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Subject : Pre-examination report of the doctoral dissertation by Mr. Jakub Wawrzyniak submitted to be awarded PhD of Institute of Fluid-Flow Machinery of the Polish Academy of Sciences (IMP-PAN).

Mr. **Jakub Wawrzyniak** has submitted a manuscript entitled "*Laser modification of the titania-based electrodes for energy conversion*" that reports on the scientific work performed at IMP-PAN under the supervision of Dr. Katarzyna Siuzdak.

The paper-based manuscript is constituted of three chapters. Each of them corresponds to one or two articles published between 2020 and 2022 in high quality journals. The three parts are organized similarly with a general introduction followed by an overview of the attached document(s). The summary can even present figures that were not published in the scientific article. It facilitates the understanding and the reading of the following paper. Finally, a short conclusion is proposed at the end of the manuscript. It would have been interesting to add some outlooks. Although the aim and scope of the thesis are clearly stated at the beginning, a general state-of-the-art would have been an added-value to the manuscript. The reader is, however, informed in the introduction of each paper. The report is clear, concise and well written.

The **first chapter** deals with optimizing the geometry of free-standing TiO_2 nanotubes (TiO_2NTs). A quick reminder on the TiO_2NTs fabrication process is given as introduction. It helps the reader to delve into the chapter. Although this group is expert in the field for a longtime, the presented findings bring significant new insights on the relation between the anodization parameters and optical or photoelectrochemical properties of the TiO_2NTs. This work lays the basis for the following. The specific tubular arrangement is peculiarly interesting because, in opposition to usual aligned TiO_2NTs, inner and outer walls are easily accessible. This leads to an interesting photoelectrochemical response.

A paper was published in **Surface Coating & Technology**.

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The **second chapter** focuses on laser-matter interactions. Mr. Wawrzyniak reports on the original morphology that they could fabricate by a well-controlled laser treatment performed after anodic oxidation of Ti. Hollow nanopillar arrays could be grown through this approach. In addition to describe, in details, the effect of several parameters on the hollow pillars' morphology, this work leads to very good photoelectrochemical performances. It also opens the way to build promising nanostructures by encapsuling another material within the pillars.

A paper was published in **Scientific Report**.

Chapter three is dedicated to water splitting. This part takes benefit of the previous findings. Mr. Wawrzyniak modify nickel-decorated TiO_2NTs by controlled laser irradiation to enhance oxygen evolution reaction (OER). This is the demonstration of the potential of the hollow TiO_2NTs. The overpotential corresponding to a 10 mA/cm^2 OER is relatively low on this system as compared to other similar electrodes geometry and composition.

A communication was published in **Advanced Materials Interface**.

The second part of **chapter three** describes further developments that were reported in the last publications. In this work, the laser-based modification technique is, indeed, applied to TiO_2NTs containing sputtered transition metal (Fe, Co, Ni, and Cu) and the electrochemical properties were assessed for both oxygen and hydrogen evolution reactions (OER and HER). The influence of the laser treatment was found to have the opposite. It promotes OER while it is detrimental for HER. A significant decrease in material resistance induces a lower overpotential (0.69 V at 10 mA/cm^2) for such nickel-modified material.

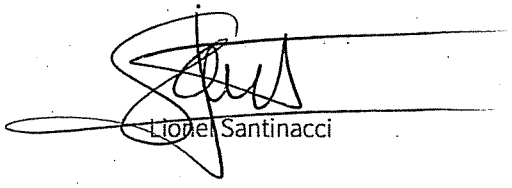
A paper was published in **Nanotechnology**.

The **conclusion** summarizes shortly the main results of the dissertation.

This manuscript reports fundamental understandings on the synthesis of TiO_2NTs and the effect of laser treatment. A unique morphology is presented. The photoelectrochemical properties constitute an evident academic interest but they can although lead to significant advancements in the PEC technology. Those findings are supported by precise and rigorous experimental works. I hope in the following work the spectacular efficiency of the hollow TiO_2NTs will be elucidated because it is a bit counterintuitive to have a higher electrochemical response with a smaller active area.

The work presented by Mr. Jakub Wawrzyniak is highly valuable. I therefore **strongly recommend** the publication of this doctoral dissertation.

Sincerely Yours,



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