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Fabrication and Characterization of Dye-sensitized Solar Cells Based on Natural Organic Dyes

In this work a prototype of the dye-sensitized solar cell based on a natural organic dye from blackberry was studied. The cell was fabricated using technologies available at Slovak University of Technology. The cell was tested by Keithley 5A Source Meter, Model 2440 and solar simulator: AM 1.5G solar simulator Oriel (Xe 1000 W, 250-1100 nm), class AAA, purchased from European Fund of Regional Development. The characterization of the cell provides I-V characteristics with open circuit voltage of 445.5 mV, short circuit current of 308.94 µA, fill factor of 40.51 %, and efficiency of 0.3345 %. The cell shows slight degradation in performance over time with a drop in the open circuit voltage to 406 mV during 15 minutes.

Keywords: dye-sensitized solar cell, blackberry dye

I. INTRODUCTION

As the storage of a fossil supply is decrescent every year the mankind must look for another source of energy. Even the most powerful source we have now will be depleted some day and there is also a problem with the nuclear waste we must consider. One option is to look for that source in renewable energy technologies such as wind or solar power.

The sun is a primary source of energy for most life forms found on the earth. It is clear, abundant and most of all renewable. Fully grasping the power of the sun we can improve our way of life, reduce our dependence on fossil fuels and stimulate economy by bringing new jobs to the industry.

Every year the use of solar energy technologies is increasing in the world. It provides people with the energy to heat the house (solar thermal energy) or change solar energy right to electricity (photovoltaics) and decrease the dependence on the other sources of power.

Ever since the invention of the silicon solar cell in the 1940s, people have acknowledged the enormous potential of photovoltaic systems for large scale electricity production. However, semiconductor grade silicon wafers are expensive so great effort has been put into developing cheaper thin-film solar cells and modules. Such films may be pure inorganic or contain organic materials as an essential part of the device. As one of the examples are dye-sensitized photoelectrochemical solar cells (DSSC).

In this communication we bring the details on the technology of fabrication such organic light – harvesting systems with the electrical characterization of the solar cells based on organic dyes extracted from fruit tissues.

II. DYE-SENSITIZED SOLAR CELL PRINCIPLES

The first panchromatic film, able to remit image in black and white, followed the work of Vofel in Berlin, in which he used dyes and silver halide grains [1]. However, clear recognition and verification of operating principle dates to 1960s, when Gerisher and Tributsh researched a ZnO photoelectrode sensitized by organic dyes [2, 3]. But these cells had low harvesting efficiencies and low photon to current conversion, because as a photoelectrode they used single crystals and polycrystalline materials. Only after the introduction of mesoporous materials such as TiO_2 and using synthesized dyes the performance of these cells improved. By using porous TiO_2 electrodes with a roughness factor of ca. 1000 Ru based on a synthesized dye and iodine I^-/I_3^- redox couple in an organic solvent that Grätzel and O'Regan reported a solar cell with efficiency of 7 to 10 % [4]. Ever since this discovery there was a continuous approach to improve performance, efficiency and stability of these solar cells.

DSSC consists of dye, nanoporous crystals, e.g. TiO_2 layer, electrolyte solution and two glass slides (electrode and counter electrode) that are coated with transparent conducting oxide.

As mentioned above, support substrate can be glass, although it is possible to use a flexible plastic substrate. The support substrate must be transparent in visible and near UV region because light is coupled into the cell through it. The anode electrode is made of a thin film of a transparent, conducting material, which is deposited on the inner side of the support substrate. For this purpose indium thin oxide (ITO) semiconductor is widely used. Although other semiconductors such as fluorine-doped thin oxide (SnO_2:F) can be used as well (FTO).

The real photoanode is formed by a porous film of nanocrystalline semiconductor (TiO_2). These films are usually few micrometers thick (between 1- 10 µm) and average particle size is 5–25 nm. This film can be fabricated in different ways. The most widely used method for fabrication of thin films is casting slurry of the nanocrystals using spray, or drag coating and then calcine the film at 400 - 450ºC. Thus structural stability can be created. The counter electrode is coated by catalyst, e.g. Pt (Platinum) or carbon to speed up the redox reaction with the electrolyte. The dye molecules are adsorbed on the surface of TiO_2 coated electrode. Between the electrode and the counter electrode a liquid electrolyte is encapsulated.

