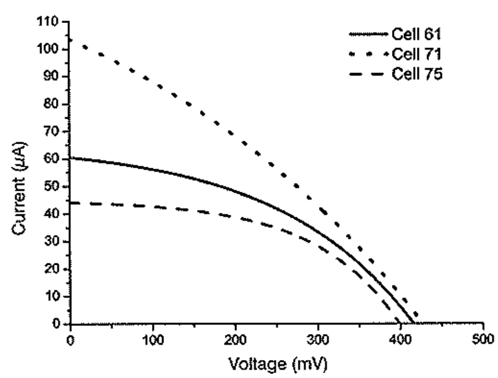

Figure 3. I-V Curves of three different SC under illumination for P_{MPP} calculations.

Table 3: Parameters of SC including the efficiency

No.	61	71	75	74
Dye	BB 50%	Achiote	BB 50 %	BB 50 %
layers	4	6	4	4
A (cm²)	1,0x1,0	1,0x1,0	0,5x0,5	0,5x0,5
J (mW/cm²)	21,6	10,9	10,9	10,9
Uoc (mV)	416,0	427,1	398,8	405
Isc (mA)	60,5	103,6	44,2	64
FF	41,8 %	32,0 %	49,8 %	49,8 %
Efficiency	0,052 %	0,130 %	0,080 %	0,118 %

4. Conclusions

Two Colombian's native fruits, Achiote and Blackberry (also known as Mora de Castilla), are used in the fabrication of DSSC as sensitizers. Both dyes have showed a relatively good efficiency (0.130% and 0.118%) and performance under controlled illumination. Exploring some variables, we have found that the greatest enhancement was achieved by increasing the number of titania layers, through the Dr Blade preparation. In our case 4 layers of TiO_2 for Blackberry and 6 layers of TiO_2 for Achiote are the best semiconductor thickness.

Another important aspect is related to the voltage and current values. In general, voltage values are relatively stables and are around 400 mV, while the current is directly affected by active area and the quality of TiO_2 deposition. We found for Achiote that the 1.0 x1.0 cm² is good size, however for Blackberry a smaller area works better. We can reasonably conclude that reducing the size of the active area improved the efficiency significantly, especially the fill factor.

References

[1] **O'Regan B, and Graetzel M,** 1991, A low–cost, high–efficiency solar cell based on dye- sensitized colloidal TiO2 films, Nature 353, 737

[2] **Ali Ram. and Nayan N,** 2010, Fabrication and analysis of dye-sensitized solar cell using natural dye extracted from dragon fruit, International Journal of Integrated Engineering, 2 55

[3] **Calogero G,** et al. 2012, Anthocyanins and betalains as light-harvesting pigments for dye-sensitized solar cells, Solar Energy 86, 1563