

## Jury Member Report – Doctor of Philosophy thesis.

**Name of Candidate:** Julijana Cvjetinovic

**PhD Program:** Physics

**Title of Thesis:** Optical and mechanical properties of diatom algae and related materials

**Supervisor:** Professor Dmitry Gorin

**Co-supervisor:** Professor Alexander Korsunsky

**Name of the Reviewer:** Prof.Vladimir Drachev

I confirm the absence of any conflict of interest.

**Date: 17.09.2023**

### Reviewer's Report

The dissertation under review studies diatom algae – unicellular microorganisms with siliceous frustule. Specific goal focuses on a combination of optical and mechanical properties of diatoms with a potential development of an artificial analogue. Quite often optical properties are strongly structure dependent, as well as their mechanical properties. Thus, both types of methods, optical and mechanical, are relevant for getting insights into materials evaluation. Through the functionalization, diatom properties and the range of applications can be further upgraded and expanded. The author involves a modification of the diatoms “fishnet” with gold nanoparticles to demonstrate material properties that can be used as surface enhanced Raman scattering (SERS) platform for sensing applications. Actual content corresponds to the topic of the dissertation work. Multiple experimental methods were used in the work which is a strength of the performed research. The thesis presents a comprehensive study of diatoms in the form of colonies in suspension, individual living diatoms, as well as purified frustules and diatomite powder.

There are quite significant scientific results in the thesis and publications related to FLIM study and mechanical properties with AFM. The thesis is based on 14th high quality publications with the key role of J. Cvjetinovic. The overall impression is very positive.

I would suggest that the author spend some time addressing issues listed below.

1. The main drawback of the thesis is the absence of detail and clearly written conclusions at the end of Chapters. Especially it concerns to Chs. 5,6,7,8. Note, if there is nothing to conclude after the presented results in a chapter, it suggests that the chapter can be omitted.

2. Several specific issues regarding FLIM results, Ch.5. (Not in the order of importance).

2a. "In living cells, the lifetime ranges from 0.3 to about 1.5 ns, because a great amount of absorbed energy is used in photochemical reactions [183]." This quote, even cited, should be explained how the absorbed energy affects the lifetimes.

2.b. FLIM images in Fig. 51-52, color bars are hardly readable. The text nearby says that life time ranges from ... to .... What does it mean? Different emitters of another reason? FLIM provides a map of life time and its variation. For instance, *K. amoena* in FLIM Fig 51 shows clear difference in life times in different locations. It is not appropriate just to say average time or life time range, in my opinion.

2.c. Another quote: "... the detection system that was used includes a 402-nm and 638-nm lasers as the excitation source and a 690-nm bandpass filter..." It makes sense to specify excitation wavelength for each image.

2.d. It must be discussed the mechanism how the fill factor of the frustule affects the life time in the following statement. "Another reason could be that in diatoms, pigments have different concentrations, and in some diatoms, they only partly fill the volume of the frustule."

2.e. One more quote: "The longest fluorescence lifetime was observed in the case of the old bacteria-contaminated culture of *E. silesiacum*, which confirms the assumption that these values may also depend on the life cycle of diatoms." That is a strange conclusion since the FLIM image for a "young bacteria-contaminated culture of *E. silesiacum*" has not been shown.

2.f. Also, here are two sentences nearby that seems contradicting each other: "Figure 52 on the left bottom demonstrates that there is no signal from the empty frustule without organic content. Fluorescence lifetime ranges from 0.4 to 0.8 ns."

3. Section 6.7 Summary says: "Static and dynamic mode AFM and in-SEM nanoindentation revealed the peculiarities of mechanical performance." Which one? More details are required.

Also: "Besides static in situ nanoindentation measurements, the behavior of the frustule was reported for the first time under the cyclic loading." What is the behavior? More specific description would be beneficial.

4. Chapter 7. No references. Fig 74 how diffraction channel was calculated versus main channel.

Fig. 83 Why x-z cross-section is shown in a different scale than y-z?

5. Sometimes the term "extinction spectra," sometimes "absorbance spectra" are used in the text. Is it intentionally done? What is the difference between spectra?

**Provisional Recommendation**

*X I recommend that the candidate should defend the thesis by means of a formal thesis defense*

*I recommend that the candidate should defend the thesis by means of a formal thesis defense only after appropriate changes would be introduced in candidate's thesis according to the recommendations of the present report*

*The thesis is not acceptable and I recommend that the candidate be exempt from the formal thesis defense*