V-Substituted ZnIn$_2$S$_4$: A (Visible+NIR) Light-Active Photocatalyst

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Abstract: ZnIn$_2$S$_4$ is known to be a visible light-active photocatalyst. In this work, it is shown that by substituting part of the In atoms with vanadium, the visible light range of photocatalytic activity of such material can be extended, using the so-called in-gap band scheme that has been shown to enhance photovoltaic characteristics. Characterization of this material using several techniques, complemented by DFT calculations, will support this statement. While here only the degradation of aqueous HCOOH in well-aerated conditions is discussed, the same material may be used, with an adequate sacrificial reagent, for photocatalytic H$_2$ generation.

Keywords: ZnIn$_2$S$_4$; substitution by vanadium; visible light-active photocatalyst; DFT

1. Introduction

Use of sulphides as photocatalysts is a well-studied subject, as shown by several very recent reviews [1–6]. In particular, ZnIn$_2$S$_4$ is known to be active in a significant part of the visible light spectrum; it has been used for H$_2$ production [7,8], microorganism inactivation [9] or dye degradation [10]. On the other hand, ZnIn$_2$S$_4$ has been combined with other semiconductors to improve photocatalytic properties. Thus, it has been combined with oxides, like in [11–15]; it has also been combined with other sulphides, as in [16–19], or even nitrides and phosphides [20,21]. Additionally, some reviews on its use, or on the use of similar materials, have appeared [22–25], and our group has done a recent publication including references to the ZnIn$_2$S$_4$ system [26].

Here, the possibility of enlarging the spectral range in which ZnIn$_2$S$_4$ is photocatalytically active will be addressed, in particular, through substitution of indium by vanadium. The idea is based on a claim made by Luque and Martí [27] that by introducing intermediate levels in photovoltaic cells it may be possible, in theory, to enhance by more than 50% the solar efficiency of such systems. In the past, our group has addressed, using DFT calculations, the possibility of achieving such an electronic structure [28–33]; using photocatalysis, this has then proven to be the case in a couple of examples [31,34], while promising experimental results indicating that a similar electronic structure has been achieved have been provided recently [35].

In the following, a recall is presented of the data obtained by our group with undoped ZnIn$_2$S$_4$, and then relevant data on V-substituted ZnIn$_2$S$_4$ (including DFT results) and on its photocatalytic properties are given in detail.

2. Experimental Section

The reactants used were ZnCl$_2$, InCl$_3$, VCl$_3$ and Na$_2$S as the source of sulfur. The solvent used, in order to avoid as much as possible the oxidation of VCl$_3$, was one with reducing characteristics, being composed of ethyleneglycol (in the following, shortened to EG) and MilliQ distilled water (to facilitate the solubility of the salts), water being present at 20% by weight. All reactants were supplied by Aldrich; the In and Zn salts had purity of 99.999%, while the others had purity of 99%, except EG, which was supplied by Panreac with purity of 99%.
The solids were made, after adjusting the pH to 3 with concentrated HCl (also from Panreac), using solvothermal treatments in the specified solvent at 180 °C during 65 h, with the objective of obtaining at the end 1 g of solid. The latter was filtered out from the solution and washed repeatedly with water and methanol, and finally with water. The objective was to prepare V-substituted ZnIn₂S₄ with a V–In ratio of 1:9.

Chemical analysis data, BET-specific surfaces, X-ray diffractograms, UV-Vis-NIR spectra and photocatalytic tests of aqueous HCOOH degradation (including spectral response profiles using a collection of filters coupled to a Xenon lamp) were obtained and analyzed as reported previously [36,37]. EPR data were obtained and analyzed as reported in the Supporting Information of Ref. [38]. DFT calculations were carried out with the VASP code [39], using the PAW method to represent the cores [40]; the cutoff energy for electron functions was set at 300 eV and the Brillouin zone was sampled with a (12 × 12 × 2) Monkhorst-Pack grid. Because this material has layers interacting only via van der Waals forces, a correction to the energy, using the method proposed in [41], was added and used in the relaxations.

Irradiation was provided by an ozone-free 450 W Xe lamp provided with a water filter (to decrease IR light) and, where necessary, with bandpass filters having FWHM = 50 nm. The magnetically stirred and well-aerated suspension, adjusted with a phosphate buffer to pH = 2.5 (the natural pH of the HCOOH 1.5 mM solution utilized) and using 40 mg of photocatalyst in 80 mL of the EG-water mixture, was sampled periodically and, after filtering out the catalyst, the HCOOH concentration was measured using the UV absorption of HCOOH at \( \lambda = 205 \text{ nm} \).

