Influence of sintering temperature on the performance of titanium dioxide anode in Dye Sensitized Solar Cells with natural pigment hypericin

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***Abstract*—Dye Sensitized Solar cells (DSSC) are very attractive due to their low cost fabricating methods and used materials. One of the most important parts of the cells is the photoanode. Many semiconducting materials are used for this purpose, but most common one is titanium dioxide (TiO_2). Optimal sintering temperature of anode plays important role in performance of TiO_2 layer in DSSC, since it provides good electrical contact between particles, which consequently leads to better electron transfer through the cell, but still restricts unfavorable phase transformation. In this paper two identical cells with natural pigment hypericin as sensitizer were assembled with anodes sintered on two different temperatures (500 °C and 600 °C), so their performance parameters could be compared. The ratios between the maximal power densities (P_{max}) and solar to electrical energy conversion efficiencies (η) for the two measured cells are 5 times in favor for the cell sintered at 600 °C, which shows the importance of temperature treatment of TiO_2 electrodes for better performance of solar cells.**

***Index Terms*— DSSC; TiO_2 anode; sintering temperature; hypericin.**

I. Introduction

Dye-sensitized solar cells (DSSC) are very popular due to a low cost of production materials and methods, compared to silicon-based solar cells. They were first introduced in 1991[1] and since then, their performance has been improving [2-4].

The operating principle of DSSC is very simple, as presented in Fig 1. It is designed to mimic photosynthesis in plants. Incident solar photon oxidizes the sensitizer, which further delivers the electron to conduction band of semiconductor. Dye molecule then gets reduced by electrolyte, and electrolyte is further regenerated at the counter electrode. Most common electrodes for DSSC are TiO_2 for anode, and platinum electrode as counter one. Widely used electrolyte is I^-/I_3^- solution in acetonitrile[5].

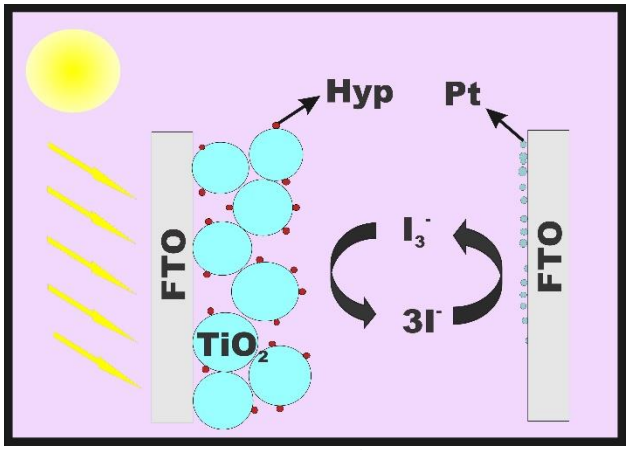

Fig. 1. Schematic representation of DSSC constituent parts

Many types of sensitizers are known and used today: organic, inorganic, synthetic, natural [5]. DSSCs with porphyrin and ruthenium dyes have the highest efficiency of conversion solar energy into electrical, reaching 11 and 13 % [6]. The price and toxicity are great disadvantages of these dyes [7]. On the other hand, natural pigments extracted from flowers, plants and fruits are affordable and widespread, but their efficiency of conversion is only a few percent [8]. The best result published so far for natural pigment sensitized solar cell reported Ghann [9] with pomegranate juice and reached the efficiency of 2 %. In the extensive study by Kumara [10], the best performance showed red turnip, and

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reached cell efficiency was 1,70 % on 470 nm. Still, review papers show that most natural pigments have low performance, with conversion efficiency somewhere between 0,013 and 0,50 % [9].

Hypericin is a photosensitive pigment which is one of the principal active constituents of St. John's wort (Hypericum perforatum). Hypericin is novelty in terms of photovoltaics [11], although it is widely used for its photodynamical and phototherapeutic properties in medicine [12]. Hypericin's molecular structure is presented in Fig.2.

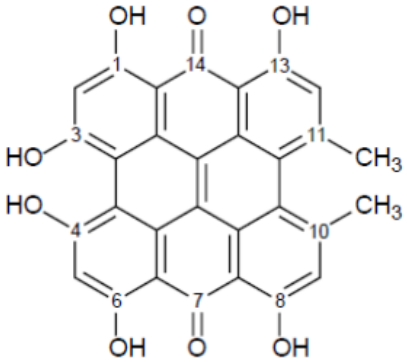

Fig 2.Molecular structure of hypericin.

TiO_2 is a stable, nontoxic oxide, which has a high refractive index (2.4-2.5) and naturally occurs in several crystal forms: rutile, anatase, and brookite. Rutile is the thermodynamically most stable form. Anatase is, however, the preferred structure in DSSCs, because it has a larger bandgap (3.2 vs 3.0 eV for rutile). In recent years, the progress has been made in the development of methods to synthesize new anatase nanostructures such as nanoparticles, nanorods, nanowires and nanotubes [13, 14]. These methods include sol-gel, micelle and inverse micelle, hydrothermal, electrodeposition and many more. One of the most important parameters of fabrication of TiO_2 anode is temperature of sintering, it provides good electrical contact between TiO_2 particles, while, carefully chosen, it does not allow phase transformation from anatase to rutile (~500 ºC) [15].

