To Professor Gr. Zywica

Institute of Fluid-Flow
Machinery of the Polish
Academy of Sciences, Gdansk,
Poland

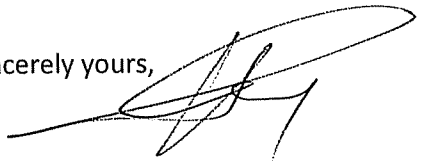
Dear Prof. Zywica,

Please, find with this submission my review of the dissertation of Mr. Jakub Wawrzyniak "Laser modification of the titania-based electrodes for energy conversion". My evaluation of the work is positive and I recommend to the Scientific Council to admit Mr. Wawrzyniak to the next stages of the PhD defense procedure. In my review, I clearly declare it and give explanation about my decision. The review is also presented in electronic version on CD.

I also include signed documents sent to me before.

Thank you for considering me in the evaluation process!

Sincerely yours,



Prof. N. Nedyalkov

REVIEW

of a dissertation for obtaining the educational degree "doctor"

Author of the PhD dissertation: Jakub Wawrzyniak

Name of the PhD dissertation: Laser modification of the titania-based electrodes for energy conversion

Reviewer: Nikolay Nedyalkov, Prof. DSc in "Academician Emil Djakov" Institute of Electronics, Bulgarian Academy of Sciences

The presented dissertation is aimed at a detailed study of the influence of the conditions for obtaining titania nanotubes, on their characteristics and development of methods for their modification. These studies are related to a specific application of these structures as electrodes in efficient water splitting. Both the scope of research and the indicated application determine its high relevance, both in an applied aspect and from a fundamental point of view, related to the detailed description and understanding of the properties of nanomaterials.

At a time when it is becoming clear that the replacement of conventional energy sources with new clean technologies is a question concerning the future of humanity, such research attracts considerable scientific interest. The presented work is focused on an effective solution in this direction – the use of new materials for efficient application in renewable and green energy sources such as water splitting and hydrogen production. Although this technology has been known for a long time, there are still a number of problems that prevent its effective use and commercialization. One such is related to the use of expensive electrode materials. The efforts of scientists and researchers are focused on the development of new, artificially created materials that have high efficiency and low cost. An idea that is attracting increasing interest is that these electrodes also possess high photocatalytic activity in the visible spectrum, that is, use sunlight to increase their efficiency in operation. Notwithstanding the process of water splitting has been studied in detail and is easy to implement, even just obtaining materials with high efficiency as electrodes, such that it becomes competitive, requires in-depth knowledge in various aspects - interaction of light, catalytic properties, electrochemical behavior, electrical properties of nanomaterials, corrosion resistance. A significant part of this knowledge has not yet been revealed.

In the presented dissertation, the solution to these problems is sought in the use of a nanostructure of titania nanotubes, a material which, in addition to the high ratio of free surface to volume, also exhibits photocatalytic properties, i.e. conditions with the potential to solve the requirements for efficient electrodes in water splitting systems. In addition, results for subsequent modification of the morphology and composition of this structure by laser impact are also presented. Changes in the optical properties of the materials, modification of the number density and evolution of the charge carriers are effects that are expected to occur by this treatment. A number of classical methods are also used to analyze the structure, composition, electrochemical activity and optical properties of the obtained materials, which provide the necessary characterization for the intended application and for an in-depth discussion of the realized fundamental physical picture. They also determine reliability and ease of interpretation of results by other researchers. The conducted experiments, characterization

of the obtained materials and the detailed discussion significantly contribute to the effective finding of optimization solutions and bring the water splitting systems closer to commercialization.

The used 66 sources specified in the dissertation work and the additional ones used in the publications on the basis of which it is built, show the doctoral student's in-depth knowledge of the main processes and problems related to the subject. The main characteristics of the anodization process and the mechanisms involved in the formation of nanotubes are shown. A clear statement of the aims and objectives of the dissertation shows that he can understand and interpret physical problems as well as carry out creative evaluation. The aims and objectives of the dissertation work are directed to: *Preparation of the substrate material consisting of the free-standing titania nanotubes and evaluation of their properties; Optimization of the processing parameters of the pulsed nanosecond laser for modification of the titania substrates; and Introduction of the sputtered transition metals from the 4th period to the surface of the electrodes and their evaluation for water electrolysis.* They are clearly oriented towards obtaining effective alternatives to the developed electrodes in water splitting systems. The applied approaches and work methodology are purposefully selected to achieve the set goals and objectives. Anodization of the titanium foil is chosen as the production method, as it is easy to perform and allows effective control of the parameters of the obtained structures. As a method for further modification of the properties of titania nanotubes, laser irradiation and its combination with previously applied metal has been considered. The choice of a method based on laser interaction is appropriate, as it offers non-contact localized impact, the result of which can be easily and effectively controlled. A nanosecond laser is also chosen, which is widely available and inexpensive. It offers also a domination of the thermal effects that would contribute to morphology and composition modification due to melting, melt dynamics and efficient element diffusion. From the results presented, it can be seen that the proposed method can lead to obtaining structures with an efficiency that cannot be obtained by other methods.

Research that has a contributing nature is reflected in four publications. The first work is focused at optimization of the anodization method of a titanium substrate. A detailed study of the influence of basic experimental parameters, such as applied voltage and anodization time, on the characteristics of the obtained titania nanotubes is presented. The choice of these parameters is appropriate because, as shown, changing the applied voltage can lead to significant modifications in the structure of the nanotubes, i.e. this parameter can be effectively used to obtain structures with desired parameters. The presented results show that the anodization time does not significantly affect the morphology, which is an important result from the point of view of the transfer of this technology in industry. Conditions are presented for well separated nanotubes, which have the potential for effective use as electrodes in photocatalytic reactions. In this regard, a number of analyzes are carried out and on their basis the structures with a maximal photoelectrochemical activity are defined. It also demonstrated a notable change of the optical properties of the system of well separated nanotubes that could contribute to more efficiency in the interaction of the system with visible light. In addition, the research in this work also provides insights into the formation processes of titania nanotubes and the relationships between their spatial characteristics and observed properties.

