Response to referee remarks and questions

Reviewer:

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I would like to thank Dr. József Sándor Pap for his insightful questions and his detailed feedback on my work. The followings are the answers to his questions.

Answers to the reviewer's questions

1. **Figure 4.13 – Good that the inhomogeneity was studied and discussed. Could the nanoscale inhomogeneity be the reason for the difference in literature RHP values despite the same average composition?**

   The inhomogeneity may be one of the reasons for the different RHP reported in the literature but its effect is not as important as the crystal structure of the catalyst. In the literature overview, I compared syntheses where intensive conditions were applied to achieve good homogeneity. When the preparation conditions were the same, the resulting solid gave very similar catalytic activity between about 2:8 and 8:2 ZnS:CdS ratios, so the inhomogeneity may have only a small contribution (10%) to RHP.
2. **Chapter 4.2.2 – The hydrothermally treated catalysts were not much affected by the presence of Ni on the surface. Does the ineffective co-catalysts indicate that charge extraction is not the rate limiting in RHP?**

   We can neither confirm nor deny if the charge extraction is the rate-limiting reaction in this case. As indicated in the STEM images (Figure 4.27), the Ni(II) was found on the surface, regardless of the modification type that was applied, but if we compare the results on the bulk- and surface-modified samples, we realize a small increase in the RHP for the former and almost no change for the latter. This suggests that Ni(II) acted as a charge scavenger and increased the speed of the charge extraction in the first case but in the second one, the charge separation was already as fast as it could be, and so the surface modification did not contribute to any increase in the RHP.

3. **Among the preliminary results, the effect of Ce is discussed. What is the possible explanation of the positive effect of Ce?**

   The possible explanation for the positive effect of Ce is that it plays a role similar to Ni(OH)$_x$ in our system, so Ce(III) is oxidized to Ce(IV) by the hole then it reacts with sulfide ions to form sulfur. Similarly to Ni(OH)$_2$ and Ni(OH)$_3$, the Ce^{4+}/Ce^{3+} ion pairs co-exist in their respective metal-doped system, which could ameliorate its activity due to the fast and repeatable redox cycles between the two. The other possibility could be the formation of cerium sulfide, which forms a type II heterojunction with the ZnS-CdS catalyst, as Bai et al. reported it. This suggests that a deeper investigation of Ce-modified catalysts to explain the difference between the obtained RHP for Ce(III) and Ce(IV) would be extremely interesting, especially since it was rarely reported in the literature.

   REF: Bai, Y., Wang, K. and Wang, X., 2018. Influence of Ce^{3+} doping on the optical and photocatalytic properties of Zn$_{0.8}$Cd$_{0.2}$S-ethylenediamine hybrid nanosheets. *Journal of Photochemistry and Photobiology A: Chemistry*, 356, pp.355-363.

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?**

   The redox potentials related to Eq. 7-10 (page 19) at pH 13.5 are summarized in the following table and figure (Table 1 and Figure 1).

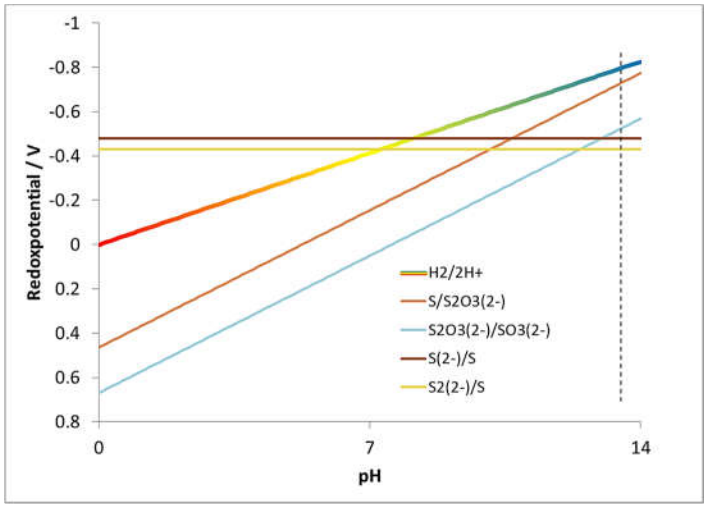

Figure 1: Redox potential of the redox system present in Eq. 7-10

Oxidized form	Reduced form	E (pH 13.5)/ V
SO_3^{2-}	$S_2O_3^{2-}$	–0.52
$S_2O_3^{2-}$	S	–0.73
S	S^{2-}	–0.48
S	S_2^{2-}	–0.43

Table 1: Redox potential of the redox system present in Eq. 7-10 at pH 13.5

Therefore, the Gibbs energy of the reaction of Eq 9 ($S + SO_3^{2-} \rightarrow S_2O_3^{2-}$) is **$\Delta G = -nFE = -2 \cdot 96500 \cdot (-0{,}52-(-0{,}73)) = -39.6$ kJ/mol**.

As a source of H_2S for the evolution of hydrogen in a liquid phase, the sulfite system (Na_2S/Na_2SO_3) is considered the most favorable in terms of safety and convenience compared to ethanolamine or hydroxide systems. However, Buehler et al. reported the use of hypophosphite ions ($H_2PO_2^-$) as alternatives to SO_3^{2-} ions and even found it to have a higher performance due to the two-step oxidation of $H_2PO_2^-$ to HPO_3^{2-} as shown in the following reactions.

$$S_2^{2-} + H_2PO_2^- + 3\,OH^- \rightarrow 2\,S^{2-} + HPO_3^{2-} + 2H_2O$$

$$S_2^{2-} + HPO_3^{2-} + 3\,OH^- \rightarrow 2\,S^{2-} + PO_4^{3-} + 2H_2O$$

According to the literature, the reduction of $S_2O_3^{2-}$ ions is thermodynamically less favorable than that of hydrogen ions, therefore, unlike polysulfides that could form if sulfur is not removed, the $S_2O_3^{2-}$ ions will not compete with hydrogen ions for electrons and will result in hydrogen gas generation. In addition to that, by introducing H_2S to $S_2O_3^{2-}$ ions, we can regenerate the original S^{2-}/SO_3^{2-} solution as indicated in the following reaction, and the sulfur product can be easily separated by filtration.

$$S_2O_3^{2-} + H_2S \rightarrow S + HS^- + HSO_3^- \quad pH < 4.2$$

REF:

- N. Bühler, K. Meier, JF Reber., 1984. Photochemical hydrogen production with cadmium sulfide suspensions J. Phys. Chem, 88, pp.3261-3268.
- Oladipo, H., Yusuf, A., Al Jitan, S. and Palmisano, G., 2021. Overview and challenges of the photolytic and photocatalytic splitting of H_2S. Catalysis Today, 380, pp.125-137.
- Dan, M., Yu, S., Li, Y., Wei, S., Xiang, J. and Zhou, Y., 2020. Hydrogen sulfide conversion: How to capture hydrogen and sulfur by photocatalysis. Journal of Photochemistry and Photobiology C: Photochemistry Reviews, 42, p.100339.