WYDZIAŁ CHEMII
Uniwersytet Łódzki

UNIC

Łódź, 09.02.2024

Prof. dr hab. Grzegorz Celichowski
Department of Materials Technology and
Chemistry
Faculty of Chemistry, University of Lodz

**Review of the doctoral dissertation of mgr inż. Krzysztof Nadolski**
**Fri "Applications of nonlinear optics methods in sensing"**

Doctoral dissertation written under the supervision of:

Dr hab. Inż. Katarzyna Matczyszyn, prof. PWr.

Wrocław University of Science and Technology, Poland

and

Prof. Pierre-François Brevet,

Institut Lumière Matière,

Université Claude Bernard Lyon 1, France

**Choosing the topic of work.**

Krzysztof Nadolski's doctoral dissertation entitled "Application of nonlinear optics methods in sensing" fits into an interdisciplinary area of scientific research, combining nanotechnology, analytical chemistry, and potentially biomedical sciences with advanced optical methods based on nonlinear phenomena. The choice of the topic of the work is interesting for several reasons.

Nonlinear optics methods combined with nanotechnology open up new possibilities in the field of sensors, allowing the development of new detection and analysis methods that can be used in various fields, from medicine to environmental protection.

(048) 042 635 57 98
Pomorska 163, 90-236 Łódź
grzegorz.celichowski@chemia.uni.lodz.pl
https://www.chemia.uni.lodz.pl/

This work introduces a new perspective on the possibilities of using the nonlinear optical properties of nanoparticles, especially gold, which may contribute to further research and technology development in this field.

The research results give hope for their use in practical sensory applications, including detecting environmental pollutants, monitoring health status, and developing new diagnostic methods.

In the scientific and social context, this work highlights the importance of research on nanotechnology and nonlinear optics in developing modern sensor technologies, which have a wide range of applications and impact on improving the quality of life and environmental protection.

In addition to potentially applicable effects, the work also expands basic knowledge from the area of physical phenomena observed during the interaction of light with metallic nanostructures.

Due to the above, the choice of the topic of the work can be considered valuable from an application and basic science point of view.

**Purpose and thesis of the dissertation.**

The doctoral student did not formulate the aim and thesis of the work and did not present a research plan. The work submitted for review takes the form of a summary of a published series of three articles, along with a theoretical introduction and a short description of each publication. However, even in this form of doctoral thesis, in the reviewer's opinion, it is worth starting the description of the achievements by presenting the purpose of the research and expectations or assumptions as to the results of the work, which can be formulated in the form of a thesis.

(048) 042 635 57 98
Pomorska 163, 90-236 Łódź
grzegorz.celichowski@chemia.uni.lodz.pl https://www.chemia.uni.lodz.pl/

**Structure and editorial aspect of the dissertation.**

The work has a classic layout that can be expected from a doctoral dissertation presented in the form of a summary of a published series of three articles, it has 122 pages, is written in English and contains the following elements:

• Table of contents in a classic form that fulfils its functions.

• 2 pages of a list of abbreviations and symbols that fully serve its purpose.

• Summary in Polish and English.

• Introduction to the work, 40 pages long. It contains a very concise description of methods of synthesis and characterizing gold and silver nanoparticles, as well as a broader discussion of nanoplasmonics and nonlinear optics. The theoretical part ends with a short description of the applications of gold nanoparticles and optical analytical methods based on plasmonic phenomena.

• The remaining part of the paper "Results and Discussion" contains descriptions of the three publications along with their complete copies.

• A two-page summary with conclusions closing the dissertation.

• List of literature references containing 190 items.

• The work does not contain a list of illustrations.

To sum up, the presented structure of the dissertation meets the expectations set for doctoral theses, although there is some deficiency with the lack of a chapter devoted to the goals, thesis and work plan.

**Assessment of the substantive content of the dissertation.**

Considering the core of the dissertation consists of three papers published in reputable peer-reviewed journals, I assume a discussion and assessment of their content might not be targeted. Therefore, I will focus on the substantive evaluation of the doctoral work itself.

