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Review of the PhD thesis of Mr. Paweł Dąbczyński from Smoluchowski Institute of Physics Jagiellonian University on "Engineering of interfaces in hybrid-organic electronic devices" Supervisor Dr Hab. Jakub Rysz.

The dissertation of Mr. Paweł Dąbczyński is composed of the 9 scientific chapters with a comprehensive description of the results and details of experiments. The results and the details of experiments are incorporated in 2 publications coauthored by Mr. Dąbczyński. The first one published in ACS Omega while the second one in Chemical Science, IF=2.58 and IF=9.5, respectively. Other his achievements are described in other 11 publications. This mature form of presentation is not very common for Ph.D. theses because it requires much effort and time than writing only the thesis. The papers must have passed a careful review process prior to publication. It makes the reviewing much easier because all the published material was already severely checked and criticized. However, in the case of Mr. Paweł Dąbczyński there is also the full text dissertation. The topic of the thesis is connected with high demand for better electronic devices (field effect transistors, light emitting diodes, and other photovoltaics) and organic and hybrid solar cells.

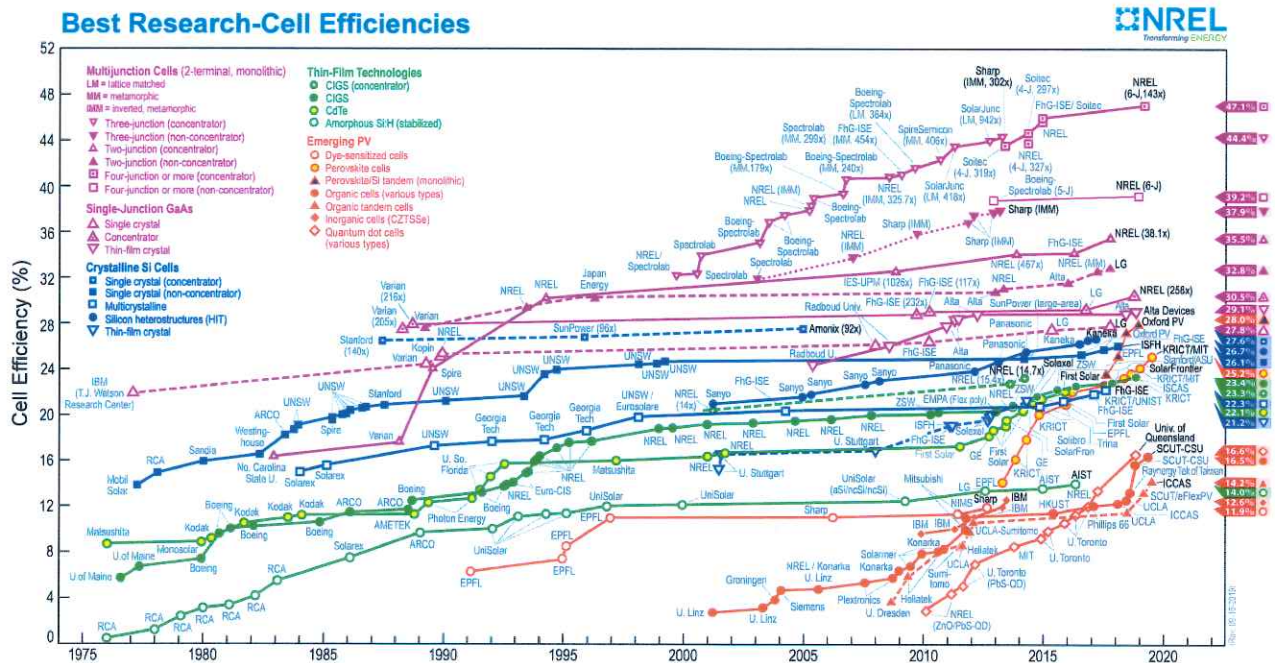
It must be noticed that the electrical energy generation from renewable resources is

dramatically increasing. For example it amounts in Germany to more than 47% in 2019 while the energy only from solar cells is approaching 11%. Any improvement in the solar cell techniques would mean significant economic advantage and saving the environment. In many applications it would be beneficial to have such devices on flexible substrates.

The description of the results of the thesis is composed of the valuable **Introduction** and in **Chapter 1** in which Mr. Dąbczyński summarized the knowledge about the need and possibility of using solar energy and outlined the principles of solar cell functioning. Early (1978, US patent, Exxon) solar cell assembly consisted only 4 layers, more layers solar cells were discovered in 1979 (US patent, Eastman Kodak), as the additional layers enhance solar cell efficiency. Today roughly 25 basic patents are covering the field of organic solar cells (US, Germany, China, Japan, Austria, Switzerland). The necessary steps for functioning the cell was clearly depicted in a drawing adapted from another PhD dissertation from Karlstad University. Five steps are needed for efficiently functioning solar cell. A solar cell may be seen as a solar-light driven electron pump: the highest voltage which the solar cell can develop is related to the maximum concentration of electrons that are pumped, while the maximum current is determined by the pump rate. The most appealing parameter is the cell efficiency defined as a ratio of the power produced by the cell to the power of incident light. The currently solar cells on the market are based mostly on silicon. More sophisticated and more efficient panels are built on copper indium diselenide, GaAs, cadmium telluride. The majority of panels range from 15% to 20% efficiency. Organic/polymer materials applied in solar cells have not been commercialized yet. The efficiency of these cells is still low, a little more

than 10%.

A graph below illustrates the efforts to achieve the highest efficiency of laboratory obtained solar cells.



