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Review of the doctoral dissertation:

“Plasmonic nanostructures supporting frequency conversion in atomic systems”

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The topic of the presented thesis is a theoretical study of the influence of plasmonic nanoantennas and metamaterials on nonlinear light-matter interaction, with particular focus on Raman scattering and multiphoton absorption. The work has been written under the supervision of prof. Karolina Słowik. The Author specifies five articles comprising the thesis, all of them from last two years. Three papers are published in very good journals with high impact factor (Optics Express, Optics Letters, APL Materials), one is currently under review. Apart from that, there are 5 other works, published mostly in post-conference materials. In total, according to Google Scholar, all of the papers have been cited 50 times, and the Author has a H-index of 3. This seems fairly typical for this stage of career. However, it should be noted that 37 out of 50 citations can be attributed to one paper from 2018, which was published before doctoral studies and is not considered to be a part of the thesis.

In general, the presented results are new and fairly original. Analysis of Authors’ and co-authors’ declarations leave no doubt that the Candidate’s contribution to these works was significant on all stages of writing and publishing. In terms of novelty, the various nanostructures developed by Author are an improvement upon existing ones, incorporating some new features such as multiresonant elements. The methods employed in their analysis are fairly standard. Ref. [20] is notable for dealing with quantum systems characterized with permanent dipole moments, which is a new and pretty unique subject as far as I could tell (there are some papers on it dating back to 1997 [Optics Communications 140 (1997) 89-92], but not many of them).

The thesis begins with a short introduction (32 pages) about key physical phenomena relevant to the presented papers as well as a brief overview of numerical methods employed in the commercial software used to perform some calculations. Then, it is followed by Author contribution statements, conclusions and pretty extensive bibliography (77 positions). Oddly, bibliography is missing in table of contents. Rest of the thesis consists of the five publications. The structure of the introductory part is logical and it Is written in an understandable way. However, there are some issues, as outlined below.

A minor problem is that some statements are incomplete or imprecise. For example, (page 12) "In this work, to ensure a fair comparison, all calculations are performed numerically using commercial software such as CST and COMSOL"... Fair comparison to what? (page13) "the field can deeply penetrate the nanosphere's metallic bulk, where the absorption appears" - This is an imprecise statement; "we introduce (a comparison?) how much the size of particles affects the optical response."; (page 20): "The spontaneous emission enhancement can then be evaluated as the ratio of total dipole powers near the nanoparticle and in free space" – I'm not familiar with the term "dipole power". Is that power of dipole radiation? (this is only clarified later, in section 1.5.3). Also, in cited Ref. [3], this enhancement is expressed in terms of displacement field **D**, which further increases the confusion whether power or polarization is discussed here. Side note, Purcell factor is often expressed in terms of effective mode volume, which can be readily calculated from energy density of the EM field in the system; any comment on applicability of such approach to studied cases? (page 23) the statement "…the presence of atomic systems near nanoparticles unlocks frequency conversion. As a result, a signal is generated in a background-free scheme, that signalizes of the occurrence of the considered process." is very confusing. (page 24) "Coherent anti-Stokes Raman scattering (CARS) is a nonlinear four-wave mixing process that has a higher sensitivity compared to Raman scattering" – an short explanation why CARS has higher sensitivity would be nice. At first glance, relying on third-order nonlinear effect dramatically lowers the output signal, and thus sensitivity? (page 25) "Two-photon absorption (TPA) is a nonlinear optical process where two photons simultaneously interact with a molecule, exciting it from the ground state to the first excited state, and then the molecule emits a photon as it returns to the ground state, producing fluorescence." – second part is not two-photon absorption anymore.

Some parts are not sufficiently explained. Example results are presented, but there is no discussion or insight into what they mean and why they are such. On page 14: "As suggested by Eq. (1.22), the geometry of plasmonic nanoparticles significantly influences their optical properties and plasmonic behavior." - It is clear that polarizability of a spherical particle depends on its radius, and all the following parameters such as RCS and ACS are radius-dependent accordingly. However, by "geometry" the Author means also shape of non-spherical particles, as evidenced by Fig. 1.6 discussed here. In such a case, it is hard to say how exactly Eqs. (1.22)-(1.28) relate to these systems. Indeed, the Author states that "Different shapes such as Plasmonic nanostructures supporting frequency conversion in atomic systems spheres, rods, cubes, and more complex geometries exhibit different plasmonic characteristics due to variations in their surface charge distributions influencing their interactions with the electromagnetic field". In general, section 1.2.5 is a little short and vague. Of course, there are no analytical solutions for these shapes, but some insight into why some particular shapes are better than others would be appreciated. Later, page 16, eqs. (1.30)-(1.33) - some symbols such as tau are not explained here, only later they are given some values but still without explanation.

