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Review of the PhD thesis of Shyantan Dasgupta entitled „*Enhancement of structural stability and operational reliability of perovskite solar cells*"

M.Sc. Shyantan Dasgupta has prepared the presented doctoral dissertation under the supervision of Prof. Alina Dudkowiak and auxilary supervision of Dr Konrad Wojciechowski at the Poznan University of Technology.

During the last decade, we have witnessed an unprecedented technological rush aimed at the development of photovoltaic devices based on lead halide perovskites, which power conversion efficiency (PCE) has now exceeded 26% for small-area cells. The outstanding performance of perovskite solar cells (PSCs) is ascribed to the excellent optoelectronic properties of these semiconductors such as sharp optical band edge, high absorption coefficients, and long carrier diffusion lengths. However, PSCs are still facing challenges including scale-up, low long-term operational stability, use of expensive blocking or transport layers and precious metals. This dissertation addresses the most relevant issues related to improvement of stability and operational reliability of PSCs, and suggests a new strategy to consider not only the new materials for device fabrication but also provides efficient encapsulation protocol to prevent degradation of devices caused by environmental factors.

The doctoral dissertation has the structure of a guide to a series of five published publications and consists of a rather condensed literature introduction, a description of the used research methodology, the author's commentary on the works included in the series, and appendices in the form of already published works. The thesis is very well written and contains in total 87 pages (5 chapters) with a list of 226 updated references.

The literature part consists of three main subchapters. The first part (Chapter 1), also called as Motivation, provides a description of growing climatic changes together with the renewable energy sources. Most attention is put on the solar energy providing short introduction to perovskite-based photovoltaic. Chapter 2 starts with the theoretical background to semiconductors and recombination mechanisms. Further, the fundamental working mechanism of solar cells based on p-n junction and description of their photovoltaic parameters is concisely described. A more detailed review on perovskite-based semiconductors and related solar cells is given in Chapter 3. Particularly, this part describes the structural and optoelectronic properties of halide perovskites, techniques for thin film formation and charge transport mechanism in a completed device. In addition, this part also provides the standard protocol to measure PSCs and collect photovoltaic parameters.

Next, the Author reports on the most significant achievements of the included publication series (Chapter 4). These works have been published in very good international journals related to energy materials (e.g., Journal of Materials Chemistry A, Energy Technology, Energy and Environmental Materials). The Author of the dissertation acts as first author in two publications, while in other three publications he is on the second position. However, based on the attached certifications, it is clear that the Author played an essential role in realizing these projects and demonstrated his excellent skills in the fabrication and characterization of PSCs with novel materials engineering.

In the first publication of the series (Energy Technology 2020, 8, 2000478), the Author demonstrated a novel synthetic route for the formation of ultra-pure and free of phosphorous-based impurities methylammonium iodide (MAI), which is essential precursor for the formation of methylammonium lead triiodide thin films. The proposed synthetic approach allows to control the colloidal perovskite precursor solution and deposit thin film with improved optoelectronic properties. Further study reveals that the controlled addition of methylammonium hypophosphite (MAH_2PO_2) to the perovskite precursor solution containing MAI synthesized with this new method plays a positive role in improving the performance of PSCs in compared to the commercially available MAI. Specifically, this modification led to the formation of perovskite films with low defect density and reduced nonradiative recombination. Notably, this synthetic route is also applicable for the formation of other important alkylammonium iodide e.g. formamidinium iodide. Reading this part of the dissertation, a question arises regarding the description of colloidal nature of perovskite solution. What does the Author mean by saying that the use of ultra-pure MAI helps to control a colloidal network in the solution (Page 61)? Does the colloid solution contain particles that are stable on time? In addition, could the Author demonstrate during public defense of his doctoral dissertation how the purity of other important precursor for the perovskite film formation i.e., PbI_2 may affect the performance of PSCs.

In another publication (Energies 2022, 15, 5397), the Author undertook the attempt to analyze the changes occurring in time in PSCs using optical reflectance in the NIR range (900-1700 nm). The as-fabricated devices with the inverted architecture were aged over one month and the reflectance spectra were monitored. Based on two-dimensional correlation spectroscopy and analysis of the ratio of distinguished peaks in reflection spectra it was possible to monitor structural stability of the device. Specifically, this contactless method allows to find a moment of device cell degradation. However, why did the Author not correlate the change in the reflectance spectra with the device performance? Did the performance of the device degrade during aging time?

