



Reviewer's report on the dissertation thesis

Thesis title: Hybrid nanomaterials for photoanodes in photoelectrochemical water splitting

PhD student: M. Sc. Ali Can Güler

Supervisor: Prof. Ing. et Ing. Ivo Kuřitka, PhD. et PhD.

Reviewer: Ing. Vojtech Nádaždy, CSc.

Dissertation thesis by M. Sc. Ali Can Güler focuses on the current issue of solar-driven water splitting. More specifically, the development of ZnO-based photoanode materials in various nanoforms to enhance light harvesting and to improve the efficiency of photoelectrochemical (PEC) water splitting. The main goal of the thesis is to investigate the role of different ZnO nanostructure morphologies on the photoanode performance, as well as the effect of Au nanoparticles on the extension of the light absorption to longer wavelengths. This work belongs to applied research with potential use in technologies of low-cost PEC cells for water-splitting.

The assignment of the dissertation thesis is adequate to the state of the art in this field. There were chosen proper methods and techniques to solve the set goals. The thesis has a standard structure with 6 chapters. Introductory chapter #1 is devoted to the short description of the need for renewable energy resources and beneficial aspects of chemical energy storage. In the chapter #2, the author reviews fundamentals of the PEC water splitting and working principle of the PEC cell for the water splitting. More particular is described photoanodes forming the heart of the water oxidation system, which is under investigation in this work. Further are discussed semiconductor materials, especially ZnO, suitable such photoanode with literature review related to present strategies used in improving of PCE performance of ZnO anode. The chapter #3 presents the aims of the PhD thesis itemized in three tasks. In fact, the three items do not represent aims, but rather what has been accomplished during the research activities on the topic. The list of materials, sample preparation, and methods employed for characterization are shortly specified in the chapter #4. The results and discussion are presented in chapter #5, which is divided into three sections. The first section is devoted to comprehensive analysis of the geometry modification of ZnO nanorods on the light absorption spectra and PEC properties. The second section deals with the ZnO nanorods gradient doped with Au nanoparticles. This modification allows formation of surface plasmons and creation of upward band bending, which results to the enhanced PCE performance. The further PCE cell improvement via successive modification of ZnO nanorods photoanode to ZnO nanodendrites and photosensitized by absorbing BiVO₄ is presented in the third section. This sophisticated treatment leads to light absorption towards the longer wavelengths in the visible light, better charge transfer as well as suppression of charge recombination rate. The limits and advantages of chosen approaches and analysis are

properly discussed. A brief summary of obtained results, their contribution to science and future prospects are given in the chapter #6. Since the nature of experimental work is mostly team affair, I appreciate the clear specification of the author's contributions to the presented results.

The most valuable original results achieved by Ali Can Güler can be considered:

1. Comprehensive investigation of ZnO nanorods geometry on the PCE performance, including the nanorods preparation and complex characterization. (A. C. Güler et al., *Nanoscale Adv.* 5 (2023) 3091).
2. Demonstration of beneficial effect of surface plasmon resonance via Au nanoparticles to eliminate partially weak visible light absorption of the ZnO nanorods. (A. C. Güler et al., *Int. J. Mol. Sci.* 24 (2023)).
3. Preparation of the BiVO₄/ZnO nanodendrite heterostructure, which shows a potential of such heterojunction photoelectrode for efficient PCE cells. (A. C. Güler et al., submitted).

The thesis is written compactly with a logical division and technically well elaborated. I would have a reservation about the presentation of data regarding the efficiency of prepared photoanodes. The text contains some comparisons of parameter values in individual parts. Photoelectrochemical properties are summarized for ZnO nanorods, ZnO nanorods/Au nanoparticles, and BiVO₄/ZnO nanostructure in Fig. 5.12, Fig. 5.24, and Fig. 5.43, respectively. Nevertheless, it would be helpful for the readers to compare the performance parameters of all the prepared photoanodes also in one place. I would have the following questions:

1. Could you prepare such comprehensive comparison of the performance parameters in your presentation?
2. The comparison of ABPE spectra shows that the efficiency should be the highest for ZnO nanorods, lower for ZnO nanorods/Au nanoparticles and lowest for the BiVO₄/ZnO nanostructure. However, conclusions from other characterization techniques shows the opposite. Can you explain this discrepancy?
3. Also, IPEC spectra should be invariant on used LED source. Why is the IPCE spectrum for ZnO nanorods/Au nanoparticles more intense than for BiVO₄/ZnO nanostructure?
4. Why did not you show chronoamperometric photoresponse for the BiVO₄/ZnO nanostructure?

Taking into account the above-mentioned review, I can state that the objectives of the PhD thesis have been met. With this PhD thesis the PhD student demonstrated the ability of scientific work, including data analysis and cooperation with other colleagues. Most of the obtained results have already been published in a couple of peer-reviewed journals that also document these capabilities. The submitted work meets the requirements for the award of the PhD degree. Therefore, I recommend the submitted thesis for the defense and after its successful defense I propose to award a Doctor of Philosophy to M. Sc. Ali Can Güler in the Degree programme of study P3972 Nanotechnology and advanced materials.

Bratislava, 16. 2. 2024

Ing. Vojtech Nádaždy, CSc.