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Evaluation report on the Doctoral Dissertation submitted by Marta Gordel, entitled: "*Synthesis, optical studies and functionalization of plasmonic nanoparticles for biological applications*".

The dissertation submitted by Marta Gordel focuses on various aspects related to applications of metallic nanoparticles in biology. Definitely, this topic is highly important and the context of this research is well embedded in current efforts of implementing nanotechnology in medicine. Carrying out such an interdisciplinary research project, which is located at the interface between chemistry, biology, and advanced spectroscopy techniques, is highly demanding an requires exceptional motivation and determination. Particularly important is continuous quest for learning new techniques of synthesis, structural and optical characterization methods, and finally applications of nanostructures in cellular systems. The research described in the thesis unequivocally shows that Marta Gordel, in the course of her PhD studies, has been able to achieve this ambitious and challenging goal. The research was carried out in two groups led by prof. Marek Samoć at the Wrocław University of Technology in Poland, and prof. Malcom Buckle at the Ecole Normale Superieure de Cachan in France, both of which have provided excellent environment for studying both the basic properties and applications of metallic nanoparticles in biological systems. And this I can see as the key achievement of the thesis prepared and presented by Marta Gordel. Namely, the development of the whole pathway, which starts from synthesis of nanostructures, then continues through manipulation of these nanostructures either using external fields or chemical functionalization, in order to reach the level of becoming imaging agent in cells, is truly amazing and very rare among PhD students not only in Poland but also internationally.

Equally important is the ability to publish research in internationally renowned journals, in particular at such an early stage of research career. I do understand, that part of this success is owed to great supervision, but 9 publications during PhD studies is an outstanding result.

In addition to this strong publication record, and I should mention here, that the results of many of these publications are included in the thesis, Marta Gordel frequently and actively participated in international conferences, presenting her work with enthusiasm and confidence. Furthermore, many results obtained in the course of her PhD were the outcome of collaborative efforts, also internationally. The ability to create such cooperation and maintain it at the fruitful level is extremely important in carrying out interdisciplinary research at the competitive level. All these aspects of scientific activity clearly show that Marta Gordel has developed the complete spectrum of knowledge and capabilities necessary to successfully pursue research career.

The research results described by Marta Gordel in her thesis are with no doubt of high quality and interest to the community. However, for some reason even Marta herself did put no particular emphasis on any of the results, making them in turn quite equally leveled with respect to each other. From one point of view this is surprising, as one could expect that a PhD candidate at the end of the studies should be able to pinpoint her/his major achievement and try to let the world know what it is. On the other hand, I can easily understand this somewhat egalitarian approach of Marta Gordel, who treats each and every of the results with equal attention. In my opinion it stems from the ladder-type character of this thesis, where in order to reach the next step, it is absolutely required to climb all the preceding steps, making them equally important and vital of achieving the final goal, if anything like this ever exists. In other words, whether we talk about synthesis and functionalization of gold nanorods or nanoshells, studying their properties in strong laser fields, understanding their non-linear properties, or applying these nanostructures in cells, we should realize and appreciate huge amount of work, dedication, patience, required for completing each and every step. And this knowledge, which is the sole privilege of Marta Gordel, perhaps makes all of the results included in the thesis equal for her. And this choice, whether conscious or not, must be appreciated.

If I were to make such a distinction, and to select the result obtained by Marta Gordel that should be considered the most important, I would also have a problem. But the origin would be – and in fact is – different. The thesis is composed of several important, mutually connected demonstrations/observations, and – as I mentioned above – all these were necessary to complete the work. But disappointing to some degree is that none of these effects is studied more systematically, to a degree that would allow to make some coherent interpretation or prediction. Perhaps the section that has the strongest flavor of coherence concerns the studies of non-linear properties of silica nanospheres with varied thickness of gold nanoislands. However, also in this case the interpretation stops at barely stating the fact of having the best properties for a structure with the thinnest Au shell, without any attempt to discuss this result in

the context of varied morphology, light absorption, etc. This is what I consider one of the major weaknesses of this thesis.

Another example of such generally inconclusive result is observation of laser-induced modifications of gold nanorods. The choice of nanorods seems to be quite accidental, in particular since the laser light of 800 nm wavelength was used, which does not correspond to any of the plasmon resonances of the nanorods. It would be highly interesting to try to probe the influence of high-power laser on the nanorods with varied morphology. Such systematic research would perhaps allow to make more general conclusions about the observed phenomena, extending beyond pure phenomenology. One of the obvious questions is why the dependence of intensity at 800 nm on the number of laser shots should be described with an exponential function? On a more formal note, it is not clear, what the numbers given in Fig. 45a mean (1.449 and 1.040). Also, in regard to this chapter, I do not understand how the values of average aspect ratios were obtained. Obviously, they cannot be derived from the data given in Table 1. It would also be extremely helpful to provide full datasets of nanorod morphology, in the form of histograms, for instance.