The dye molecule is excited from ground state by absorption of light photon. This leads to electron being transferred into the conduction band of the semiconductor layer which leaves the dye in an oxidized state. Thus oxidized dye molecule cannot accept another light photon. The oxidized dye is reduced to the ground state by taking in donor electron that is present in iodide/iodine electrolyte. After reaching the FTO/ITO electrode, the electrons pass through an external circuit, thus making external work and arrive at the counter electrode, where they are accepted by electrolyte, catalyzed by platinum and recombine with triiodide into iodide again. Thus conversion of sunlight to electrical energy can be made.

In this paper antocyanine extracted from blackberry was used instead of widely used dyes based on Ru and N3 complexes such as N3, N719 or "black dye", on which one of the highest efficiencies where measured (10.0 % to 11 %) [4, 5]. The structural formula for some N3 based molecules are in Figs. 1 and 2.

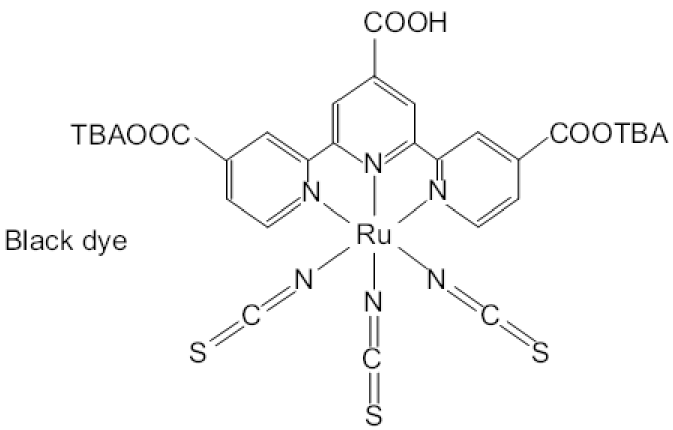

Figure 1 Structural formula of organic dye - “Black dye”.

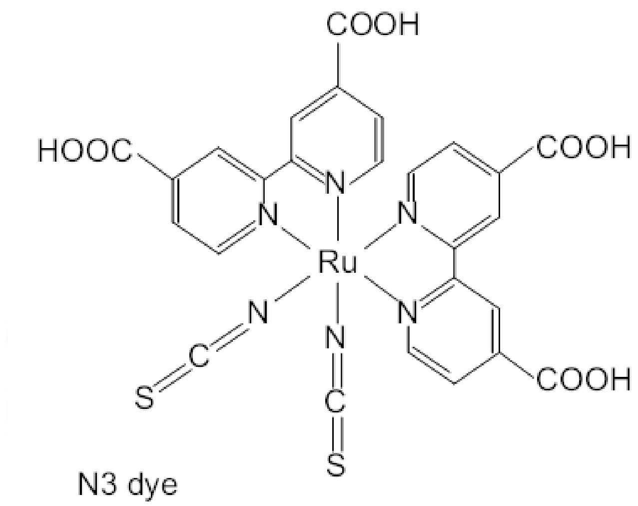

Figure 2 Structural formula of organic dye - N3.

Although DSSC using these dyes can achieve high performance, there is a problem with Ru at the center of the molecule, whose price is very high and such molecules are artificially prepared which raises a cost of the final product even higher. Therefore, we decided to use antochyanine dye, which can be found in nature in abundance. The structure of antochyanine is depicted in Fig. 3.

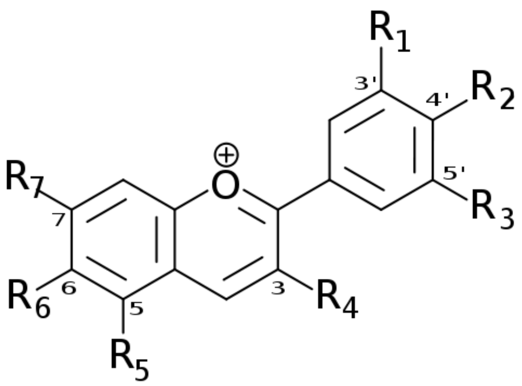

Figure 3 Structural formula of natural organic dye – anthocyanine.

