



Opponent's review on the PhD dissertation

"The effect of the preparation conditions on the photocatalytic H₂ production of noble-metal free Zn_{0.75}Cd_{0.25}S semiconductors"

by Maali-Amel Mersel

Maali-Amel Mersel – supervised by Prof. Ottó Horváth and Dr. Lajos Fodor – submitted her PhD dissertation to the Doctoral School of Chemistry and Environmental Sciences in the branch of Chemical Sciences. The dissertation summarizes the work that she carried out at the Center for Natural Sciences, Environmental Photochemistry Research Group of the University of Pannonia. In my preliminary evaluation, I have already explained that the topic of the dissertation – photocatalytic H₂ evolution from alkaline aqueous solution of sulfide – is highly relevant. I agree that CdS would be an excellent photocatalyst. However, as the Candidate correctly highlights, the toxicity of Cd cannot be omitted and complicates a broader use. Such problems had not been always considered before implementing new technologies and thus, our society is now facing serious consequences of mass occurrence of polymers, persistent drugs, toxic waste in sweet water and soils. The 'dilution' of Cd using Zn seems to be a reasonable approach to mitigate this issue, and the Candidate in her dissertation showed convincing results that the photocatalytic activity of 3Zn:1Cd sulfides may be improved by applying a Ni-based co-catalyst. In the Conclusions, the Candidate summed up her achievements to the point and I would not repeat those here.

First, the publication requirements with the two first-authored papers in two acclaimed, international, peer-reviewed journals are fulfilled. I underlined in the preliminary review that the work was carried out systematically, the Candidate's – and that of the group behind – scientific logic and depth of insight in photocatalysis and material preparation methods are very convincing. The same applies to the safe handling of modern analysis methods. I highlight again that for me, the calculations on the precipitation driving forces were the most remarkable achievements beyond the fact of finding efficient photocatalysts. I found this part especially interesting as this careful consideration is rarely seen in the literature.

Second, the dissertation is precisely constituted, both the text and the illustrations are focused to the main points. The 120 numbered pages – including a ToC, a short abstract and introduction, a literature review on 29 pages, research objectives, experimental descriptions and calculation methods on 10 pages, discussion of the results on 49 pages, conclusions on two pages, a list of 139 relevant literature references, figures, own publications and conference appearances, and the five thesis points – fulfill the formal requirements of the doctoral school. All structural elements of the dissertation, especially the insightful literature outlook, place the new achievements in right scientific context.

In my preliminary review, I made a list of remarks and I thank the Candidate for carefully considering all concerns before submitting the final version. Now I failed to find typos, mistakes or editing issues in the final dissertation. Thanks to the improvements she made,



the result can be set as a good example both in terms of appearance and professionally edited contents.

Lastly, I accept all of the thesis points as new, independent scientific results. Her statements are appropriately supported by the results. I made some formal suggestions in the preliminary evaluation, and the candidate considered and wisely modified the points accordingly.

My questions to the candidate:

1. Figure 4.13 - Good that the inhomogeneity was studied and discussed. Could the nanoscale inhomogeneity be the reason for the differences in literature RHP values despite the same average composition?
2. Chapter 4.2.2 - The hydrothermally treated catalysts were not much effected by the presence of Ni on the surface. Does the inefficitive co-catalysts indicate that charge extraction is not the rate limiting in RHP?
3. Among preliminary results, the effect of Ce is discussed. What is the possible explanation of the positive effect of Ce?
4. Eqns. 7-10 and also, chapter 3.4 raised a question in me - what is the energy balance of using sulfite as sacrificial oxidant? What else could be used in practice to remove sulfur deposits, are there any viable alternatives? Is thiosulfate a useful product?

Altogether, the Candidate's results as presented in the dissertation and the thesis points leave no doubt, that she can earn PhD in Chemical Sciences. Her work is a remarkable contribution to hydrogen-producing Zn/CdS photocatalysts, in which she devoted attention to the effect of Ni-based co-catalysts. The dissertation and the theses are suitable for a final defense.

I, the undersigned, declare that I recommend the PhD thesis for acceptance.

Budapest, 24th of March 2022

József Sándor Pap
opponent