This remark brings me to the second key issue of this thesis. While Marta Gordel was extremely successful in publishing her research in regular articles, she decided to construct her PhD thesis as a compilation of articles. There are many unwanted and unfortunate implications of such an approach. I will list just a few of them, but I believe they provide sufficient evidence that extreme care has to be taken in the process of compiling separate works into a single – presumably coherent – thesis.

a) There is no abbreviation list, and as a result, A denotes both absorbance and a parameter in equation 5.
b) Introduction is extremely brief and there are many aspects that are missing or described inadequately (e.g. dielectric functions of metals should be shown). I admit that this is one of the major difficulties of highly interdisciplinary work to include sufficient information in the introductory chapters to allow for understanding the content.
c) I am not fully convinced that the excitation in a metallic nanoparticle with a size less than the wavelength of light can be described and surface plasmon resonance, as written in several places in the thesis.
d) The chapter, where experimental techniques are described, contains only the presentation of the Z-scan and time-resolved luminescence. Thus, it was highly surprising to find that at various places throughout the thesis, a number of other experimental techniques was used (atomic force microscopy, transmission electron

microscopy, confocal fluorescence microscopy, etc.). As a result, the description of all these techniques is very brief, journal-style. But more importantly, such non-structured structure makes it rather difficult to follow the experiments that are of varied character and complexity.

e) Subchapter V.3, where non-linear properties of organic dyes are described, breaks the coherence of this work. Neither these dyes nor the results are used elsewhere in the thesis, the context for including these experiments is completely unclear.

f) Final, and perhaps one of the most important consequence, of structuring the PhD thesis as a compilation of research articles, concerns very sterile presentation of the results, as well as its strong selectivity and lack of showing statistical data. In addition to showing histograms of length, width, aspect ratio of Au nanorods (mentioned above), it would be highly interesting to see more AFM images, similar to the ones displayed in Fig. 79, more TEM images, similar to the ones displayed in Fig. 54, and alike.

g) Inclusion of numerical simulation (which were not done by Marta Gordel herself) in many of the chapters, as they were also part of the papers/manuscripts, is also disputable. In fact in the context of the results presented in the thesis, the results provide minute information, or at least this is not readily noticeable. I do not understand why the chapter of aligning nanorods, where essentially microscopy images are shown, should end with the result (standard and expected) that there are hot-spots forming at the connection points. But what is really curious, is the origin of strong asymmetry of electric field distribution in the case of Au nanoshell (Fig. 67). It is not clearly explained in the text, while it is quite counterintuitive.

h) Regarding the results discussed in Chapter V.2, I would like to ask about checking whether the properties of both nanorods and nanoshells were indeed unaffected during the measurement. Also, it is not clear why such nanostructures were selected for these studies and how the results can be extended toward other similar systems.

i) The final critical comment I would like to make concerns the results obtained for Au nanorods conjugated with Cy dyes using DNA. Typically, in order to observe fluorescence enhancement due to increase of fluorescence quantum yield, it is required to use metallic nanoparticles characterized with plasmon resonance at wavelengths shorter than the emission of a fluorophore. In this work the choice is reversed. Furthermore, the analysis of fluorescence decays is extremely vague, despite the fact that the TCSPC technique was described at length. I think that in order to make the numbers listed in Table 7 convincing, presentation of both, the raw

time-resolved data and analysis thereof is absolutely required, particularly since the analysis seems to be not straightforward (i.e. the decays seem not to be single exponential). It is also not clear, where the errors of estimating fluorescence decay times originate from. Obviously, the data displayed in Fig. 82 is not in agreement with the numbers given in Table 7, and the values of quantum yield are not plotted as a function of separation between nanorods and Cy dyes.

There are of course typos, grammar and stylistic errors throughout the thesis, but I would say, this is natural and expected. I decided not to list them in the report.

Summing up, I value the science described in the thesis of Marta Gordel very high, in general all of the results are original and interesting to the community. However, I believe that the choice of presentation of these results is quite unfortunate, and some negligence in keeping the thesis coherent, decreases somewhat my very positive opinion thereof. Nevertheless, with all confidence, I know that Marta Gordel is a highly-qualified, young scientist with virtually unlimited potential of tackling the most difficult, thus interesting problems in interdisciplinary science, and of searching for answers to key questions. She deserves with no doubt the award of the PhD degree.

S. Maćkowski