The goal of this paper is to compare the performance of two cells, almost identical, with the difference only in sintering temperature of anode, one at 500 °C, and the other at 600 °C. The motive can be found in the fact that the temperature of 500 °C is recommended as optimal for anatase electrode preparation, but the DSSC devices showed better performance when TiO_2 was sintered at 600 °C, although it showed phase transformation to rutile [16].

II. Experimental

TiO_2 paste was prepared as described by Ito in ref. [17]. TiO_2 powder (P25, Sigma) was transferred into alumina mortar and grinded, with addition of acetic acid, water and ethanol, respectively. After the transfer into the beaker with ethanol, it was stirred with a magnetic tip and sonicated with an ultrasonic horn. After this set of treatments, terpineol was added, and the mixing and sonication procedure was repeated. Then, the ethyl cellulose was added, and the sonication treatment was performed once more. At the end, the paste was evaporated from solvents.

TiO_2 paste was coated onto fluorine doped thin oxide glass (FTO), previously cleaned and treated with UV lamp and $TiCl_4$ treatment, by screen-printing. The photoanodes were then gradually heated under an airflow at 325 °C for 5 min, at 375 °C for 5 min, at 450 °C for 15 min and 500 °C for 15 min. One more step was performed on the electrode sintered at higher temperature – 600°C for 30 min. The exact temperature at the sample position was measured with a K-type thermocouple, Ni/NiCr.

The thickness of the TiO_2 layer was measured on comparator Iskra NP37 (15 µm).

X-ray diffraction (XRD) measurements were performed. (phase composition) using Rigaku Ultima IV X-ray diffraction instrument in thin film geometry with grazing incidence angle of 0.5°, using Ni-filtered CuKα radiation (λ = 1.54178 Å). Obtained data was analyzed with PDXL 2 software. Afterwards, the $TiCl_4$ treatment was conducted once again on TiO_2 anodes. Right after programmed heating to 500 ºC/600 ºCand cooling at 80 ºC, the electrode was immersed into 10^{-4} M hypericin solution in acetone and kept at room temperature for 20 h.

The counter electrode was prepared on cleaned FTO glass, and treated with a solution of HCl in ethanol. Then, after heating at 400 ºC a drop of H_2PtCl_6 solution in ethanol was applyed and heated under an airflow again at 400 ºC [17]. I^-/I_3^- electrolyte solution in acetonitrile was also prepared.

TiO_2 electrode, sensitized with hypericin, counter Pt electrode were assembled as a sandwich type cell with the sealing tape. A drop of electrolyte was put onto the hole on the Pt counter electrode, and then the cells were ready for measurements.

Photovoltaic characteristics of DSSC were examined with the solar simulator Abet, LS series 10500 at 1.5 AM, at 23˚C (measured with IR thermometer) controlled with circular thermostat Julabo F12 (under illumination).

Illumination of the system produces additional heat, so the assembled solar cell was thermostated at the steady state temperature of 23 ± 1 ºC. After achieving steady state temperature, photovoltaic measurement was performed by Gamry electrochemical devise, Gamry Series G 300 potentiostat, with Linear sweep voltammetry (LSV).

III. Results

The aim of this research was to investigate the influence of sintering temperature of TiO_2 layer on the performance of DSSCs with hypericin. Two identically prepared TiO_2 anodes were sintered at different temperatures—500 and 600 °C.

As seen in Fig. 3., XRD patterns of the two anodes feature three different peaks, from left to right: anatase form, substrate and rutile phase. The XRD measurements were performed to ensure that the majority of crystalline form is anatase, which was proven as better choice for DSSC than rutile even at 600 °C.

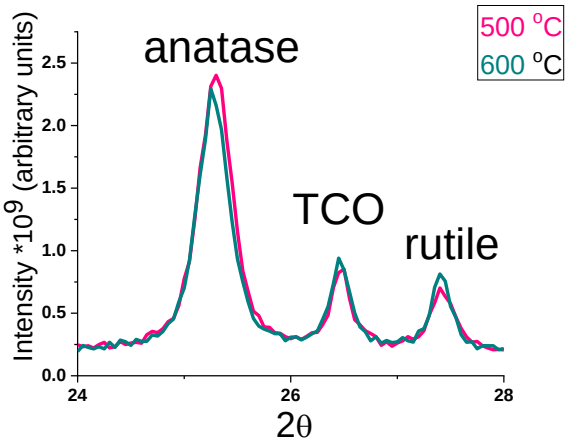

Fig. 3. Fractions of different crystal phases of TiO_2 and substrate TCO, sintered at 500 and 600 °C.

