

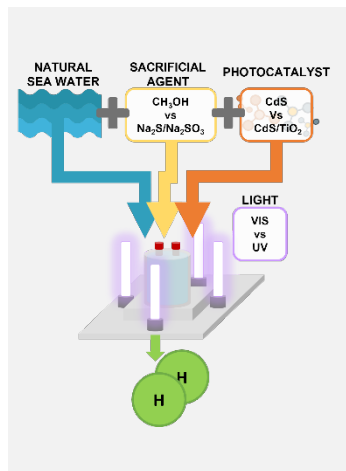
Understanding the Role of Sacrificial Agents in the Photocatalytic Generation of Hydrogen from Seawater with Cadmium Chalcogenides as Photocatalysts

POSTER

Ph.D. Student: N

Journal: NONE

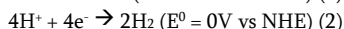
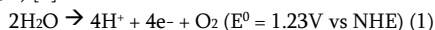
M.J. Rivero¹, D. Pelayo¹, G. García-Basté¹, I. Ortiz¹. (1) Departamento de Ingenierías Química y Biomolecular, Universidad de Cantabria, Avda. Los Castros, s/n, 39005 Santander, Spain, mariajose.rivero@unican.es.



One of the key elements to increase stability in the photocatalytic hydrogen (H_2) generation is the sacrificial agent (SA). SAs are electron donors and play a crucial role to prevent charge recombination and photo-corrosion of the catalyst, and thus, improve the process efficiency. So far, different SAs have been used, such as alcohols, organic acids, and sulfide/sulfites pairs, and its effect depends mainly on the affinity of the SA for the catalyst and its redox potential. However, their role in the charge transfer mechanisms is not yet fully understood. As part of a broader scope work on photocatalytic H_2 generation using cadmium chalcogenides based photocatalysts, CdS and CdS/TiO₂, the role of two common SAs, CH₃OH and Na₂S/Na₂SO₃ is analyzed in this work. For this purpose, photocatalytic experiments of H_2 generation from seawater have been carried out under visible and UV light. Using Na₂S/Na₂SO₃ as SA yields the highest H_2 production with both photocatalysts under both light spectra, that is explained through its effect on charge transfer and photocorrosion inhibition.

Introduction

Photocatalytic hydrogen (H_2) production involves the simultaneous reduction and oxidation of water as a complex multistep reaction involving four electrons (eqs. 1, 2) [1].



Moreover, while TiO₂ has been widely used as photocatalyst, its wide bandgap and charge recombination rate reduce the process performance. CdS has become a promising material, active under visible light and with a more negative conduction band (CB) than TiO₂ [1]. With this starting point, the heterojunction CdS/TiO₂ shows potential to improve H_2 production because of the separation of e^-h^+ pairs.

The use of sacrificial agents (SAs) reduces the charge recombination rate and photo-corrosion phenomena in the catalyst, as these molecules scavenge the holes in the semiconductor. It is known that methanol (CH₃OH) and sodium sulfide/sodium sulfite (Na₂S/Na₂SO₃) are the most commonly used SAs for oxides and sulfide photocatalysts, respectively. CH₃OH is commonly used with TiO₂, as it helps to replenish OH ions at the photocatalyst surface. Na₂S/Na₂SO₃ effectively consumes the holes in the CdS particles and the produced S²⁻ ions bind tightly to the catalyst surface, preventing its photo-corrosion and regenerating the catalyst [2].

Within this framework CH₃OH and Na₂S/Na₂SO₃ were selected as SAs to assess the performance and identify

the charge transfer mechanism in H_2 generation from seawater with CdS and CdS/TiO₂ as catalysts. Therefore, the objective of this study is to unravel the phenomena that occur during the use of CdS and CdS/TiO₂, together with the performance of each target photocatalyst with different SAs.

Material and Methods

CdS and CdS/TiO₂ were synthesized by hydrothermal method with CdCl₂ and CH₄N₂S, and CdS and TiO₂ P25, respectively. Seawater (NSW) containing 25 mg L⁻¹ of CdS or 50 mg L⁻¹ of CdS/TiO₂ (50/50) together with a SA: 20% CH₃OH or 0.1M Na₂S/0.1M Na₂SO₃ was treated. The experiments were carried out in a 250 mL photo-reactor in batch mode, with UV or visible (VIS) lamps operating at 12 W m⁻². H_2 production was determined during 24 h, taking samples every hour that were analyzed in a GC-2010 Plus gas chromatograph provided with a thermal conductivity detector. In addition, ·OH radicals were analyzed in an Agilent 1100 series HPLC [3].

Results and Discussion

The charge transfer mechanism in CdS/TiO₂ catalysts could be explained through a type II heterojunction or Z-scheme (Figure 1). ·OH radicals were analyzed to help screening the mechanism. It was observed that ·OH generation increased over 240 min due to water oxidation, allowing to conclude that charge transfer

occurs through the Z-scheme mechanism (Figure 1C and 1D) as $\cdot\text{OH}$ could only be formed by oxidation of water in TiO_2 surface due to the redox potentials. This mechanism improve the separation efficiency of photogenerated charges and has stronger redox capacity than conventional heterojunctions (as type II).