In the rest of the works, various approaches leading to modification of the morphology and composition of titania nanotubes are examined and it is presented in detail what changes in their properties this leads to. In the second work, a case of obtaining a new morphology of nanotubes

is considered. It manifests itself in obtaining closed hollow structures after irradiation of the nanotubes with laser radiation. Although no improvement in photoactivity is observed with these structures, they have specific optical properties and the potential to obtain complex composite materials.

In the following work, a method for obtaining titania nanotubes with Ni addition is developed. The deposition of nickel itself does not lead to an improvement in the electrochemical activity of the material, but such an effect is achieved after irradiation with laser radiation. It leads to a change in the morphology of the material and to modifications of the chemical composition. A significant increase (two orders of magnitude) of the current densities in anodic regime is observed. Results of basic experiments demonstrating high efficiency of oxygen evolution reaction are presented, and on their basis an explanation for the observed effect is given. The ideology presented in work 3 is expanded in work 4. In it, results of the use of other metals such as Fe, Co, Cu are presented in addition to Ni. Within a number of experiments, optimal characteristics of the obtained structures are defined, and in the next step, the efficiencies of hydrogen and oxygen evolution reactions are estimated. On the basis of detailed analyses, the obtained results are discussed, and although material performance needs additional optimization, the directions in which this could be achieved are indicated.

The general impression of the works presented is that they give a thorough picture of the process of formation and modification of titania nanotubes with a specific application as electrodes for photo-assisted electrolysis systems. A good impression is made by the fact that in all the works there is a thorough discussion of the causes of the observable properties, rather than a mere listing of the observed properties. The research can be the basis for building a complex fundamental physical picture of the properties of nanostructures and their inclusion in more complex systems, as well as for the optimization of real systems. It should be mentioned that the reliability and credibility of the presented study is confirmed in the dissertation based on comparisons with results from the literature, demonstrating a good agreement.

Based on the above-mentioned, several main contributions of the presented dissertation work can be formulated:

Obtaining and proving new data

The results of obtaining closed hollow tubes and combining them with different metals can be mentioned here. Demonstration of high efficiency of oxygen evolution reaction in structures with Ni + laser treatment is also an original and important result for applications and understanding of the physical picture involved. The conducted research presents a complex view of properties of nanomaterials, which can be effectively transferred to specific practical applications and to other systems. This expands the scope of the conducted research.

Enriching existing methods with new results

The presented possibility of modification of the morphology of titanium nanotubes and optimization of their structure and composition significantly enriches the knowledge obtained so far. A significant contribution in this direction is the detailed study of the influence of laser radiation with a wide range of parameters and the optimization of the dimensions of the nanotubes through the applied voltage. Combination of titania nanotubes with different metals and a subsequent laser treatment is also a novel recipe for their performance efficiency manipulation.

The dissertation presents declarations of each author's contribution to the publications on the basis of which it was developed. From that, and from the fact that the doctoral student is the first author in all publications, it follows that he has a significant contribution to the conducted research, processing the results and summarizing them into publications. There are four publications on which the dissertation is based. All are in well known, highly ranked journals as Nanotechnology IF = 3.874, Adv. Mater. Interfaces IF = 6.147, Sci. Reports IF = 4.379, Surface and Coatings Technology IF = 4.158. Two of the publications have citations, as the one in Surface and Coatings Technology has 10. This is a proof of the relevance of the work, credibility of the presented results, significant scientific contribution and significant interest in the subject. It can be concluded that the PhD student has acquired skills and experience in working with various analytical techniques, conducting precise experiments and critically analyzing the obtained results. As proof of this is also his co-authorship in 7 more scientific publications published in peer-reviewed journals. His active participation in international conferences shows the ability to communicate and present scientific results. He has co-authored one patent and a number of awards, which confirm the belief that the PhD student is an active and capable scientist.

The topic developed in the dissertation has significant potential for development. The obtained results are a solid basis for future development of research and applications of titania nanotubes. Potential directions are optimization as photocatalytic systems, including water splitting systems, resistive and optical gas sensors, new biomaterials.

Technical implementation, critical notes and questions

The dissertation is written clearly and it is easy for the reader to follow the logic of the research conducted.

Questions:

- The number of pulses at which the laser irradiation experiments were performed is not given. Has the influence of this parameter been investigated and what is its effect on the morphology of the resulting structures?

- Some of the experiments with laser processing were carried out in air, others in vacuum. What is the role of the environment on the electrochemical activity of the structures.

- What is the morphology of the nanotubes at a shorter deposition time? This is essential for the possible production of such structures.

- Has the efficiency of the considered electrodes been evaluated compared to the standard ones used for water splitting?

Conclusion

Based on the above, I believe that the dissertation work "Laser modification of the titania-based electrodes for energy conversion" by Jakub Wawrzyniak contains substantial contributions to the science and practice in the field of preparation, characterization and application of titania nanotubes. The doctoral student has acquired skills, knowledge and scientific experience with

which this knowledge can be effectively applied in development of the field and also in other topics. The quality of the presented research is a demonstration that the candidate has the necessary training to organize and conduct independent research at high international level. These fully cover the requirements for a scientist to obtain the educational degree "doctor". I express my convinced opinion to recommend to the Scientific Council to admit Jakub Wawrzyniak to the next stage of the doctoral procedure and finally to be awarded with the scientific degree "doctor".

Sofia, October 11, 2022

N. Nedyalkov