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Łódź, March 13, 2025

Review of the doctoral dissertation
MSc Dujearic-Stephane Kouao

Titled: "Processing and diagnostics of semitransparent photoelectrodes based on titania for energy conversion applications."

prepared under the supervision of:
PhD DSc Eng. Katarzyna Siuzdak Professor IMP PAN
(supervisor's name and surname)

1. Basis for the development of the review.

The assessment was made based on letter no. RN-421-6/24 sent by the Director of Scientific Affairs, Dr. Hab. Eng. Grzegorz Żywica, professor of IMP PAN, dated January 10, 2025.

2. Characteristics and description of the dissertation.

The industry based on advanced material technologies forces a redefinition of the current economic and technological system. Geopolitical changes that determine access to raw materials while simultaneously requiring improving performance parameters and reducing production costs pose many problems not only for a given industry but also for the technology's final recipients or users. Additionally, changing, shortening, and diversifying supply chains requires companies to make excessive investment outlays.

Such phenomena are observed, among others, in the broadly understood energy industry and related renewable energy sources. The energy industry, apart from the arms or space industry, has the fastest investment growth outlays and is a key element of the independence strategy according to the reports: ***Bloomberg: Energy Transition Investment Trends 2025, Tracking global investment in the low-carbon transition***:

Quote: "Energy transition investment Global energy transition investment has surpassed $2 trillion for the first time and more than doubled since 2020, but growth slowed to just 10.7% in 2024, from 24-29% in 2021-23. The largest sectors are electrified transport at $757 billion, renewable energy at $728 billion, and power grids at $390 billion. "All three sectors grew to new records in 2024, as did energy storage, which shrugged off headwinds to reach $54 billion."

These actions in Europe have translated into tangible savings, as confirmed by the ***European Electricity Review 2025 report, January 23, 2025, Dr. Chris Rosslowe, Dr. Beatrice Petrovich***:

Quote: "11% Share of solar in EU electricity in 2024, higher than coal; Avoided fossil fuel import €59 bn costs due to new wind and solar since 2019."

Unfortunately, the main factors that inhibit this growth are the relatively low efficiency of alternative PV cells, the periodicity of the current generation, and the frequent energy generation during periods of low consumption. This fact makes using energy storage necessary, increasing the investment cost. These factors cause many problems when creating competitive prices for the final product. For this reason, many leading research centers worldwide conduct research on materials for broadly understood energy conversion. In this case, we can mention such research centers as:

- TU Delft, EEMCS, Photovoltaic Materials and Devices, The Netherlands.
- University of Southampton, United Kingdom
- Virginia Institute for Photovoltaics, USA
- University of Central Florida. The Florida Solar Energy Center (FSEC)
- Key Laboratory of Optoelectronic Devices and Systems of Ministry of Education and Guangdong Province, College of Physics and Optoelectronic Engineering, Shenzhen University, China

In connection with this, the research topic being implemented is in line with global trends in the development of material and technical solutions to increase the efficiency of materials using the effect of solar energy conversion. These activities aim to achieve energy sovereignty in the appropriate urbanized regions, regardless of the worldwide geopolitical actions.

Based on the above, the doctoral dissertation presents the doctoral student's general theoretical knowledge in the disciplines of mechanical engineering and materials engineering and, therefore, meets the statutory requirements in this part.

The reviewed doctoral dissertation concerns the production and diagnostics of semitransparent TiO_2-based substrates with potential use as a photoanode for solar energy conversion. For this purpose, the doctoral student defined four research hypotheses:
Hypothesis 1: The optimization of the anodization conditions will allow to form semitransparent ordered titania nanotubes with aligned or spaced architecture out of Ti film sputtered onto the transparent conductive oxide substrate.
Hypothesis 2: Effective control of the tubular morphology on the both sides of the planar substrate will offer efficient and sequential light harvesting.
Hypothesis 3: it will be possible to fabricate uniform semitransparent layers of aligned or spaced titania nanotubes with well-dispersed heteroatoms in titania via anodization of Ti alloy films. Obtained semitransparent materials will exhibit superior light harvesting properties compared to the bare tubular layers.
Hypothesis 4: It will be possible to increase the incident photon-to-current conversion efficiency of the anodic tubular layers through its functionalization with laser-treated MXenes.

Leaving aside the detailed information about the technical layout of the reviewed work (the doctoral defense is public with full access to the work and reviews), it is worth noting that the research results constitute a collection of 5 scientific articles with appropriate comments and are supplemented with additional research results that were not included in them. The collection of these publications consists of:

A1. Kouao D.-S., Grochowska K., Siuzdak K.: The Anodization of Thin Titania Layers as a Facile Process towards Semitransparent and Ordered Electrode Material, *Nanomaterials* 2022, *12*(7), 1131; https://doi.org/10.3390/nano12071131

A2. Kouao D. -S., Hanus J., Kylian O, Simerova R., Sezemsky P., Stranak V., Grochowska K. Siuzdak K.: Double-sided semitransparent titania photoelectrode with enhanced light harvesting, Renewable and Sustainable Energy Reviews, Volume 197, June 2024, 114390

A3. Hankova A., Kuzminowa A., Hanus J., Sezemsky P., Simerova R., Stranak V., Grochowska K., Kouao D.-S.: TiO2/Ag nanostructured coatings as recyclable platforms for surface-enhanced Raman scattering detection, Surfaces and Interfaces, Volume 35 December 2022 Article number 102441

A4. Kouao D. -S. Hanus J., Kylian O, Simerova R., Sezemsky P., Stranak V., Grochowska K. Siuzdak K.: Photoelectrochemical and Electrochemical Activity of Anodic Semitransparent Aligned and Spaced Titania Nanotubes Formed out of Titanium–Silver Alloys, ACS Applied Nano Materials, 2024, 7 (2), 1548-1561.