Theoretically, depending on the SA, H_2 would be produced due to the affinity of the SA for the catalyst and their relative redox potentials. Then, experiments with CdS and CdS/ TiO_2 with both SAs under VIS and UV light were carried out; results are detailed in Table 1. Regarding CH_3OH , the highest H_2 production was achieved with the composite CdS/ TiO_2 and UV light, as alcohols are strongly adsorbed on the surface of oxides due to their hydroxyl groups [4], and the oxidation of the SA occurs in TiO_2 whereas reduction of H^+ takes place in CdS. However, CH_3OH is not adsorbed on the surface of CdS, and H_2 is not generated when this catalyst is excited, as the e^-h^+ pairs recombine fast.

Regarding the use of $\text{Na}_2\text{S}/\text{Na}_2\text{SO}_3$ pair as SA higher production of H_2 was obtained relative to CH_3OH with both catalysts. The highest production was achieved with CdS, mainly because of the affinity of the SA to CdS. This SA is more unstable than CdS, causing photogenerated holes more proned to oxidize the SA inhibiting photo-corrosion of the catalyst [4]. Using CdS/ TiO_2 charge transfer mechanism follows a Z-scheme, as previously mentioned, resulting in lower charge recombination rate. The SA is adsorbed in the

surface of CdS/ TiO_2 and its oxidation would occur in TiO_2 , which on the other hand has greater affinity for alcohols; the anti photocorrosion power of CdS would be reduced. According to the results collected in Table 1 it is concluded that in the case of the composite catalyst the loss in photocorrosion power has a more pronounced influence on hydrogen generation than the gain due to charge transfer mechanism. These are preliminary results that could help understand the combined role of SA-photocatalyst systems in the hydrogen generation from seawater, helping in decision making in the selection of process components.

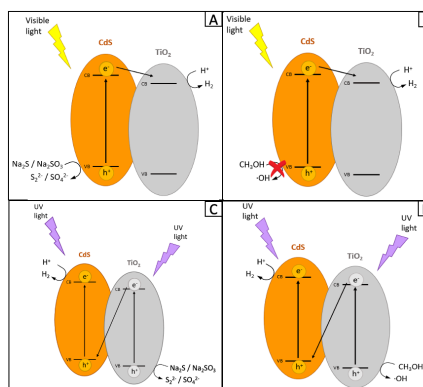


Figure 1. Charge transfer mechanism in CdS/ TiO_2 with (A) $\text{Na}_2\text{S}/\text{Na}_2\text{SO}_3$ and VIS, (B) CH_3OH and VIS, (C) $\text{Na}_2\text{S}/\text{Na}_2\text{SO}_3$ and UV, and (D) CH_3OH and UV.

Table 1. Hydrogen production rates with 12 W m^{-2} of irradiance.

Sacrificial agent	Photocatalyst	Light	H_2 production rate ($\mu\text{mol H}_2 \text{ g}_{\text{cat}}^{-1} \text{ h}^{-1}$)
CH_3OH	CdS	VIS / UV	0 / 0
	CdS/ TiO_2	VIS / UV	0 / 5.22
$\text{Na}_2\text{S}/\text{Na}_2\text{SO}_3$	CdS	VIS / UV	232.11 / 1677.30
	CdS/ TiO_2	VIS / UV	76.92 / 120.70

Conclusions

The performance of photocatalytic H_2 production with cadmium calcogenides and two different SAs (CH_3OH and $\text{Na}_2\text{S}/\text{Na}_2\text{SO}_3$) is reported. The analysis of the results concluded a Z-scheme charge transfer mechanism for the CdS/ TiO_2 composite, where reduction and oxidation reactions take place in the surface of CdS and TiO_2 , respectively. However, the best results were obtained with the CdS and $\text{Na}_2\text{S}/\text{Na}_2\text{SO}_3$ system, that were attributed to the stronger influence of SA on the inhibition of catalyst photocorrosion.

Acknowledgments

These results are part of the R&D projects PLEC2021-007718 and PDC2022-133563-100 funded by MCIN/AEI/10.13039/5011000110033 and European Union NextGenerationEU/PRTR.

References

- [1] D. Pelayo, E. Pérez-Peña, M.J. Rivero, I. Ortiz. *Catal. Today*, 433 (2024) 114672.
- [2] J. Corredor, M.J. Rivero, C.M. Rangel, F. Gloaguen, I. Ortiz. *J. Chem. Technol. Biotechnol.*, 94 (2019) 3049.
- [3] C. Tai, J. Peng, J. Liu, G. Jiang. *Anal. Chim. Acta.*, 527 (2004) 73.
- [4] V. Kumaravel, M.D. Imam, A. Badreldin, R.K. Chava, J.Y. Do, M. Kang, A. Abdel-Wahab. *Catalysts*, 9 (2019) 1.