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Review of doctoral thesis by Saeid Izadshenas Jahromi titled
Plasmonic nanostructures supporting frequency conversion in atomic systems

The doctoral dissertation, submitted to me for review, was written in the Department of Quantum Physics, Faculty of Physics, Astronomy and Informatics at the Nicolaus Copernicus University in Toruń under supervision of dr hab. Karolina Słowik, prof. UMK. The thesis describes ways of nonlinear optical processes enhancement by use of specially-designed plasmonic nanostructures. The discussed processes include Raman scattering, THz emission from polar quantum systems and multi-photon absorption. The presented research is focused on theoretical and numerical modeling of plasmonic nanostructures of different shape and made from various materials. The proposed solutions have practical implementations allowing for the detection of weak signals – not possible without optical processes enhancement.

The dissertation is composed of the collection of four thematically-related published articles supplemented by an unpublished manuscript and an extensive introduction. The introduction has 50 pages and includes fundamental information on the effects studied in the articles. It is written in English with additional abstract provided in Polish. There is a brief description of plasmonic metasurfaces, followed by information on surface plasmon polaritons and localized surface plasmon resonances with examples illustrating electric field enhancement by plasmonic nanostructures, including the impact of their geometry, size and material. Next part of the introduction covers influence of the electric field enhancement on the atomic systems with subsequent part describing nonlinear optical effects, including coherent anti-Stokes Raman scattering, two-photon absorption and generation of radiation at Rabi frequency in polar molecules. It is followed by the presentation of analytical and numerical methods: Finite Integration Technique and Finite Element Method, together with the description of software used in the simulations (CST

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Studio Suite and COMSOL Multiphysics). Next, there are listed articles comprising the thesis, the other articles published by the Author (with short descriptions), summary of Author's research work, the Author's contribution statements, conclusions and bibliography. The layout and appearance of the introduction is refined, lacking only some separation between the paragraphs (indentation or space). It provides comprehensive introduction to the physics of plasmonic structures with noticeable Author's understanding of the presented information. It has also high substantive value for students as an introduction to plasmonic nanostructures. There are some minor issues like introducing graphene as a metal (on page 16), despite not overlapping valence and conduction bands, but the overall level of the introduction is high. There were also included signed declarations of all the co-authors describing their contributions to the articles in the collection. From all the provided declarations of contribution it is clear how the work was divided, with the Author of the dissertation emerging as the main contributor guided by the Supervisor.

The first article in the collection is published in APL Materials and presents research on plasmonic nanostructures for spectrally-broad enhancement of coherent anti-Stokes Raman scattering. The proposed design consists of a metasurface with a unit cell composed of two gold nanodisks separated by SiO_2 layer from a gold film at the bottom. The proposed design provides broad near-field enhancement exceeding a factor of 100 over 140 THz range. For the coherent anti-Stokes Raman scattering enhancement the metasurface aims to support independently excitation (laser) and emitted (anti-Stokes) signals and is studied in a function of the molecular position, gap size, disk radius, disk thickness, gold film thickness, spacer thickness and unit cell size. Ultimately, the predicted coherent anti-Stokes Raman scattering reaches enhancement factor of 19 orders of magnitude, significantly exceeding 10 orders of magnitude threshold for single-molecule detection. At the same time, the broadband operation of the proposed plasmonic nanostructures could support Raman signal enhancement for different molecular species with no spectral tuning necessity. The required precision of the investigated molecule placement is high – how could it be placed within the single-nanometer-wide gap? And, since it is a metasurface, what would be the impact of different molecule misalignment in subsequent unit cells? Is it possible to improve the structure design to allow for higher molecule placement inaccuracy? And would the presence of the investigated material within the gap impact the obtained results? Finally, could the unit cell size be smaller, to form gaps directly with the neighboring nanodisks, possibly providing higher signal from the illuminated area of the same size?