Graph illustrating development of solar cells based on different materials and different techniques. *Author: Nikos Kopidakis, National Renewable Energy Laboratory, Golden, Colorado, Sep.16, 2019*

As one may see from the above graph the organic/polymer solar cells, that are being developed in the labs and being the subject of Dąbczyński dissertation, hardly exceed 10% limit of efficiency. However, they may have other features that could be beneficial, for example low costs.

The presented description indicates that the aims of the thesis concern the issues still at the laboratory level facing many problems with easiness or difficulty of fabrication, stability, water resistance, apart from low photovoltaic efficiency. Nevertheless, the efforts of controlling each of the vital elements and steps in photovoltaic cells may lead also to the improvement of other elementary electronic devices built of organic/polymer principal materials.

The thesis is concentrated on modification of interfaces which are the vital elements of multilayered construction of the photovoltaics. There are at least 4 different interfaces that can be considered, each one facilitates a different function.

Four theses of the dissertation are outlined: i) a surface of complex polymer thin film PEDOT:PSS, serving as anode, can be modified regarding to its surface energy and work function by absorption of trifluoropropyl-trimethoxysilane, ii) transparent indium tin oxide, ITO, electrode can be modified by sedimentation of nanoparticles of zinc selenite doped with manganese, again surface energy and charge transfer properties can be changed, iii) modification of bilayer of polyvinylpyridine and polythiophene may change conductivity of that semiconductor, and iv) the exposure to vapor of a solvent can modify element susceptible to a chosen solvent. All four efforts aimed at making changes to interfaces with the expectation of positive effects. The following three chapters are devoted to the materials used in the studies, sample preparation methods and characterization techniques, including SIMS, AFM, XPS and UV photoelectron spectroscopy. To my surprise there is no description of photovoltaic tool to determine the efficiency of introduced changes in working assemblies of a solar cell. In fact the information on improvements of four interfaces by applied procedures were collected mostly from XPS binding energy and depth profiles, contact angle measurements, etc. The exception is Figure 36 in which current-voltage characteristics for PEDOT:PSS assembly is plotted for various exposure times to trimethoxysilane vapor. However, it is not characteristics for the assembly as solar cell: the independent variable is voltage and there is no illumination. Instead a "solar simulator illumination" is used for predicting the influence on the virtual solar cell efficiency. That is discussed

based on predictions in Figure 37. It is the pity that there is no reference to the description of “solar simulator illumination” software. By the way, Figure 37b and 37c are identical.

The deposition of nanoparticles of zinc selenite doped with manganese on indium zinc oxide layers is the subject of the next chapter of the dissertation. The deposition was performed by dipping the electrode in a suspension of nanoparticles. The purpose was to increase the open circuit voltage and to decrease the work function, similarly as it was demonstrated by others when using deposited zinc sulfide nanowires. Current-voltage characteristics indicates that ZnSe:Mn nanoparticles forms a hole blocking layer while do not decrease the light transparency.

Polymer surface crosslinking with transition metal halides is another path of interface modification. Cobalt halides (bromine and chlorine) were used for the purpose. Here ellipsometry appeared as another technique used for characterization. Profiling indicates that polyvinylpyridine can be easily crosslinked to a depth of roughly 50nm with cobalt halides. Here the PhD candidate did demonstrate the positive action of crosslinking on binding energy by XPS technique.

Next chapter of the dissertation concerns the conduction increase due to incorporation of metal complex into organic semiconductor (polyvinylpyridine). The experiments in this chapter were performed with great care, not to observe undesired effects of orientation, the influence of used solvents and others. The conductivity of $1 \cdot 10^{-2}$ Siemens/cm was obtained which according to the literature it is one of the highest conductivities observed for R-P3HT without doping. For lamellar systems it was shown that the conductivity increase can reach 10^{+2} times.

Casting/removal/recasting experiments undoubtedly showed that the conductivity increase is caused by P4PV modified layer. The model is proposed to explain the observed conductivity changes by electric field caused by dipole moments of pyridine and bromine complexes. The conclusion is supported also by the dependence on film thickness.

The last chapter of the dissertation is related to interdiffusion of fullerene derivative in thin films made of conjugated materials under the action of solvent vapors. The interdiffusion is triggered by administering vapors and depends on type of solvent, exposure time and obviously the vapor concentration. The phenomena may serve for obtaining interpenetrating nets of donors and acceptors in organic solar cells. The author claimed that he built a solar cell based on system with penetration of fullerene derivative with the efficiency around 1%. This is not an enchanting result. It is not clear from the description whether the solar cell was physically built and tested or only constructed by "illumination simulator".

Several possibilities to modify interfaces were explored in the research undertaken in the frame of Mr. Dąbczyński Ph.D. thesis. In many cases the problems formulated and approaches developed are pioneering in the field and open widely a new possibilities of further research. New applications of conjugated polymers with their surfaces modified are now also possible.

Mr. Dąbczyński proved that any single modification can lead to the improvement of performance of photovoltaics. Then it would be natural consequence to apply several discovered modification to a single solar cell in order to observe their joint action. The potential of the methods could be illustrated in a series of experiments including two, three or four modifications simultaneously.

In my opinion, all the declared objectives of the thesis were fulfilled.

The overall impression of the thesis is very positive. I have to emphasize a very high quality of the experiments and careful interpretation of results with a great concern to limit uncontrolled parameters and to separate really acting factors.

Apart from some of my criticisms I consider the work of Mr. Dąbczyński as an outstanding contribution to the material and physical sciences.

Andrzej Gostek

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