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Review of doctoral thesis
Application of nonlinear optics methods in sensing

by Krzysztof Nadolski, M.Sc., under the direction of
Prof. Ph.D. Katarzyna Matczyszyn
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Faculty of Chemistry, Wrocław University of Science and Technology
and
Prof. Pierre-Franęois Brevet,
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The reviewed dissertation is written in English in 122 pages.

The dissertation is divided into 7 main chapters. It is based on a thematically coherent set of 3 publications indexed in the Journal Citation Reports (JCR) database:

1. ***K. Nadolski,*** E. Benichou, N. Tamowicz-Staniak, A. Żak, C. Jonin, K. Matczyszyn*, P.-F. Brevet, Adverse Role of Shape and Size in Second-Harmonic Scattering from Gold Nanoprisms, The Journal of Physical Chemistry C, 2020, 124, 27, 14797-14803
2. ***K. Nadolski,*** Ch. Jonin, E. Salmon, Z. Behel, K. Matczyszyn, P.-F. Brevet, Sensitivity of gold nanoparticles Second Harmonie scattering to surrounding medium change, Journal of Molecular Liąuids, 2023, 388, 122704
3. ***K. Nadolski,*** F. Rondepierre, Ch. Jonin, T. M. Goszczynski, K. Matczyszyn, P.-F. Brevet, Sensing Copper(II) lons with Hyper Rayleigh Scattering from Gold Nanoparticles, The Journal of Physical Chemistry C, 2023, 127, 27, 13097-13104

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It is worth noting that Mr Nadolski, M.Sc., is the first author in each of the published papers. The total IF of the published papers is 13.4, which, for a PhD student's output, it is a very good result.

The work focuses on the use of centrosymmetric and non-centrosymmetric gold nanoparticles in hyper Rayleigh Scattering (HRS) phenomena. This work is part of the current research trend of understanding the phenomena of non-linear optics in depth and then using them to detect various chemical entities even in the extremely low concentration range.

As mentioned earlier, the reviewed dissertation is written in English on 122 pages and consists of 7 main chapters. In the first chapter, the author elaborates on the abbreviations used later in the text, the next two chapters are summaries, first in English and then in Polish. Chapter 4 is the Introduction, where the author describes chemical methods for the synthesis of colloidal gold nanoparticles, as well as methods used in the characterisation of nanoparticles, such as UV-Vis spectroscopy, transmission electron microscopy, zeta potential measurements and dynamic light scattering. Further subsections of the Introduction describe the issues of nanoplasmonics and nonlinear optics with special emphasis on Rayleigh hyper-scattering and the application of gold nanoparticles in this field. The last subsection also describes other sensing (detection, analysis?) methods using gold nanoparticles by nonlinear optics methods. Then, from chapter 5 onwards, the work contains the publications that form the basis of the dissertation. The very important subsection 5.1 describes the contribution of Mr Nadolski, M.Sc. to the resulting publications. As can be seen from the description, the PhD student in each case was responsible (or co-responsible) for the measurement and analysis (although always with the help of other researchers) of HRS, and also analysed the morphology of the Au nanoparticles used (based on SEM/TEM measurements). In the first two publications, M.Sc. Nadolski took a leading part in writing the text of the publication (together with one of his promoters) and in publication no.2 he was the originator of the research carried out together with his promoters. Chapter 6 of the work is a summary and conclusions.

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The publications presented as part of the dissertation constitute an interesting and logical series of publications.

In the first publication (5.2), the author describes the role of non-centrosymmetric gold nanoparticles (nanotriangles) in the HRS phenomenon. This type of system has not been studied to date, so the research presented here is characterised by great scientific novelty. Moreover, the gold nanotriangle colloids studied also contained a fraction of spherical gold nanoparticles. Based on the study, the author concludes that non-centrosymmetric Au nanoparticles, are not optimal for detection by the HRS method, due to the low value of the first hyperpolarisability, although the presence of sharp vertices may be an advantage. This raises the question of the behaviour of a system composed only of non-centrosymmetric Au nanoparticles.