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In the second article, published in Optics Express, the Author investigates means to control emission from polar quantum systems, where low-energy emission is observed at Rabi frequency. The goal is to shift this signal to the THz range by taking advantage of its dependency on Rabi frequency, which can be controlled by the illumination field amplitude, and to enhance this THz emission intensity. The system is intricate but there are identified ways of obtaining these goals, which are addressed by two different plasmonic nanostructures. There are proposed silver nanorods, designed to enhance the electric field amplitude (in near-infrared range), changing the Rabi frequency and shifting the emission to the THz range. Additionally, electrically-tunable graphene microdisks are aimed to improve the THz emission intensity. The tunability of the graphene structure allows adapting to the emission energy, which depends on the strength of the field illuminating the structure. As an example in the study there is used a BaF molecule, which transition energy is matched with silver nanorods. The electric field enhancement simulations are performed for different silver nanorods radius, length and gap size between the nanorods. Similarly, for the graphene microdisks the simulations of the radiated power take into account disks' radius and electrical tuning. There is an information (on page 83) on the improved radiated power for larger radius of graphene microdisks, which, however, seems to not agree with the spectra presented in Fig. 9 – it would need clarification. For the optimized parameters of both system components there is demonstrated shift of the emission frequency to the THz range with simultaneous emission power enhancement of a few orders of magnitude. It would be interesting to discuss how realistic is fabrication of the proposed structure and what problems can appear – for example graphene disks with radii of 1 μm and the thickness of 1 nm may be challenging to produce and align. And what inaccuracy in construction of such system would be allowed? As the proposed systems requires relatively high excitation power density of 75 kW/cm^2 it would require comment not only on the silver nanorods durability (as discussed in the article) but, above all, whether the investigated molecule could withstand such high power densities.

The third article is published in EPJ Applied Metamaterials and presents, again, study of the coherent anti-Stokes Raman scattering enhancement. As a matter of fact, this article should be presented as the first position, as it shows an earlier stage of research described in the already-discussed article published in APL Materials. Here, the proposed design of the structure is similar, but instead of a gold film at the bottom, there is a grating. Its role is to provide enhancement spectral tuning by utilizing different angles of illumination of the structure. The enhancement provided by the system is simulated for different gap size between the disks, their different radius, varied grating height and for different distance between the

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grating's slabs, with rhodamine 6G as an exemplary molecule. The optimized structure provides coherent anti-Stokes Raman scattering signal enhancement of more than 13 orders of magnitude, significantly exceeding the single-molecule detection threshold. It was assumed that the surrounding medium is air, however it would be difficult to fabricate and use such a fragile structure with thickness of about 300 nm. Would the deposition of the structure on a substrate (of notable thickness) impact the signal enhancement?

In the fourth article, which is published in Optics Letters, there is proposed a way of enhancement of multi-photon absorption and subsequent emission. The structure consists of a graphene disk, which is electrically-tunable to support different number of absorbed photons, and four gold nanobars enhancing the emission. Both elements are separated by SiO_2 spacer. The electric field enhancement by the graphene disk is simulated in a function of its radius and the chemical potential (corresponding to the applied voltage). It is shown that this solution can provide electric field enhancement at the middle of the gap between the gold nanobars, where the investigated molecule should be placed. There is also investigated the influence of the gap between nanobars, their radius and length on the radiated power, with the gap size identified as the most influential parameter. The obtained enhancement is a few orders of magnitude, depending on the specific nanobars' geometry. The total effectiveness of the proposed structure is evaluated with an exemplary dye molecule, showing the enhancement dependence on the number of absorbed photons in a multi-photon absorption process with the highest signal enhancement above 13 orders of magnitude. In the description of graphene disk simulations there is initially a bit of confusion as to where the field enhancement occurs. First, the analyzed electric field enhancement seems to be located below the graphene disk (line 112 on page 97 and Fig. 1(e)), however it should be located above the disk – between the nanobars, where the investigated molecule will be located. I could not also find the red dot, which should indicate the molecule placement in Fig. 1. However, the following discussion seems to properly localize the electric field enhancement (40 nm above the graphene disk). In the final discussion part there is also mentioned that for energies corresponding to two-photon absorption, the graphene disk is no longer metallic but still providing electric field enhancement factor of about 5. What is the nature of this enhancement?

