UNIVERSITY OF CHEMISTRY AND TECHNOLOGY, PRAGUE
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The Habilitation Thesis Review

Title of the habilitation thesis: **Isotopic labeling and in situ Raman spectroscopy in graphene research**

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Name of the reviewer: prof. Dr. RNDr. Pavel Matějka

The habilitation thesis of Dr. Kalbáč entitled "*Isotopic labeling and in situ Raman spectroscopy in graphene research*" is focused on novel graphene 2D materials and their investigation mainly using Raman scattering spectroscopic techniques. Hence, the habilitation thesis deals with a progressive interdisciplinary area of material and spectroscopic science combining (i) advanced techniques of 2D graphene materials preparation including isotopic labeling and rational modification, and (ii) structural and chemical analysis mainly focused on Raman spectroscopy/microspectroscopy.

The habilitation thesis covers 40 pages commenting on the general aspects and key results of 30 collected publications of the author. The introductory part comments graphene layered materials and the structure of the habilitation thesis. The second chapter describes the studies on single-layer graphene starting from preparation of samples to showing the role of Raman spectroscopy (especially in the context of graphene doping, strain effects and general interactions with the supporting substrate) and emphasizing some key results. The third chapter is about graphene multilayers emphasizing the usefulness of isotope labeling to study various properties of the multilayered systems, e.g. their growth, doping, the formation of defects and functionalization of graphene layers. Two short subchapters are related to (i) the enhancement of the signal by surface-enhanced Raman scattering using a gold nanolayer and (ii) the formation of sandwich structures. Finally, relevant conclusions are drawn and future prospects are mentioned. The text is well-structured, readable and accompanied by relevant figures. It demonstrated the excellent expertise of the author. Nevertheless, from my point of view, the description is sometimes quite phenomenological. I miss critical comments related to the collection of commented studies and some consequential discussion in individual chapters. It is clear the author is an outstanding expert in the field of Raman spectroscopy of graphene materials with a very broad knowledge of physicochemical consequences. However, I guess that the information from 30 commented papers could be reviewed more analytically to provide a new perspective view. Of course, the thesis contains the concise chapter "Conclusions and outlook" with relevant comments which I appreciate.

Regardless of some critical comments, the thesis is a novel and brilliant contribution to the notable and rapidly developing field of graphene materials demonstrating the importance of their detailed chemical/structural analysis by spectroscopic and microscopic techniques. I would like to say, that I recommend the habilitation thesis for further procedures (see the conclusion).

Comments and questions

1) Single-layer graphene is introduced as the archetype of 2D materials without their clear definition. Of course, "Mathematics is good at rigorous definitions, but this isn't mathematics; it's chemistry and physics," says Boris I. Yakobson, a Rice University theoretician and materials scientist who studies 2D materials. "It's good to have definitions, but often, they're not flexible enough to reflect reality." (https://cen.acs.org/articles/95/i22/2-D-materials-beyond-graphene.html). Nevertheless, I guess that some short comment on the general definition of 2D materials can be helpful for the reader (see the weblink mentioned above, or some other web pages:

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https://www.nature.com/subjects/two-dimensional-materials, or http://pubs.rsc.org/en/Content/ArticleLanding/2011/NR/C0NR00323A#!divAbstract).

2) The reversibility of strain and doping effects is mentioned in chapter 2.3. What is the extent of reversibility? How it can be viewed from the thermodynamical point of view and considering the mechanisms of doping and strain effects? The role of substrates is mentioned in the chapter. What is the role of substrate surface morphology? Are there "flat substrates" in the nanoscale?
3) Frequency shifts and intensity changes are mentioned in chapter 2.3.1. I would like to ask about the evaluation of half-widths of bands (see chapter 2.3.1 and for example Fig. 3). What is your opinion about the use of some multivariate statistical data algorithms for data evaluation and interpretation?
4) An illustrative figure should be helpful in chapter 2.3.3 or a link to Fig. 5 which is related to the topic discussed in chapter 2.3.3.?
5) I guess that the preparation of well-defined mixed layers containing a specific ratio of ^{12}C and ^{13}C is not simple. What is the (spatial) distribution of the two isotopes in the mixed layer? Is there some evidence of clustering of the atoms of individual nuclides? Did you observe some "clustering" using Raman microscopy? Do you suppose that some TERS mapping experiment will be helpful to investigate structural details of mixed layers?
6) I would like to ask what is the future of composite materials containing graphene layers and metallic plasmonic nanoobjects.
7) I miss a list of abbreviations and symbols. There are a lot of abbreviations in the text and it is helpful to summarize and to explain them in one place.
8) Some minor mistakes occur in the case of figure captions. I miss a detailed description of the figure content in several cases. Especially, the data given in Fig. 3 should be described in details. The colors used in Fig. 5 are not optimal for me as the reader.

Conclusion

The habilitation thesis provides a lot of original and significant information about the topic demonstrating the outstanding expertise of the author in the field of graphene materials and their advanced Raman spectroscopic investigation. **I recommend** the habilitation thesis for further consideration of the habilitation board and the scientific board of the faculty and **I recommend** to award to RNDr. Ing. Martin Kalbáč, Ph.D. the title "docent" ("associate professor") in the field of inorganic chemistry.

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