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Photocatalytic H_2 production from H_2S decomposition

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Introduction

Photocatalytic H_2 production by H_2S decomposition is regarded to be an environmentally friendly process to produce a carbon-free energy through direct solar energy conversion **[1]**. For this purpose, sulfide-based materials, as photocatalysts, were widely used **[2]**. The loading of proper co-catalysts on those semiconductors was shown to improve their efficiency by trapping the electron that reduced the H^+ to H_2 **[3]**.
In this research, ZnS-CdS composite was studied because of its controllable band gap and excellent performance for H_2 evolution under visible light irradiation. The influence of the preparation parameters and the metal modification on the H_2 production activity of this catalyst was investigated.

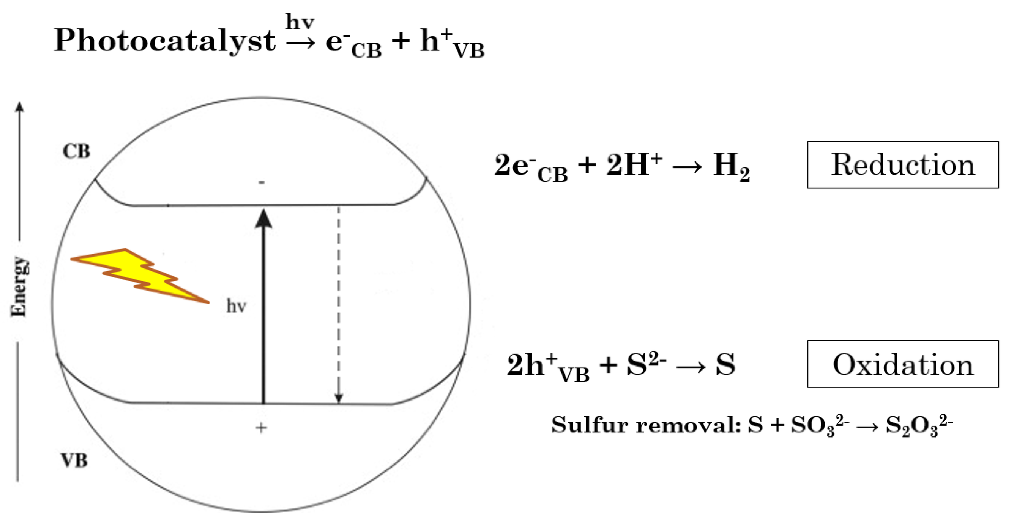

Fig **1**. Mechanism of heterogeneous photocatalytic H_2 production

Materials and methods

Metal solution: $Zn(CH_3COO)_2 + Cd(CH_3CO_2)_2 + NH_4OH$

Sulfide solution: Addition of a stoich. amount of Na_2S

ZnS-CdS Yellow ↓

Hydrothermally treated (170°C)

Fig **2.** Photochemical experiment

The ZnS-CdS catalyst was modified with different materials on the surface and in the bulk, as summarized in the table below (tab **1**.).

Metal	Ni	Cu, Mn, Co, Ag
X% Metal mod. (bulk + surface)	0.1 to 1%	0.1%

Tab **1**. Modification of ZnS-CdS with different types of metals

Results and discussion

Figure 3: The dependence of the photoactivity of ZnS-CdS on the hydrothermal treatment and the initial amount of NH_4OH (used during preparation) was investigated. It was proven that this later could highly influence the rate of H_2 production of the catalyst, and that the hydrothermal treatment is a vital step for a good efficiency; a stoichiometric amount of NH_4OH is recommended in this case.

Figure 4: XRD measurement was performed to explain this dependence. It was found that the rate of H_2 production is in good correlation with the crystallite size of CdS. Also, the absence or excess of NH_4OH was proven to favor the growth of ZnS crystals and inhibit that of CdS. Furthermore, the hydrothermal treatment was shown to increase the crystallite size of both ZnS and CdS, as expected.

Figure 5: The rate of H_2 production has increased when the ZnS-CdS catalyst was modified with Nickel either on the surface or in the bulk compared to other metals (Ni< Mn< Cu< Co< Ag), suggesting that Nickel is the best candidate for further investigations.

Figure 6: The modification of ZnS-CdS with Nickel in the bulk is more favorable than that on the surface. This suggests that Nickel is better as a dopant than as a co-catalyst.

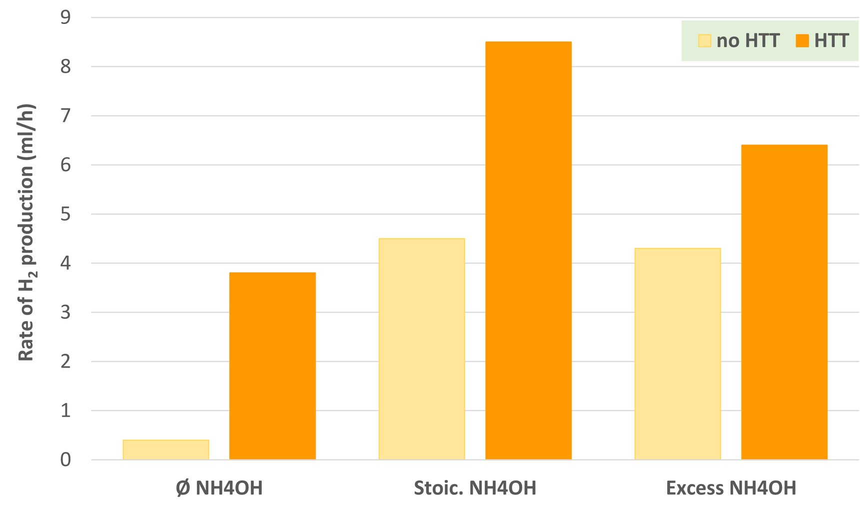

Fig **3**. The rate of H_2 production as a function of the NH_4OH content and the Hydrothermal treatment (HTT) of ZnS-CdS

