Response to referee remarks and questions

Reviewer:

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I would like to thank Dr. Károly Mogyorósi for his detailed feedback on my work and his insightful questions. His remarks (1-3) are also highly appreciated and will be taken into account in future publications. The followings are the answers to his questions.

Answers to the reviewer's questions

1. **How did the Candidate select the concentration of the photocatalyst suspension for a given irradiation power in these experiments?**
   The concentration of the photocatalyst was previously investigated in our research group, and it was found that the rate of hydrogen production increased with the amount of photocatalyst used in the reactor until it reaches an optimal value, for which increasing the concentration of the catalyst does not cause any further improvement. 18 mg of catalyst in 30 ml of the reaction mixture (0.6 g/l) was in that range.
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 hydrogen production in these photocatalytic systems? This might be important for solar photocatalytic applications.**
   Unfortunately, the effect of the temperature during the irradiation of the catalyst was not investigated, but we suspect that increasing the temperature would increase the charge separation rate, decrease the solubility of H_2, and the probability of recombination, which could result in a small increase in the RHP. Also, we designed a photoreactor, in which the temperature could be controlled, but we could not find any glass manufacturer that was willing to produce it.

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?**

   In our study, Pt was only used as a means of comparison with Ni therefore, it was not deeply investigated. Additionally, due to the small concentration of Pt applied during the modification (0.1%), it is extremely hard to check the photoreduction of platinum through a characterization technique. However, it was previously reported in the literature that the photoreduction of $K_2[PtCl_6]$ produces metal Pt.

   REF: Jin, J., Yu, J., Liu, G. and Wong, P.K., 2013. Single crystal CdS nanowires with high visible-light photocatalytic H_2-production performance. *Journal of Materials Chemistry A*, 1(36), pp.10927-10934.

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)?**

   The investigation of the stirring effect was not deeply discussed, its only aim was to show that the stirring is not required and to approach the conditions of an industrial application. In addition, in the case of the stirred system, after it was stopped, the stirring was never restarted, so the RHP was left to reach its equilibrium on its own, we can see that the increasing rate is similar at the beginning of the unstirred system and in the stirred system after the stirring was stopped.

   The stirring is found to increase the nucleation and cause a fast release of H_2 bubbles after their formation on the surface of the catalyst, but once stopped, we notice a dramatic decrease in the RHP, this could indicate an abrupt stop in the release of H_2 bubbles. After the stirring was stopped, it had a 20% lower RHP than the stirred system at the end of the reaction. This can be due to the sedimentation of the catalyst on the sides of the reactor, therefore, decreasing the surface coverage and the ratio of the absorbed photons.

5. **How fast is the sedimentation of the photocatalyst particles without stirring? Did the Candidate apply stirring during the QY determinations?**

   The sedimentation of the catalyst is quite fast, in certain cases it even happened before the beginning of the illumination. Conditions similar to those of the original measurements were used for the QY determination, so no stirring was applied to approach industrial circumstances.

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?**

   We did not investigate the oxo/hydroxo to sulfide conversion, but according to the literature, during the sulfide precipitation in the aqueous solution, the surface is covered with oxo/hydroxo groups that are slowly replaced with sulfide during the illumination, but there is no direct evidence of this phenomenon.

   Yes, it is possible to achieve this change under dark conditions, but the increase during the first hours is not only due to this factor, it is also related to the temperature increase and the release of H_2 bubbles from the surface of the catalyst. That is why the average RHP is only estimated after ~ 3 h of illumination and the first hours are often neglected.

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 opinion about the influence of pressure on the crystallization of the product and the achievable photocatalytic activity?**

   In a system like ours, it may not be possible to measure the pressure inside the Teflon-lined autoclave during the HTT, we can only calculate the theoretical value, which is around 8 bar at 170 °C. However, we know that the pressure increases with the temperature, the effect of which is much more important on the recrystallization of the prepared photocatalyst.

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?**

   In the XRD patterns (Figure 4.8), we can see a sharp peak of the cubic zinc blend for the sample Cat-0N that is consistent with its determined crystallite size in Figure 4.9. The explanation could be that the initial pH for the preparation of the sample Cat-0N was more acidic (pH 6) than for the others (pH 10 or 11), and the precipitation of ZnS is slower in acidic conditions than in basic ones. This suggests that ZnS hardly precipitates in the beginning compared to CdS, so only a part of it is precipitated at this stage. Later, after the depletion of Cd, the ZnS precipitation becomes faster, which results in an inhomogeneous structure as confirmed in Table 4.4 (Cat-0N sample has the highest inhomogeneity among the hydrothermally treated samples).

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?**

   These results only show the correlation between STEM and XRD data, therefore, we cannot give an optimal value for the particle size of the ZnS-CdS photocatalyst. The structure of the crystals is probably more important than their size. This latter could influence the required minimum amount of catalyst relative to the surface of the reactor, but it was not investigated.

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)?

It is true that trioxalatoferrate(III) could absorb at only up to 550 nm, but in the actinometry, we took into account the dependence of the QY for the reaction of trioxalatoferrate(III) (Φ), the ratio of the photons absorbed by trioxalatoferrate(III) (I_A), and the normalized spectra of the light sources on wavelength. Equation 13 from section 3.5 shows that Φ_{Fe} was weighted by the ratio of the photons absorbed by trioxalatoferrate(III) (I_A) and with the normalized spectra of light sources ($c_{Ph,in}$) (see page 48). Therefore, the results obtained from the different light sources are indeed comparable.