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Referee Report on Doctoral Dissertation „From selected lead halide perovskite materials to solar cell devices" by Rashmi Runjhun supervised by Professors Janusz Lewinski and Michael Grätzel

Transformation of energy supplies from fossil fuels to renewable sources such as wind, sun or water is currently emerging issue both in terms of the shortage of fossil fuels as well as need for environmental protection. However wind does not blow, sun does not shine on demand and therefore there is a need for highly efficient devices capable to both convert and stored produced energy. Assuming an enormous and unlimited availability of the sun energy photovoltaic cells seems to be one of the most promising devices considering renewable energy production. These solar cells can easily be coupled with energy storage devices such as batteries for home applications or redox flow batteries when megawatts photovoltaic farms are considered. However number of question remains unsolved if the solar cell technology have to be successfully widely applied. Among them following issues has to be addressed:

- efficiency of the conversion of solar energy to electrical
- production of large area devices from environmentally friendly components
- long time stability of the device

The work performed by Miss Rashmi Runjhun under supervision of leading experts in the filed of solar cell Technology (prof. Michael Grätzel) and synthesis of new innovative materials (prof. Janusz Lewinski) try to answer these hot issues and in my opinion is absolutely in line with the ongoing research towards improvement of the solar cell technology.

To solve above mentioned problems metal halide perovskites as components of solar cells were deeply studied in the reviewed Thesis. Particularly the problems related to substituting toxic Pb as a part of perovskites, long time stability of the devices, as well as fabrication of large area devices has been addressed. Metal halide perovskites have emerged as a new class of revolutionary optoelectronic semiconductors promising for various applications. Over the last decade, they have attracted particularly considerable attention for use as the active layer in solar cells and to a lesser extend in energy storage devices. The preparation of halide perovskites commonly relies on solution-based methods, however the solution-based approach faces challenges, such as limitation in their both compositional engineering and long-term storage. Moreover, the low solubility of some organic/inorganic additives in common used solvents limits further progress in compositional engineering. Therefore, there is a continuous great challenge to develop efficient synthetic strategies affording a vast array of high-quality perovskite materials prospective for applications in large are devices with a long working time. To solve this problem under the scientific guidance of Prof. Lewiński doctorate candidate suggested the use of mechano chemical synthesis as a new route of preparation of metal halide perovskites. The solid-state chemical reactions induced by mechanical forces have emerged as an efficient and simple method for the solvent-free compositions engineering of high-purity metal halide perovskite in a relatively short time. Notably, this approach also provides an efficient one-step general method for incorporating poorly soluble salts into multi-component perovskite crystal lattices. Moreover, the use of mechanoperovskites for thin films formation revealed the advantage of providing a higher degree over control of the stoichiometry, higher reproducibility, stability and material phase purity. As a result, the solar cell devices made from mechanoperovskite particles exhibited superior photovoltaic performance compared to conventional devices made using similar materials obtained by the wet method. All the advantages of mechanoperovskites make mechanochemical synthesis appealing for upscaling their fabrication. A new generation of perovskite solar cells (PSC) that have increased their power conversion efficiency (PCE) from 3,9% to over 25% has been described in the Thesis. The one-step solution process can be further enhanced by using perovskite inks resulting from the mechanochemical method instead of the solution of substrates like methylammonium and lead iodides. To gain a better understanding of this behaviour, detailed studies on solar cell parameters including crystallinity, grain size, absorption/emission properties, and impedance spectroscopy was carried out and concluded that it leads to thin films of better quality, bigger grain size, and lowered charge accumulated in ionic defect states.

The reviewed Thesis is very well organized and all aspects related to the synthesis, studies and application in solar cells of newly design perovskites are described. The variety of techniques used is impressive. I also like the way when doctorate candidate generally describes the methodology of experiments in separate section and thereafter refers to it when experiments on particular systems are described.

The experimental part starts from the description of the synthesis and characterization of lead based halide perovskite materials first in the form of polycrystalline materials followed by the investigation on single crystals. In the subsequent section studies on a modified approach to tailor mixed-cation perovskite films are undertaken. A part of this section is devoted to the research on improvement of the solar cell performance by passivation of perovskite layer. The important part of the Thesis are studies on engineering issues related to comparing of the mechano chemical synthesis with tradition wet synthesis of perovskites as well as optimisation of the preparation of thin perovskite films on the surface of solar cell electrodes. In the final section the use of ZnO quantum dots as an efficient way of increasing electron transport in the perovskite film has been successfully studied.

The Thesis are organized in such a way that reader gets an impression of each following step being a consequence of the results achieved in the former one. Although the solar energy transfer efficiency becomes higher when going through the Thesis with the final result over 25% as mentioned before. I personally gain a lot of knowledge having an opportunity to act as a reviewer. The doctorate candidate took an advantage of being supervised by the world class leaders in the field of solar energy conversion and material synthesis.

However, I do have one concern regarding the use of Eléctrochemical Impedance Spectroscopy (EIS) to study perovskite materials and solar cells incorporating them. This issue is just briefly mentioned in the Thesis but it is a vital part of several papers published by the research groups involving doctorate candidate three of them being on the list of her scientific achievements (papers 1,2, and 3 on the top of page 12 in the section Publications included in the Thesis). The comments below do not change my very high opinion on the Theis but I hope my help the doctorate candidate in her future works.

I spent some time going through the appears listed on page 12 and manage to found the paper by P. Yadav et al. Crystals 7 (2017) 252 which has been claimed to be an original work with the use of EIS. My general remark is that in none of this works the cell which has been used to EIS studies has been described. From the Nyquist plot shown in the original publication one can find out that most probably the studies were performed in the symmetrical blocking cell configuration. What was the material use as electrodes, stainless steel, platinum or others. It might be important for the quality of impedance data. The quality of these data presented in publication 1-3 is by far lower than in the original paper. Therefore it do not justify use 5 parameters equivalent circuit as suggested in supporting material to publication 1. Moreover all equivalent circuit parameters should be defined (not the case of any papers here) and have physical explanation. Even the original paper suffers from parameters not being fully justified. I personally will try to use the simplest three components equivalent circuit describing double layer capacity in series with parallel combination of bulk conductivity and geometrical capacity. Due to the semicircle distortion both capacity will probably be represented as constant phase elements. Are the authors completely sure that the iodide anion is the only conducting species? What is the proof of this? If there is no proof so discussion on changes of iodide mobility should not be included. Is the frequency range is sufficient to see diffusion effect? The lowest frequency is only 0.2 Hz far higher than that at which diffusion effects are usually observed. Although performing research within wide voltage range 0 to 1V might results in red-ox reaction undergoing in the material. Do the voltage stability window of the perovskites studied has been defined? Also I suggest to study high frequency part of the impedance spectra to find out whether there is an electronic contribution to the conductivity. These are just major concerns. Generally I will not recommend to use EIS data of such low quality to explain phenomena in solar cells.

At the end I would like to conclude that despite above remarks work performed within this Thesis shows high innovation potential and it will have high impact on the research society. It is of good quality and I recommend allowing Miss Rashmi Runjhun to publicly defend it. It should also be mentioned that the Thesis presented satisfies all requirements included in Ustawa o Stopniach i Tytule Naukowym oraz o Stopniach i Tytule w Zakresie Sztuki z dnia 14.03.2003 Dz. U. Nr 65 Poz. 595 z późniejszymi zmianami (tekst ujednolicony) related to procedure leading to award of the PhD degree. Moreover due to high quality of the Thesis and design and development of novel class materials for application in solar cell devices of enhanced energy efficiency hereby I strongly support the distinction of the reviewed Thesis.

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