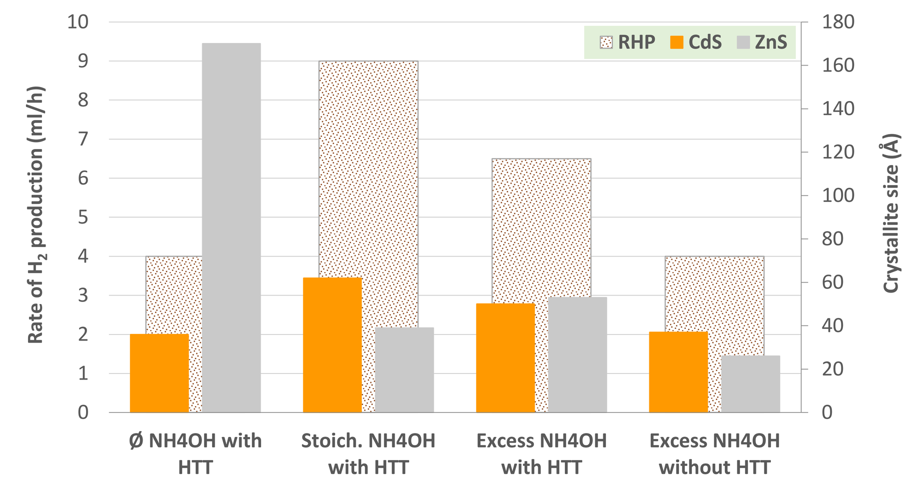

Fig **4**. The rate of H_2 production (RHP) and the crystallite size (CS) as a function of NH_4OH content in ZnS-CdS and the Hydrothermal treatment (HTT)

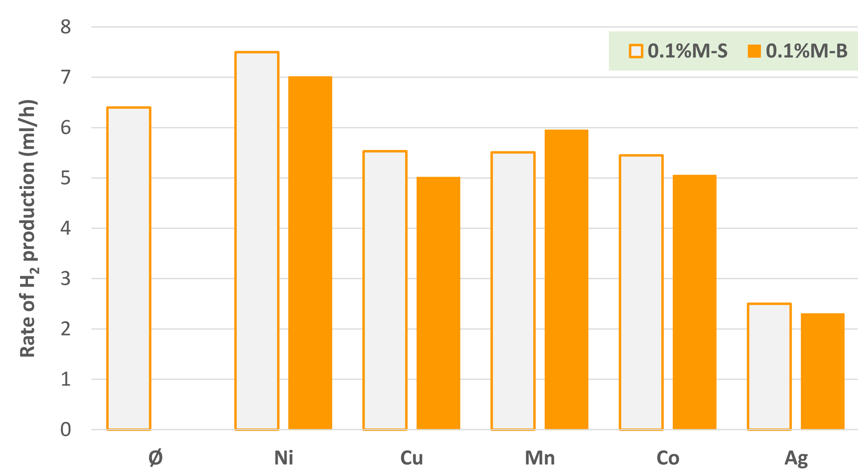

Fig **5**. The rate of H_2 production as a function of metal modified ZnS-CdS – 0.1% metal in the bulk or on the surface

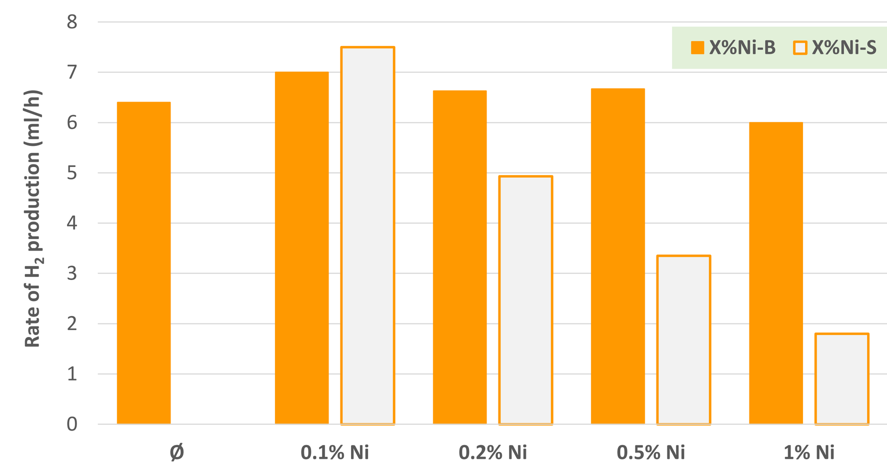

Fig **6**. The rate of H_2 production as a function of Ni modified ZnS-CdS – 0 to 1% of Ni in the bulk or on the surface

Conclusion

- The optimal ZnS-CdS catalyst is hydrothermally treated and prepared from a stoichiometric amount of NH_4OH.
- Modifying the surface of the ZnS-CdS semiconductor with the investigated metals (Ni, Mn, Co, Cu and Ag) always resulted in a decrease in the photocatalytic activity. However, the modification in the bulk seems very promising especially with Ni.
- The excellent photoactivity of the ZnS-CdS catalysts encourages further investigations to enhance the H_2 production by optimization of the reaction conditions and its modification with other metals.

References

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[3] X. You, X. Rong, Appl. Surface Sci. 2015, 351, 779-793

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