A5. Kouao D.-S., Grochowska K., Strunak V., Sezemsky P., Gumieniak J., Kramek A., Karczewski J., Coy E., Hanus J., Kylian O., Sawczak M., Siuzdak K., Laser-treated MXene as an electrochemical agent to boost properties of semitransparent photoelectrode based on titania nanotubes, ACS Nano 18 (2024).

The candidate's participation in creating these articles, as presented on pages 243-244, is usually dominant. This includes developing the research concept, conducting it, and preparing responses to reviewers. I have no comments in this respect.

3. Substantive evaluation of the work.

The work is written very carefully, but I will ignore the issue of language errors. The reader is led logically through all stages of its implementation. This is also evidenced by the periodicals in which these results were published. These are journals with very high IF values. This results from, among other things, the use of many modern research methods: X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), UV-Vis spectrophotometer, scanning electron microscope (SEM), transmission electron microscope (TEM), cyclic voltammetry (CV), Electrochemical impedance spectroscopy (EIS), Linear

Sweep Voltammetry (LSV), Intensity-Modulated Photocurrent Spectroscopy (IMPS) and correct interpretation of the obtained research results. **This fact confirms the candidate's ability to conduct scientific work independently.**

The work is interdisciplinary. However, I missed a transparent structural and mechanical element in the work, which would clearly emphasize the implementation of the work in the mechanical engineering discipline. The work concerns issues related to the development of manufacturing processes, which is included in production engineering, which is an element of the discipline of mechanical engineering. **For this reason, I classify this dissertation as being on the border of mechanical engineering and materials engineering.**

Regardless of the above, the following issues require additional discussion and detailing by the doctoral student:

1. One of the key stages of the work was the deposition of ITO, TiO_2, etc. coatings on selected substrates. This process later determined the desired morphology of the synthesized nanotubes. Were any undesirable phenomena identified during deposition, e.g., dripping (spraying entire material fragments rather than individual atoms), coagulating the material on the coated substrate, etc. (chapter 6.2)?
2. The magnetron method can cause many problems with large-scale substrate modification by applying ITO, TiO_2, etc. layers for the subsequent production of nanotubes. Therefore, would other methods make it easier and cheaper to use a TiO_2 coating?
3. Are these nanotubes since their cross-sections are about 1 μm? Fig. 59 p. 98.
4. Do "exfoliated" nanotube systems interact physically? If so, were the effects of mutual polarization depending on the distance tested?
5. The diameters of the produced nanotubes were examined in the work. However, was the effect of their height on energy conversion observed? (Page 97).
6. How were the samples protected from interaction with moisture from the air?
7. Does the laser processing not change the chemical phase structure of both the nanotubes and the incorporated MXenes phases?
8. How can the photovoltaic effect be described in the produced mirror nanotube systems?

To sum up, the following achievements of the doctoral student are worth emphasizing:

1. A method was developed for producing semitransparent hybrid materials with a nanotube structure while maintaining appropriate distances between them. In this case, the produced materials were recognized by a photocurrent twice as high as a substrate overgrown with symmetrically spaced nanotubes.
2. Production of functionalized silver-modified nanotubes. The synthesized titanium nanotubes (TNT) showed an increase in the band-gap energy values of the TNT due to the incorporation of Ag atoms into the structure and to obtain a specific architecture of the synthesized nanotubes. In addition, the produced materials showed a self-cleaning effect, enabling their reuse.
3. Preparation of structures with MXenes phases has revealed an increase in the photon-to-electron conversion efficiency of about one order of magnitude compared to the unmodified TNT.

The above achievements constitute an original solution to the scientific problem, which is also confirmed by the published articles marked in the submitted dissertation A1-A5. Moreover, the obtained results are the main contribution to the ongoing CEUS-UNISONO project "Semitransparent titania nanostructures on complex geometry surfaces for enhanced light harvesting and sensing," financed by the National Science Centre in Poland, project no. 202/02/Y/ST8/00030.

4. Conclusion:

The reviewed work fits the global research trend concerning developing processes for producing hybrid materials exhibiting quantum photoconversion properties. The research's undeniable substantive value is the complete characterization of the properties of the produced composite materials constituting titanium nanotubes and the developed and verified procedures for creating materials with repeatable structural and current properties. The PhD student demonstrated independence in planning and experimenting using advanced research methods and techniques. The aim of the work was achieved (hypotheses 1-4). The obtained results contribute to further research and analysis, including research using, for example, physical and chemical modeling methods that allow for optimizing the produced materials' chemical structure and phase boundary.

In conclusion, I state that the reviewed dissertation meets the requirements of Article 187 of the Act of July 20, 2018 - the Law on Higher Education and Science (as amended). I request its admission to further stages of the proceedings for the award of the degree of doctor in the engineering and technical sciences in the mechanical engineering discipline.

Considering the high level of content, broad scope, topicality of the subject matter, and the publication of its results in journals of high scientific reputation, I classify the dissertation as exceptionally good and deserving of distinction. I request that the doctoral thesis of Mr. MSc Dujearic-Stephane Kouao be recognized as outstanding.

Prof. PhD, DSc, Eng. Łukasz Kaczmarek