The second publication (5.3) addresses the influence of the medium, specifically the refractive index, on the HRS process. Commercially available Au nanoparticles with diameters of 40 and l00nm were used for the study. Different amounts of glycerol were then introduced into the system, resulting in changes in refractive index. Interestingly, for both types of nanoparticles tested, the largest signal decrease was observed for small amounts of glycerol, while the signal changes were smaller for larger amounts of glycerol. Based on the experiments, the author presents a mechanism for the observed phenomenon - he relates the changes in the HRS response of the system to the viscosity of the solution. For small amounts of added glycerol, the first hyperpolarisation changes expotentially, while for large amounts of added glycerol we are dealing with aggregation of nanoparticles.

The third publication (5.4) describes a method for the detection of copper (II) ions by HRS using 50nm Au nanoparticles. Copper (II) ions were introduced into solution in the form of copper (II) bromide. M.Sc. Nadolski concludes on the basis of his studies that the system’s behaviour can be divided into two parts: below and above a concentration of ImM. Above this value, the aggregation of nanoparticles and the formation of dimers and trimer is dominant. Below this value, the behaviour of the system is different; the author draws conclusions on the basis of his data.

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It is the duty of every reviewer to point out minor flaws, typos or language errors. The work is written neatly, with correct language - I found only a few typos (page 10 - line 31, page 14 - line 8). The above minor typos and linguistic errors do not in any way affect the high scientific level of the reviewed work. However, in my opinion, the weakest point of the reviewed work is its title. In the English version, the title is very general and it is not entirely clear what the reviewed paper will be about, there is no information that it is mainly HRS measurements, and there is no mention of the use of gold nanoparticles. The Polish title unfortunate use of the word 'sensorics', where the Dictionary of the Polish Language suggests that sensorics is a branch of science that studies how humans and other animals interact with their environment, while the adjective sensory is used in the context of feeling through the senses. This is too much of a loan translation from the English language. The word could be replaced by another loan translation, *in sensing*, but the Polish language has other phrases, such as in demodulation, or in analysis. The title of any paper, whether scientific or not, is of course a very important matter, and an utmost care should be taken that the title prepares the reader for the subject matter covered in the paper and that it is correct. However, I must make it clear that the rest of the work stands at a very high level.

After reading the thesis, some questions of a debatable nature came to my mind and I would ask the doctoral student to address them:

1. In publication 5.2, a mixture of Au nanoparticles with two different shapes was used. What was the reason for that choice? Could the author consider a hypothetical situation where only Au nanoparticles were used for the experiment? (This immediately raises the question of the method to remove the spherical Au nanoparticles from the mixture).
2. Publication 5.4 describes a method for the detection of Cu ions^{2+} using spherical Au nanoparticles, with copper (II) bromide as the introduced analyte. Was the effect of different salts investigated (the SI shows data for copper (II) chloride, but there are many more copper salts? Was the process selective only for copper (II) ions, what other cations were tested?

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3. Based on the research carried out and the knowledge available, could the author present all the factors positively influencing the HRS process that could lead to its analytical usefulness.

I assess the dissertation very well and I am confident that it meets the requirements for doctoral theses. The research carried out is innovative, addresses very interesting issues, and fits in very well with current scientific trends. Much of the research presented was pioneering for the field in question. The dissertation is coherent, excellently planned experimentally and contains a very interesting interpretation of the obtained results. In conclusion, I believe that the submitted dissertation fully meets the requirements for doctoral theses set out in *Article 187(2) of the Act of 20 July 2018. Law on Higher Education and Science (i.e. Journal of Laws of 2023, item 742, as amended)* and I request that Mr. Krzysztof Nadolski, M.Sc., be admitted to the further stages of the doctoral thesis.

Krajczewski Jan

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