Catania
July 12, 2023

Ph. D. Thesis Defense-Reviewer's report

Ph. D. Candidate: Łukasz Haryński
Doctoral Dissertation Title: "Scalable modifications of optical and electronic properties of TiO_2 nanotubes for solar electrochemistry"
Reviewer: Prof. Francesco Ruffino

SUMMARY OF EVALUATION:

	Excellent	Good	Fair	Poor
Technical quality		x		
Novelty	x			
Relevance	x			
Clarity of presentation	x			
Length of the thesis		x		

DETAILED COMMENTS ON THE THESIS:

I have carefully read with interest the thesis by Łukasz Haryński that mainly reports on: a) the synthesis and a scalable method for pulsed laser-induced structure modulation of TiO_2 nanotubes towards effective photoresponse; b) the study of the optical and electronic properties of TiO_2 nanotubes combined with thin films of chromium, molybdenum, and tungsten oxides.
In particular:

- Chapter 1 reports a general overview focused on the motivations of the work related to the global energetic issue, on the interest and peculiar proprties of TiO_2 nanotubes in connection to their use in devices constituting potential technological solutions, on planned strategies, approaches and methodologies.
- Chapter 2 reports, schematically, the objective and scope of the work, inserted within a well-focused scientific and technological framework.
- Chapter 3 describes, in a detailed and critical way, the experimental methods and approaches which appear, always, reliable and strongly founded.
- Chapters 4 and 5 report a guide to papers (chap.4) and published papers (chap. 5) based on the results and findings of the work. In chapter 5, in particular, four high-quality and interesting papers are reported.
- Chapter 6 is a conclusion and perspective chapter which closes the thesis summarizing the obtained results and step forwards with respect to the literature and briefly introducing some perspectives.

The PhD thesis presented by Łukasz Haryński is really well written, well organized and structured. In particular, the structure of the Thesis is very well cared for in detail. The new data are solid and

based on a great number of experimental results. The scientific approach is correct and always based on the attentive study of the Literature in the field. The material proposed (TiO_2 nanotubes) is duly presented in a detailed introduction where also a general framework on the nanotechnology and nanostructuring fields are presented.

Each chapter of the Thesis is always framed in the scientific literature and in the actual real-world problems. The used methodological approach is rigorous. The chosen subdivision into chapters is appreciable and renders the thesis very clear. The introduction is complete and well conjectured, giving all the fundamentals to understand the reasons behind the investigated systems and the parameters changed in the different experiments.

The candidate adopted a multi-technique approach (Scanning electron microscopy, Raman spectroscopy, X-ray diffraction, X-ray photoluminescence spectroscopy, UV-visible spectroscopy, Density functional theory calculation, Electrochemical and Photoelectrochemical tests tests), which demonstrate his capacity of taking profit of various instrumental and calculations methods. The candidate demonstrates an impressive control over the fabrication and characterization of the proposed systems. The methodology applied for the investigations presented in this thesis is adequate and all the main objectives of the proposed investigation have been reached. The strongest areas of the thesis are the high amount and high-quality data obtained, the in-depth analysis of the results, the large degree of control that could be obtained in the production of the diverse nanoarchitectures.

I conclude that the candidate for the Ph.D. degree evidences a high level of expertise, ripeness and independence, which will certainly grow as a successful independent scientist.

For all the above reasons, I think this work is excellent and worth discussion in the PhD defence.

The Reviewer, Prof. Francesco Ruffino