Review Report on PhD Thesis of Maali-Amel Mersel

entitled

„The effect of the preparation conditions on the photocatalytic H_2 production of noble-metal free $Zn_{0.75}Cd_{0.25}S$ semiconductors”

The PhD Thesis is dealing with different synthesis methods and thorough characterization of $Zn_{0.75}Cd_{0.25}S$ type photocatalysts with high visible light activity for hydrogen production. The Candidate explored the influence of many synthesis parameters on the photocatalytic activity, such as the molar ratio of ammonia and the metal precursors, the pH of the precursor solution, the zinc and cadmium molar ratio, the order of mixing of the reactants, the hydrothermal treatment. The photocatalysts were also additionally metal-modified with different metal ions. The photocatalytic activity was tested by monitoring the hydrogen evolution with an interesting gravimetric method from the solutions containing Na_2S, Na_2SO_3 and $Na_2S_2O_3$. The tests involved the precise determination of the apparent quantum yields with different light sources, including UV and visible LEDs, and an Hg-Xe lamp. The samples were characterized with many techniques, including ICP, SEM, DRS, XRD, TEM, and STEM-EDS. The best efficiency was found to be 14.9 % quantum yield at 380 nm irradiation when the surface was modified with 0.1 % Ni(II) ions that was mostly in NiO and $Ni(OH)_2$ form on the surface. The re-usability of the photocatalysts and their high activity after long term (12 months) storage was also confirmed. The PhD thesis is very well written, proportionally structured in a detailed Literature chapter (30 pages), *Experimental Part* and *Results and discussion* chapters (50 pages). The selected 139 references are well representing the literature. The thesis points are summarized in a straightforward format. Very briefly, the Candidate determined the key preparation conditions that affect the photocatalytic hydrogen evolution efficiency of the composite; the relationship between the structure and the photocatalytic activity of the unmodified $Zn_{0.75}Cd_{0.25}S$ catalyst by several techniques; the modification

of $Zn_{0.75}Cd_{0.25}S$ catalyst with Ni(II) increased its photocatalytic efficiency; provided an explanation of the efficiency-enhancing role of Ni(II) and both unmodified and Ni(II)-modified catalysts were shown to be stable in several catalytic tests, even after long term storage.

The research was performed at the Environmental and Inorganic Photochemistry Research Group (Faculty of Engineering, Center for Natural Sciences, University of Pannonia) supervised by Dr. Ottó Horváth (DSc) and Dr. Lajos Fodor (PhD). The Candidate learned many characterization techniques, evaluation methods and proved her ability to use them in research. The results were published in two articles in high impact journals and presented on several conferences. It is very important that Candidate also considered potential health and environmental risks with the cadmium containing photocatalysts when suggesting the optimal composition. The topic is very important and the Doctoral thesis provide significant contribution to the research field of visible light driven photocatalysis for hydrogen production by eliminating toxic H_2S.

I have few questions and remarks:

1. How did the Candidate select the concentration of the photocatalyst suspension for a given irradiation power in these experiments?
2. It is mentioned that *„The illumination was always started at room temperature, which increased to about 45 °C in the first hour of illumination."* (Page 40). Do we consider the higher temperature beneficial for the hydrogen production in these photocatalytic systems? This might be important for solar photocatalytic applications.
3. On page 41, it is indicated that *"In this case, irradiation was applied for the deposition of Pt and it was finished within the first 8 h of illumination (under the circumstances used for hydrogen generation)."* Did the Candidate use any material characterization technique for checking the photoreduction of platinum on the surface? Is it in metallic platinum form?
4. In Figure 3.4, the effect of stirring is presented on the Rate of H_2 production (RHP) and the volume of the evolved H_2 gas (page 47). The green curve represents the values measured with stirring. It is indicated however with a dashed line that the stirring was stopped at about 3.5 hours of irradiation. This resulted in a relatively rapid decrease in the rate of H_2 evolution from 130 μmol/h to 25 μmol/h. In the same time period the data points without stirring show higher H_2 evolution rate values. What is the explanation for this difference? Supposedly, the stirring was then re-started in about 15 minutes that caused the reaction rate to increase to 100 μmol/h level (green curve). What is the reason for the lower H_2 evolution rate compared to that measured for the non-stirred photocatalyst suspension (red curve)?
5. How fast is the sedimentation of the photocatalyst particles without stirring? Did the Candidate apply stirring during the QY determinations?
6. In Figure 4.2. (page 52) there is an initial rapid increase in the H_2 evolution rate that is considered as a result of the oxo/hydroxo surface groups being replaced by sulfide during irradiation. Is there any direct evidence of such surface modification? Is it possible to achieve this change under dark conditions before the irradiation is initiated?
7. Is there any measured or estimated pressure value inside the Teflon-lined autoclave when the samples are treated at 170 °C? What is your oppinion about the influence of pressure on the crystallization of the product and the achievable photocatalytic activity?

8. In Figure 4.9. (page 62) the crystallite size of ZnS is significantly larger in the sample prepared without added ammonia solution (CAT-0N) compared to the Cat-1N sample. However the CdS crystallite size is smaller for the CAT-0N sample. What is the reason for this difference?
9. It is stated that *„These results are in accordance with the previously discussed XRD data, which showed the highest crystallite size in ZB (Zinc blende (sphalerite)). The large particle size may be one of the factors that decreased photocatalytic performance."* (Page 66) Is it possible to determine an ideal size of the $Zn_{0.75}Cd_{0.25}S$ photocatalysts for hydrogen production?
10. It is mentioned that *"Although the QY should be independent of the light source, our calculations resulted in lower QYs for the Hg-Xe arc lamp and the visible LED."* (page 71) When QY values are compared, should not we also mention the actual wavelength range applied for the determination? If we consider a Xenon lamp as light source with four main peaks in the 400-600 nm range or a UV LED with relatively narrow emission spectrum in the 370-420 nm range, do you think it is directly comparable? Based on the trioxalato-ferrate(III) actinometry, do we also measure photons in the spectral range that is not suitable for excitation of the photocatalyst (for example below 2.44 eV, above 510 nm)?

Few remarks about figure formats:

1. In Figure 4.7. (page 59), both the wavelength (nm) and the Photon energy (eV) values are shown. This is very useful and could be applied in other similar figures or tables.
2. In Figure 4.12. (page 67), the scale bar of the STEM images should be larger.
3. The element label in the STEM images (Figure 4.27. and 4.28., page 86-87) should be larger for the better visibility.

The experiments, syntheses and characterization measurements were performed very accurately and reproducibly. The theoretical background is also nicely presented. The schemes, tables and figures are shown properly with all necessary explanations. The results are well documented and accurately summarized in the Thesis points (5 main points and 16 sub points). I accept all the Thesis points as new scientific results. The PhD Thesis written by Maali-Amel Mersel is therefore eligible for public defense and it fulfills all requirements for obtaining the PhD degree.

Szeged, 23 March 2023

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