Laurent BIGOT
Laboratoire PhLAM
IRCICA, Campus CNRS de la Haute Borne
50, avenue Halley
59658 Villeneuve d'Ascq
France
Tel : +33 (0)3.62.53.15.35
email : laurent.bigot@univ-lille.fr

To the attention of Dr. Robert GÓRA
Chairman of the Scientific Discipline Council
Chemical Sciences
Wroclaw University of Science and Technology

Object : Report related to the PhD thesis manuscript of Mr. Krzysztof NADOLSKI on the subject "Application of nonlinear optics methods in sensing"

Dear Sir,

The doctoral dissertation by Mr. Krzysztof NADOLSKI is entitled "Application of nonlinear optics methods in sensing". It reports on a thesis works that has been performed between October 2018 and September 2022, under the co-supervision of Prof. Katarzyna Matczyszyn from Institute of Advanced Materials, Wroclaw University of Science and Technology, Poland, and Prof. Pierre-François Brevet from Institut Lumière Matière, Université Claude Bernard Lyon 1, Villeurbanne, France. This work was part of the "BioTechNan" (program of interdisciplinary cross-institutional post gradual studies KNOW in the field of Biotechnology and Nanotechnology), co-founded by the European Union on the period 2018-2023.

The thesis works of Mr. NADOLSKI focused on the study of the nonlinear response of metallic nanoparticles. More particularly, the aim of this research project was to analyze the intensity and polarization-dependence of a specific nonlinear property, namely the Hyper Rayleigh Scattering (HRS), of metallic nanoparticles of various shapes submitted to various surrounding media. The originality of this approach lies in the fact that the nonlinear properties of metallic nanoparticles are often less studied than the linear ones (e.g., surface plasmon resonance) whereas they are very sensitive to shape, size and surface quality of the nano-objects. Beyond a contribution to general understanding in physics and chemical sciences, such a work also presents application-oriented opportunities. More precisely, the proposed work is above all experimental work but, as we will see, still requires some theoretical support. The aim of the work both consists of increasing the general understanding of the nonlinear properties of nanoparticles (especially the impact of their shape and their surrounding medium) and of analyzing how these properties, through their sensitivity to the nanoparticles themselves and to the environment which surrounds them, makes it possible to envisage applications in the field of sensors.

The 122-page manuscript proposed by Mr. NADOLSKI is made up of 7 sections. It is written in English and also includes an abstract written in Polish. The sections 4 to 6 contain the core of the thesis work (scientific part) while the other sections relate to complementary elements for the reader (abbreviation in section 1, abstracts in sections 2 and 3, and list of references in section 7). Concerning the scientific part, the choice was made by the author to report as is, three of the publications resulting from the thesis work, accompanied by their supplementary material. These publications constitute three sub-parts of section 5 and are each preceded by an introduction page explaining their content. Before this, the contribution of the author to each publication is clearly explained. The bibliography presented at the end of the document counts 190 references and seems very complete. The whole thing is fluid, well-illustrated and pleasant to read. The bound document which was provided to me is of very good quality. It might be interesting to increase the resolution of some images reported in the section 5 (e.g., page 80 and pages 82 to 88) in the final version so as to facilitate the reading. I will now focus my report on the sections 4 to 6.

The section 4 contains, in 39 pages, a set of general reminders on notions which might be necessary for the reader to fully understand the work proposed. It begins with a quick overview of nanomaterial manufacturing methods. Mr. NADOLSKI explains clearly that this part of the work was not the original and main point of the thesis but we understand that sub-section part is intended to give some basic elements to the reader. The reader's attention is particularly drawn to soft chemistry methods which provide access to a wide range of shapes and sizes. The presentation continues with a review of different characterization methods commonly applied to the case of metallic nanoparticles. UV-VIS absorption, electronic microscopy, zeta potential measurement and dynamic light scattering (DLS) are thus briefly presented accompanied by a few elementary equations or figures. These methods are commonly used in the community to know, directly or indirectly, the size, shape or surface condition of metal nanoparticles. It would have been interesting to have some details on the instruments used by Mr. NADOLSKI during his work. The reading continues with some theoretical reminders concerning the linear optical properties of metallic nano-objects. The notion of Local Surface Plasmon Resonance (LSPR), is thus presented and the Maxwell Garnett equation, Drude free electron gas model and Mie theory, used to explain color of metallic nanoparticles, are recalled. The general properties of the LSPR are also briefly presented. The following sub-section (4.4) constitutes the largest part of the section and concerns general reminders of nonlinear optics which will be applied to the case of nanoparticles. More particularly, Mr. NADOLSKI focuses his presentation on Hyper Rayleigh Scattering, a non-coherent version of Second-Harmonic Generation (SHG), and gives some general equations and presents characterization techniques, including polarization-resolved analysis, associated to it. He then recalls the state-of-the-art of the study of HRS of metallic nanoparticles and illustrates his point with several figures taken from literature. The section ends by some consideration on the applications of gold nanoparticles, especially for sensing, when the position of the LSPR peak or the Surface-Enhanced Raman Scattering spectra of the nanoparticles are monitored. My main regret after reading this section is that I would have liked it to conclude with a clear presentation of the problem Mr. NADOLSKI faced at the start of his work. A reminder of the scientific objectives with regard to the state-of-the-art of research on the subject would thus have made it possible to understand the intended goal which we will discover, finally, upon reading the three publications presented in the next section.