The last manuscript is an unpublished work, which was uploaded to an open-access repository. It is thematically-related to the topics presented in the articles with the research presented in the manuscript expanding the two-photon absorption and the subsequent emission enhancement analysis. Compared to the structure proposed in

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the previous article, published in Optics Letters, where the system was based on a graphene disk and gold nanobars, here the structure consists of silver nanobars, separated by SiO_2 from a silver film. The silver nanobars form a plus-shaped nanostructure with two sets of opposite nanobars of different length – one pair supporting two-photon absorption and the other enhancing the emission at two-times higher energy. Their independent and collective operation is checked with different polarizations of the incident beam. However, since the enhancement of both the two-photon absorption and the emission requires specific polarization of the illuminating beam, it may not always be the most efficient polarization for the excitation of the investigated dye molecule. There is analyzed the influence on the enhancement, provided by the structure, of different length of the nanobars, their width, the gap size between the nanobars and the silver film presence. It would be interesting to examine also the impact of the SiO_2 layer thickness on the silver film effectiveness. The system is then tuned to match three different dye molecules with the resulting overall enhancement factor above 10 orders of magnitude in the approach called "classical". The optimal geometry of the system is provided with the accuracy of 0.1 nm, which may be difficult to obtain in a real structure. To verify the assumption of the independent enhancement of the absorption and the emission processes, next analysis is performed in the quantum-mechanical approach. The enhancement is at first applied to the absorption and to the emission separately to finally simulate both of the processes simultaneously. The observed decrease of the emission due to the Purcell effect is, however, unclear. Even for the case of limited reservoir of electrons in the excited state, the Purcell effect should not decrease the emission, as compared to the free-space case, and in the least efficient case it should have no impact on the emission intensity. It is explained by the decrease of the excited state population but this Purcell-effect-driven decrease should be through photons emission, so the overall emission intensity should not be lower than in a free-space case. It needs clarification as this observation impacts the conclusions of the manuscript.

The doctoral dissertation consists of four published articles preceded by the introduction and supplemented by an additional unpublished manuscript. The introduction provides an extensive and thorough preface to the articles, explaining in an approachable way all the topics necessary for understanding the performed research. The articles comprising the thesis were published in APL Materials (Impact Factor: 5.3), Optics Express (Impact Factor: 3.2), EPJ Applied Metamaterials (Impact Factor: 1.5) and Optics Letters (Impact Factor: 3.1) with the Author always on the first position. The articles, together with the unpublished manuscript, form a thematically-related series investigating ways of enhancement of nonlinear optical processes by specially-designed plasmonic nanostructures:

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coherent anti-Stokes Raman scattering, THz emission from polar quantum systems and multi-photon absorption. The structure supporting coherent anti-Stokes Raman scattering allowed for the enhancement factor of 19 orders of magnitude and broadband operation with an additional grating-enabled spectral tuning possibility in a similar system. The emission from polar quantum systems was both shifted to THz range and enhanced a few orders of magnitude, whereas the structure with electrically-tunable multi-photon absorption enhancement led to the overall signal enhancement above 13 orders of magnitude. Finally, the structure based on silver nanobars made possible study of the independent enhancement of the absorption and the emission processes. This original research, although theoretical and numerical, aims at real experiments, including actual molecules' parameters and problems arising in the fabrication of the plasmonic nanostructures, like sharpness of their edges. The obtained results may lead to the tremendous increase of sensitivity of the optical techniques used for molecular study.

The presented doctoral dissertation clearly shows that the Author has developed the ability of performing independent research and has an extensive knowledge on the theory of the plasmonic nanostructures and the underlying physics. The performed research and its results are original solutions of scientific problems and I request that Saeid Izadshenas Jahromi be admitted to further stages of the proceedings. Furthermore, taking into account a high level of the performed research, which was published in high-impact scientific journals and with clearly main role of the Author (especially the articles on the coherent anti-Stokes Raman scattering in APL Materials and on the THz emission from polar quantum systems in Optics Express) I request that the dissertation be distinguished.

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