Moreover, I have several questions regarding some assumptions and results. On page 18: "Fabricating individual nanoantennas presents greater challenges compared to the metasurfaces, due to the smaller size scale." - Aren't individual elements of metasurface just as small? Related to that, I have several questions regarding Fig. 1.9:

-Does the specified size (352 nm) apply both to single antenna (d) and metasurface element (a)?

-The advantage of metasurface, both in terms of bandwidth and field enhancement, seems rather small; is there really any advantage?

-It is expected that individual elements of metasurface will have some variability in size. How much of broadband advantage comes from that? This is a general comment about all numerical results. Actual, fabricated nanostructures are never perfect; is the possible variability in various dimensions taken into account? This is particularly important considering the pretty bold claims regarding signal enhancement; the proposed nanostructure may very well be a “one-point wonder”, so to speak. A good illustration of this is Fig. 5 in reference [9], which displays an array of seemingly identical nanostructures, and yet the measured SECARS signal varies greatly between them. In general, all of the Author’s papers contain some discussion of the impact of various dimensions of the system on its performance, but how about imperfections/uneven shapes?

In section 1.3, the Author discusses the coupling between plasmons and atomic systems. An electric dipole approximation is used, where the size of the atomic system is assumed to be much smaller than the spatial variation of electric field. However, given the significant confinement of the plasmon field and the fact that the “atomic emitter” can represent an entire molecule, the validity of the assumption is not obvious. The Author briefly mentions some papers about extension of dipole model [42-45], but I’d like to hear more about it; specifically how well the assumptions hold in the cases analyzed in the five papers contributing to the thesis. For example, in the Author’s APL Materials paper [18], The plasmonic structure features a 3 nm gap where field is focused. In this gap, field strength is highly variable on sub-nm scale. The proposed application involves Rhodamine 6G ($C_{28}H_{31}ClN_2O_3$) organic molecule, which is quite large; according to [J. Bain et al, Journal of Chemical Physics 112, 23 (2000)] it is about 1.6 nm long, so it seems it would barely fit the gap?

Equation (1.43) shows the total enhancement factor of SECARS process as a product of individual enhancements of emissions/absorptions. This is only true when all the probabilities are statistically independent. How well does this assumption hold? By significantly enhancing every constituent process, the Author claims a total enhancement factor of 10^{20} in his paper [18], which seems somewhat optimistic; in supplementary material, there’s a comparison with earlier works; most of them are characterized by less than 10^{10} enhancement factor and only one theoretical study comes close with 10^{18}. Indeed, In that study, they claim 10^{6} improvement over other similar nanostructures, which seems a little dubious. Such a huge amplification raises a few questions:

-does this imply that the process is basically impossible to perform without enhancement?

-how such enormous amplification affects noise? Aren’t external factors such as thermal radiation a problem?

The discussion of numerical methods is very brief but pretty well written. However, in the finite integration technique section, there’s no mention of numerical accuracy, stability or algorithmic complexity. In short, nothing that could allow the reader to evaluate the strong and weak points of the approach. A comparison to other methods, such as FDTD, would be nice as well. Given how important this tool is in obtaining results in all Author’s manuscripts, this section should warrant more attention. I’d like to hear more about the features and limitations of the algorithm, in particular the issues of above-mentioned accuracy, stability and numerical complexity. The second section about finite element method is very general and has no mention of where this method is applied – to what kind of problems?

In conclusion, despite some minor issues the presented work is a good overview of the Author’s research subject, it is written in a clear way and definitely meets the criteria for doctoral dissertation. The Author clearly understands the discussed topics and his skill with designing plasmonic nanostructures and using various numerical tools to analyze them is evident.

I conclude that the presented dissertation meets the formal requirements for a Ph. D and is a new and original contribution to the field of nanostructure-enhanced Raman scattering. I recommend admission of the candidate to the subsequent stages of the procedure, including the public defense.

Przedstawiona praca spełnia wymagania ustawowe stawiane rozprawom doktorskim i stanowi nowe, oryginalne podejście do projektowania struktur plazmonicznych stosowanych w badaniach rozpraszania Ramana. Wnioskuję o dopuszczenie doktoranta do dalszych etapów przewodu doktorskiego.