Current density–voltage curves for the cells with anodes sintered at two different temperatures are presented in Fig. 4 and Fig. 5.

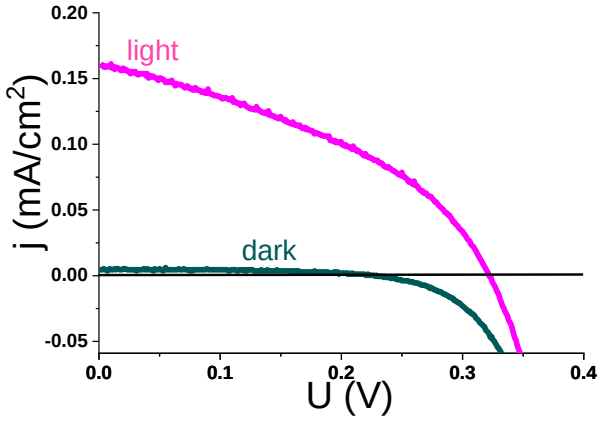

Fig.4. Current density–voltage characteristics of the cell sintered at 500 °C in the dark and under 100 mW cm^{-2} of simulated AM1.5 illumination for the illuminated device.

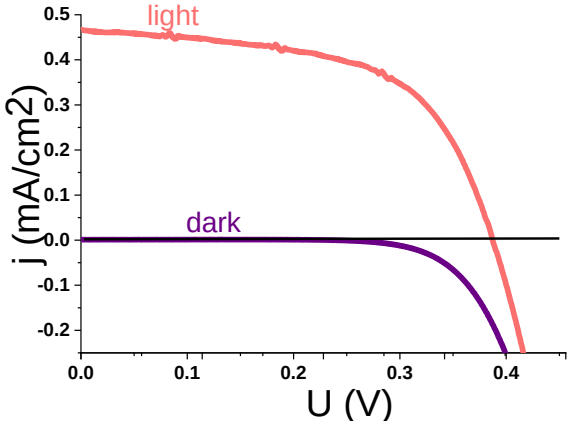

Fig.5. Current density–voltage characteristics of the cell sintered at 600 °C in the dark and under 100 mW cm^{-2} of simulated AM1.5 illumination for the illuminated device.

Comparing Fig. 4 and 5 it is noticeable, that the cell with the anode sintered at the higher temperature has far better performance. It has higher values for short circuit current density (j_{sc}) and open circuit voltage (U_{oc}). For better insight, the cells' performance parameters are given in Table 1 bellow.

TABLE I
IE CURVES PARAMETERS FOR MEASURED CELLS

	500 °C	600 °C
j_{sc} (mA/cm^2)	0.162	0.468
U_{oc} (mV)	322	387
P_{max} (μW/cm^2)	20.7	106.1
FF	39.7	58.6
η (%)	0.021	0.106

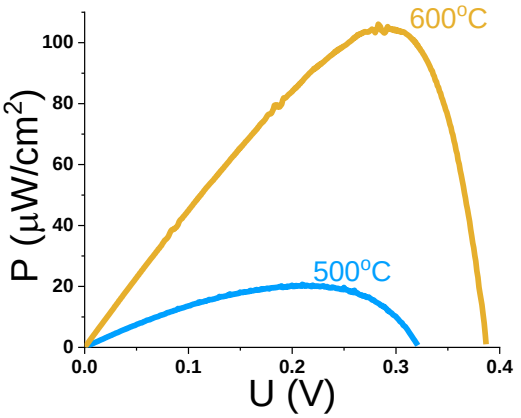

Fig.6. Power density-voltage characteristics of the cells sintered at 500 °C and 600 °C under 100 mW cm^{-2} of simulated AM1.5 illumination.

The ratios between the maximal power densities (P_{max}) and solar to electrical energy conversion efficiencies (η) for the two measured cells are 5 times in favor for the cell sintered at 600 °C, as seen in Fig. 6. It shows the importance of temperature treatment of TiO_2 electrodes for better performance of solar cells.

IV. Conclusion

The goal of this work was to present the importance of sintered temperature for an adequate performance of TiO_2 electrodes in dye sensitized solar cells. Two identical cells, with natural pigment hypericin as sensitizer and different sintered temperature were compared. The result showed five times higher value of maximal power density for the cell with the higher sintering temperature of 600 °C at given conditions. Despite that much lower temperature of electrode preparation is recommended in literature, obtained results show that anatase phase may be preserved even at much higher temperatures, depending of heating procedure. The reason for better performance of the cell treated with higher temperature is better electrical contact between TiO_2 particles, which provided better electron transfer through the anode, and

therefore lower resistance of the cell. This experiment was conducted on P25 TiO_2 particles, but it would be interesting to observe and compare optimal sintering temperatures for other nanostructures such as nanoparticles, nanorods, nanowires, nanotubes, etc.

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