III. MEASUREMENT OF ABSORPTION OF THE DYE

Before preparation of the cell, the absorption of the dye extracted from blackberry was measured. After blending and filtration of the dye from the fruit it was rinsed in ethanol. The absorption spectrum of the prepared solution was measured by UviLine 9100 spectrophotometer in the range between 320 nm and 1100 nm. The absorption spectrum of pure ethanol was recorded as well as that of blackberry dye linked to TiO_2 nanoparticles sintered on glass sheet. All the results were put to chart and are presented in Fig. 4. The absorption maximum of the anthocyanine dye solution extracted from blackberries is 545 nm which is in accordance with literature [6]. The absorption maximum of the linked dye to TiO_2 showed a slight shift to the lower wave lengths with a value of 540 nm.

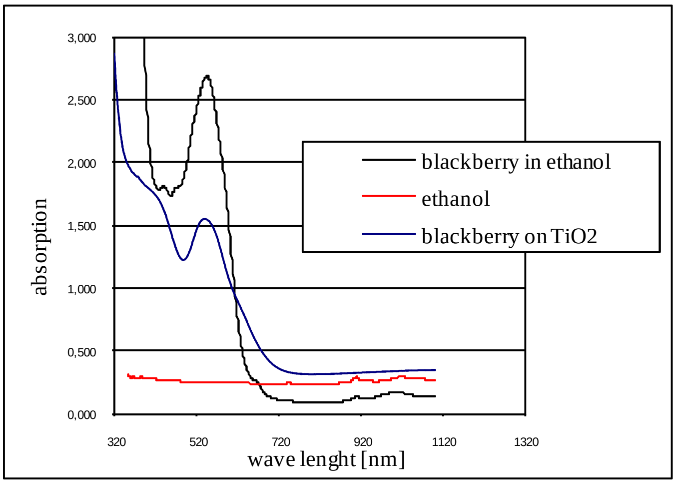

Figure 4 Absorption spectrum of blackberry dye solution in ethanol (black line), pure ethanol (red line) and blackberry dye linked to TiO_2 nanoparticles sintered on glass sheet (blue line).

IV. MATERIALS AND THE FABRICATION OF THE DSSC

Materials used for preparation of DSSC were obtained from SOLARONIX. Titanium paste for preparations of an electrode was Ti-Nanoxide D 20g. As the electrolyte Iodolyte AN 50 was used. For a counter electrode Pt-Catalyst T/SP was used. A conductive glass was also purchased from SOLARONIX – TCO 30-8 5x5cm. As a dye, antocyanine extracted from blackberries was used.

The fabrication of the DSSC followed these steps:

1. Preparation of TiO_2 film
2. Staining of TiO_2 film with dye
3. Pt coating of the counter electrode
4. Assembling process of the cell

Preparation procedure of DSSC film is :

1. First, the TCO glass sheet was gently cleaned with ethanol and paper towel.
2. Deposition area on the conductive side of the glass was defined by using scotch tape 3M. The size of the final open area was 2 cm x 3 cm.
3. Then, 3 or 4 drops of TiO_2 suspension was added onto the deposition area. The suspension was smoothed evenly by using a glass stiring rod. The slide was allowed to dry for approximatelly 5-10 min before removing the tape.

4. After the tape was removed the glass was put on the hot plate and dried of 30 min at 100 ºC. The glass slide was then fried at 450 ºC for other 30 min.
5. After frying, the glass slide was allowed to cool down to room temperature.

The staining process was as followed:

1. First, blackberries were blended in petri dish and filtered through a filter paper.
2. Then, ethanol was added to the juice and poured onto a small shallow dish.
3. Finally, the cool glass slide with TiO_2 was placed in a dish containig the blackberry juice and kept immersed for 30 min.