As can be deduced from the description contained in the publication "Adverse Role […]", the dissertation's author independently synthesized the nanomaterials used for the research and participated in their characterization. In this context, the introduction part concerning this

(048) 042 635 57 98
Pomorska 163, 90-236 Łódź
grzegorz.celichowski@chemia.uni.lodz.pl https://www.chemia.uni.lodz.pl/

topic appears very modest. The author did not describe the synthesis process itself or the factors determining such nanoparticle parameters as their size, shape, and distribution of these parameters.

For the studies described in the other publications included in the thesis, commercially available gold nanoparticle colloids are used. Even for such materials, it would be worthwhile to perform their characterization independently before using them for further work. In my opinion, such a minimum should include at least three techniques such as UV-VIS, SEM (preferably STEM) or TEM imaging, and DLS.

It is good practice to perform imaging with an electron microscope (SEM, TEM) at several distant points of the applied sample and to image several hundred nanostructures. Such studies will allow for a better understanding of the material, especially in terms of its monodispersity regarding both the size and shapes of the nanoobjects.

Therefore, I have a question: How do you assess the potential impact of the heterogeneity of the studied nanomaterial on the recorded optical properties?

The schematic of the HRS measurement setup presented in section 4.4.2 is quite symbolic, and it is hard to imagine the procedure for conducting measurements and the devices used therein. How are the HRS measurements related to polarization recorded?

Since, according to suggestions from the third described publication, this technique can be used for measuring copper ion concentrations in analyte solutions, I would ask for a comparison of the technical difficulties and cost of this method in relation to classic spectrophotometric measurements. Does this method have the potential to be used for measuring concentrations of other metals, and how specific is it? Would the presence of other dissolved substances in the analyzed solution interfere with its studies using the HRS technique in the context of measuring concentrations of copper or other metals?

I would also like to ask a more general question regarding the possibility of using nonlinear optical phenomena for the studies of the close environment of metallic nanoparticles in colloidal systems. One of the more interesting issues of colloid chemistry is the possibility of creating layers of organic compounds on metallic surfaces allowing for their stabilization

and/or functionalization. This opens the path to a range of important applications of gold and silver nanoparticles, including the construction of systems for targeted drug delivery (targeted therapies). However, as described regarding nonlinear optical phenomena, they occur at high power densities of the illuminating sample light. Does this not cause decomposition or photochemical reactions of the studied compounds? From reading the work and the publications attached to it, it does not emerge (or I did not find such information) how long the measurement lasts and what could be the dose of energy absorbed by the studied nanoparticles. Please provide a broader comment on this matter and take a position regarding the possibility of studying systems containing organic compounds.

Are there any limitations? Do the observed nonlinear effects change during longer measurements? Were there attempts at imaging (SEM, TEM) nanoparticles of different geometries after their exposure to laser light? If such measurements were not performed, what is the author's opinion on the usefulness of such measurements?

From an editorial point of view, the work does not raise concerns. The only weak point is the size reduction of the reproduced publications, making them practically unreadable. This forced me to download the works from the Internet to familiarize myself with them.

The literature included at the end of the work is extensive and contains many works published in the last few years, indicating its currency.

**Summary of the dissertation.**

The work ends with a summary in which the PhD student summarizes the most important achievements. The potential of using HRS methods in analytical applications was also indicated. The fact that the author of the work recognizes that many answers need to be found before this method can be more widely applicable proves his scientific maturity.

(048) 042 635 57 98
Pomorska 163, 90-236 Łódź
grzegorz.celichowski@chemia.uni.lodz.pl https://www.chemia.uni.lodz.pl/

**Conclusions.**

The presented results of the work constitute interesting and valuable scientific material with a high level of originality. The doctoral student has valuable publications, including 3 works related to the topic of the presented dissertation. Total 4 publications.

Taking into account the above facts, I declare that the doctoral dissertation meets all the requirements of the Act of July 20, 2018, Law on Higher Education and Science, and I am appealing to the Wrocław University of Science and Technology's Discipline Council for the admission of mag. inż. Krzysztof Nadolski to the next stages of the doctoral process.

Prof. dr hab. Grzegorz Celichowski

(048) 042 635 57 98
Pomorska 163, 90-236 Łódź
grzegorz.celichowski@chemia.uni.lodz.pl https://www.chemia.uni.lodz.pl/