As previously explained, the section 5 is a collection of three of the author's publications (where Mr. NADOLSKI appears as first author) with some explanations in the preface. The selection of articles retained by Mr. NADOLSKI is the following:

- Paper #1 (section 5.2): *Adverse Role of Shape and Size in Second-Harmonic Scattering from Gold Nanoprisms*, Krzysztof Nadolski et al. The Journal of Physical Chemistry C 124 (27), 14797-14803 (2020)
- Paper #2 (section 5.3): *Sensitivity of gold nanoparticles Second Harmonic scattering to surrounding medium change*, Krzysztof Nadolski et al., Journal of Molecular Liquids 388, 122704 (2023)
- Paper #3 (section 5.4): *Sensing Copper(II) Ions with Hyper Rayleigh Scattering from Gold Nanoparticles*, Krzysztof Nadolski et al, The Journal of Physical Chemistry C 127 (27), 13097-13104 (2023)

This collection is preceded by a clear description of the author's contributions to the three publications. We then understood that Mr. NADOLSKI contributed at one time or another to all major stages related to his thesis work, namely:

- the preparation and structural characterizations of the samples (paper 2# and #3);
- analysis of results of characterization of structural properties of samples (paper #1 and #3);
- the measurement of the nonlinear properties of gold nano-objects (paper #1, #2 and #3);
- the analysis and theoretical treatment of the nonlinear measurement (paper #2 and #3);
- co-writing articles (paper #1, #2 and #3);
- was at the origin, with his supervisors, of the work which was the subject of the article (paper #2).

The proposed selection of articles constitutes a coherent whole which gives the feeling of a complete vision on the subject with:

- the study of Hyper Rayleigh Scattering (HRS) of non-centrosymmetric gold nanoparticles, in paper #1. Here, HRS response of solutions containing gold nanospheres and nanoprisms has been measured, together with the its polarization-resolved dependence. The first hyperpolarizabilities values deduced from the measurement for the nanoprisms appear to be lower to that reported in the literature for other nanoparticles. This suggests a strong role of the nanoparticle's surface in the case of the study, which is confirmed when normalizing the first hyperpolarizabilities values per surface unit. A discrete nonlinear dipole model has been considered in order to interpret these somewhat counterintuitive results and it is concluded that surface effects are therefore dominant for non-centrosymmetric particles while it is rather volume effects which dominate for centrosymmetric ones.
- the study of the sensitivity of the second harmonic response from gold nanoparticles to the nature of the surrounding medium, in paper #2. Unlike colorimetric approaches based on the study of SPR, this work aims at evaluating the sensitivity of the nonlinear response of gold nanoparticles to their environment (modification of the refractive index) by monitoring the HRS intensity. Nonlinear response of commercially-available gold nanoparticles dispersed in aqueous solutions with varying glycerol concentrations have been recorded and strong variation of the HRS signal is reported for small glycerol concentrations. This highlights the better sensitivity of this approach compared to a simple analysis of linear absorption changes. The HRS signal change is attributed to a modification occurring close to the surface of the nanospheres, which is confirmed by polarization-resolved analysis that does not show any volume effect.

- the study of the sensing of divalent copper ions by gold nanoparticles through the analysis of the HRS properties of solutions containing gold nanospheres in which copper(II) bromide salts are added, in paper #3. The general philosophy of this work is similar to that of the previous article, namely exploiting the very good sensitivity of the nonlinear response of gold nanoparticles to surroundings changes (especially when compare to the monitoring of the plasmon peak properties), with the aim to detect low concentrations of $Cu^{2+}$ ions. HRS intensity and polarization-resolved HRS maps have been recorded as a function of copper concentration. Based on DLS and zeta potential measurements, the hypothesis of a competition mechanism between the formation of corona-like structure around the nanoparticles (at low copper concentration) and nanoparticles aggregation (above 1 mM copper(II) bromide) is discussed. It is concluded that the sensitivity of the HRS method is particularly adapted to study low-concentration case thanks to its high sensitivity to surface effects.

In conclusion, Mr. NADOLSKI offers us the results of a work that is predominantly experimental but based on solid theoretical bases. This results in a pleasant to read manuscript, in which the results are presented in a clear and convincing manner. The research subject matter he addressed is original and he obtained new results compared to the state-of-the-art. To achieve this, Mr. NADOLSKI had to develop practical and theoretical skills in physics, chemical and materials sciences. Through this doctoral dissertation, he demonstrates that he has the general knowledge in those disciplines and that he has acquired the ability to carry out comprehensive research work by being trained in its different aspects. Considering the quality of the manuscript, the raw results obtained and their promotion in four quality international journals (Mr. NADOLSKI being first author for three of them), I issue a favorable opinion for the thesis defense of Mr. NADOLSKI with a view to obtaining a doctor's degree from the Wroclaw University of Science and Technology, Poland. I am in favor of indicating that this thesis dissertation deserves a distinction.

Villeneuve d’Ascq, February 5, 2024

Dr. Laurent BIGOT
Director of Research at CNRS