Pt coating of the counter electrode:

1. Another TCO glass slide was cleaned gently by ethanol and dried with paper towel.
2. Then, an entire surface of the conductive side of the glass was coated by Pt-Catalyst T/SP and fried at 400 ºC.

Assembly process was:

1. The assembly process began with taking the TiO_2 coated glass slide, which was stained in blackberry juice, and putting it face to face with the Pt coated glass slide. The glass was put slightly offset to allow enough room for electrical contacts.
2. After that, both sides were hold together using binder clips and a drop of Iodolite electrolyte was put and one end of the glass. The electrolyte solution penetrated into the cell by capillary effect and stained entire cell. By attaching contacts to both sides of the cell, this was ready for subsequent electrical characterization.

IV. CHARACTERIZATION OF THE DSSC

The performance of a solar cell is defined by several parameters such as short-circuit current I_{sc} and open-circuit voltage V_{oc} obtained under standard illumination conditions (AM 1.5). Fill factor (FF) under standard conditions is a measure of a diode behavior of the cell. It is obtained using a full current-voltage characterization as follows:

$$FF = \frac{P_{max}}{V_{OC} I_{SC}} = \frac{(VI)_{max}}{V_{OC} I_{SC}} \quad (1)$$

The global power conversion efficiency of energy to electricity conversion efficiency (η) of the cell with Pout electrical power under standard illumination conditions is given by:

$$\eta = \frac{P_{out}}{P_{in}} = I_{SC} V_{OC} \frac{FF}{P_{in}} \quad (2)$$

where P_{in} is incident optical power.

The measurements of I-V curves were carried out using Keithley 5A Source Meter, Model 2440. The samples were illuminated by AM 1.5G solar simulator Oriel (Xe 1000 W, 250-1100 nm), class AAA. I - V characteristics of the solar cell are displayed in Fig. 5.

Table 1 shows the parameter values as a function of time after assembling the cell. From values in Table 1 can be seen that parameters of DSSC (V_{oc}, I_{sc}, V_m, I_m, FF and efficiency) are slightly degrading over time; degradation of the efficiency is of exponential character.

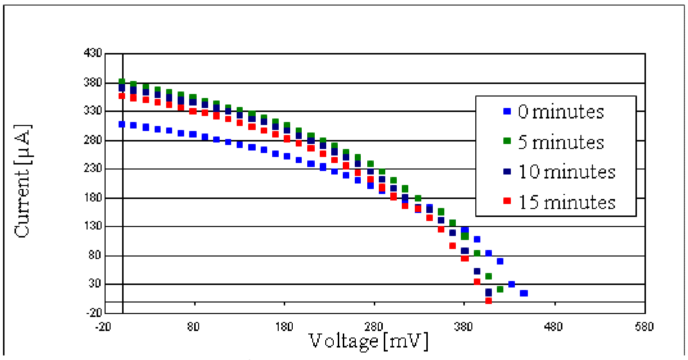

Figure 4 I-V characteristic of the experimental data.

Table 1: Degradation of solar cell's parameters.

time [min]	I_{sc}[μA]	U_{oc}[mV]	I_{max}[μA]	U_{max}[mV]	FF[%]	η [%]
0	308.940	445.5	202.740	275.0	40.51	0.334
5	380.400	419.0	238.800	275.0	41.20	0.262
10	371.520	406.0	238.740	261.5	41.39	0.249
15	358.120	406.0	224.650	261.5	40.40	0.234

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V. CONCLUSION

The absorption spectrum of both the blackberry solutions rinsed in ethanol with maximum at 545 nm and that as linked to TiO_2 nanoparticles sintered on a glass sheet with maximum at 540 nm. Slight shift to the lower wave lengths was observed.

DSSC were successfully fabricated using anthocyanine dye extracted from blackberries. The open circuit voltage of 445.5 mV, short circuit current of 308.94 μA, fill factor of 40.51 % and efficiency of 0.3345 % were evaluated. The cell shows degradation in performance over time of the exponential type with a drop in the open circuit voltage to 406 mV in 15 minutes.

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