In the third publication (J. Mater. Chem. A 2022, 10, 11046), the Author reported on the use of three perylene diimide derivatives as electron transport material in PSCs. The motivation of this work was to found alternative materials to replace the commonly used PCBM in inverted PSCs. The synthesized perylene diimide derivatives differ from each other by having different substituents in their bay positions. These compounds were thoroughly characterized using DFT calculations and various spectroscopic techniques. It was demonstrated that the engineering of the molecular structure not only affect the electron mobility but also change their LUMO levels. The energetically favorable band alignment with the perovskite layer is critical for efficient charge transfer and critical achieving high-performance PSCs. In this work, the compound named as **PDI-3** revealed promising potential for utilization in PSCs. After optimization procedures, the best device based on **PDI-3** yielded a power conversion efficiency (PCE) of 16.8%, which was comparable to the PCBM-based device with a PCE of 17.3%. It was interesting work to show that the change in the electronic nature of the substituents in perylene diimide semiconductors can tailor the charge extraction and band alignment. However, I would like to ask the Author to further specify some statements during public defense of his doctoral dissertation. Firstly, what are the desired advantages of replacing fullerene material (PCBM) with organic molecules (e.g. perylene diimide), especially in devices with inverted architecture? So far, the most efficient devices reported in the literature have still used fullerene-based materials as ETL. Secondly, it is not clear for me what changes in the device fabrication based on **PDI-3** were applied to reach PCE of 16.80 % (Table 4), which highly improved from that PCE shown in Table 3 (9.80%).

The fourth publication (ACS Appl. Energy Mater. 2022, 5, 15114) focuses on improving the interface between hole transporting and perovskite layers through deposition of bulky organic ammonium molecules. The Author rightly noticed that the interface tailoring is crucial for improving the efficiency and stability of PSCs. The proposed modification led to the formation of 2D perovskite phase at the buried interface, which not only improved the hole extraction ability but also reduced nonradiative recombination. As a result, the device on flexible PET/IZO substrate and modified with the 4-fluorophenethylammonium iodide (FPEAI) yields a PCE of 18.66%, which was significantly higher than the pristine device without interface modification (16.03%). Notably, the formation of 2D phase at the interface results also in a significantly enhanced thermal and light-soaking stability of fabricated devices. This study was continued in the last fifth publication of the series (Energy Environ. Mater. 2023, 6, e12434) where the Author developed encapsulation protocol for flexible PSCs enabling good stability in various stressing environmental conditions. It was found that the use of proper polymer-based barrier foils, edge sealants and UV-curable adhesives can provide robust hermetization of device against environmental factors. These works open new directions to form highly stable p–i–n PSCs by modifying the HTL/perovskite interface and providing sufficient lamination protocol. However, did the Author consider to study the effect of applied modification and encapsulation on the device's bending stability? The study on the mechanical properties and fracture behaviors of perovskites are essential for flexible solar cell applications.

Chapter 5 summarizes the most important results of this doctoral dissertation and also provides future challenges and perspectives of perovskite-based photovoltaic.

To sum up, the research undertaken by the Author concerns essential issues in the constantly developing field of photovoltaic cells based on halide perovskites, mainly focusing on their stability aspect. The doctoral dissertation of Shyantan Dasgupta is very coherent in terms of topic demonstrating rational engineering of materials and modification of solar cell components. The Author demonstrated very good skills in the fabrication of PSCs and their characterization using various spectroscopic and optoelectronic methods. The results presented in the dissertation open up new possibilities and perspectives in the rational fabrication of stable PSCs and toward commercial viability. I rate the scientific level of the thesis as very high and I'm sure that the doctoral dissertation of Shyantan Dasgupta fully complies with the conditions set out in Art. 187 of the Law on Higher Education and Science in Poland of July 20, 2018 (in Polish: Prawo o szkolnictwie wyższym i nauce, Dz.U. z 2018 r. poz. 1668 ze zm.) In view of the above, I am applying for admission of Shyantan Dasgupta to the next stages of the doctoral dissertation defense.

Daniel Prochowicz