3. Results and Discussion
3.1. Previous Data on Undoped ZnIn₂S₄

As reported in [26], the diffractogram, UV-Vis diffuse reflectance spectrum and spectral dependence of the photocatalytic activity for the degradation of aqueous HCOOH against wavelength were as depicted in Figure 1. It can be seen that the diffractogram presents well-resolved peaks. This contrasts with the diffractograms shown below in Figure 2, the reason being that, because there was no need to keep a reducing environment, only distilled water was used in that case for the solvothermal synthesis. The bandgap measured with the Tauc plot (2.6 eV) allows a significant use of visible light; the spectral response for photocatalytic degradation of aqueous HCOOH matches well the spectrum of ZnIn₂S₄, once the width of the filters used (FWHM = 50 nm) and the possibility of a few defects narrowing a bit the bandgap are taken into account.
3.2. New Data on V-Doped ZnIn$_2$S$_4$

3.2.1. Characterization of V-Substituted ZnIn$_2$S$_4$

Chemical analysis yielded a result close to the intended one (V–In ratio = 1:8.6). However, its diffractogram, shown in Figure 2, displayed peaks less resolved than in Figure 1a above; indeed, they are much closer to those of undoped ZnIn$_2$S$_4$ prepared using Na$_2$S as well and the same EG-water mixture. This probably means that these systems contain more defects than the undoped ZnIn$_2$S$_4$ material. In any case, these diffractograms are very close to those reported in Figure 3 of Ref. [10] and Figure 10A of Ref. [22]; all of them correspond to the hexagonal phase of ZnIn$_2$S$_4$. On the other hand, the peaks for the system containing V appear displaced to slightly higher angles, as expected considering the smaller ionic radius of V in comparison with In.

The diffuse reflectance spectrum of V-substituted ZnIn$_2$S$_4$ prepared solvothermally with Na$_2$S and the EG-water mixture, after obtaining the Kubelka-Munk transform and plotting it against the photon energy, is presented in Figure 3. It can be seen that, in comparison with the same data presented above for undoped ZnIn$_2$S$_4$, absorption is much extended into the visible and even IR range (it must be noted, however, that the small peaks below 0.7 eV are overtones of vibrations). No data are available on diffuse reflectance spectra upon substitution by V in this sulphide; the closest examples are probably those found in Figure 5b of Ref. [31] and Figure 3a of Ref. [38].

EPR spectra were also obtained for this V-substituted sample; they are shown below in Figure 4. Several things must be noted: (a) The shape of the spectra, showing hyperfine peaks, is typical of V$^{4+}$ (V$^{3+}$ is normally not seen in EPR, since the high fine structure leads to having all features outside the normal magnetic field range); indeed, it is very similar,
except for the sharp peak at $g \approx 2.00$ (surely due to some type of defect), to that found in the Supporting Information of Ref. [38], which shows the $V^{4+}$ spectrum in V-substituted In$_2$S$_3$. (b) The ratio between doubly integrated areas of the spectra at 77 K and ambient temperature is close to 4:1, as can be expected for a normal paramagnetic system. (c) Most importantly: quantification of the absolute number of spins in comparison with a CuSO$_4$ standard indicates that not more than 14% of vanadium is present as $V^{4+}$, which means that the rest is present as $V^{3+}$, as expected considering the reducing power of EG at the temperature of the solvothermal treatment.

Figure 4. EPR spectra of V-substituted ZnIn$_2$S$_4$.

DFT calculations were carried out for this V-substituted ZnIn$_2$S$_4$. Here, $V^{3+}$ species substitute for In$^{3+}$ octahedral cations. Indeed, $V^{3+}$ ions usually prefer octahedral coordination, and it must be noted that the layered structure of ZnIn$_2$S$_4$ has all Zn cations in tetrahedral coordination while 50% of In cations are in octahedral coordination and the other 50% are in tetrahedral coordination. In this case, a V–In ratio of 1:7 was chosen, to approach the 1:8.6 ratio found experimentally. The result of this calculation is presented in Figure 5. It can be clearly seen that an in-gap band appears (separated from the valence and conduction bands) that is partially occupied, i.e., is crossed by the Fermi level (represented by the dashed vertical line). This in-gap band is rather close to the valence band, which explains that the transitions from its empty part to the wide valence band may cover completely the visible range and a substantial amount of the IR range, as shown in Figure 3. On the other hand, the distance between the conduction band and the filled part of the in-gap band justifies the small hump appearing in Figure 3 around 1.9 eV. The main rise in the absorption spectrum corresponds, obviously, to the main bandgap of ZnIn$_2$S$_4$. On the other hand, it is well known that DFT calculations at the PBE level significantly underestimate bandgaps in semiconductors; where the in-gap band induced by vanadium might appear once the bandgap widens is still an unresolved question.

3.2.2. Photocatalytic Activity of V-Substituted ZnIn$_2$S$_4$

The photocatalytic activity of this material for the degradation of aqueous HCOOH was then examined. First, the decrease in HCOOH concentration was determined for a series of bandpass filters (and also with no filter); the result in each case is displayed in Figure 6a. Then, each curve was fitted assuming first order kinetics; the results of rate constant $k$, compared with the same result obtained for the undoped ZnIn$_2$S$_4$, and also compared with the absorption spectrum of each sample, is shown in Figure 6b. It is clearly seen that the spectral response of V-substituted ZnIn$_2$S$_4$, although somewhat smaller in the 400–500 nm range (which can be ascribed to the presence of defects, including those introduced by vanadium), is on the other hand widened, reaching even the NIR range (as observed for the small photoactivity found at $\lambda = 750$ nm). This is just what can be expected considering the DFT results in Figure 5, which indicate a transition of lower energy from
the filled part of the in-gap band to the conduction band (one must recall that spin flips during light absorption events are not allowed). Therefore, the effect of the in-gap band on the general electronic structure is confirmed by the photocatalytic experiments.

Figure 5. Density of states plot showing the results of the DFT calculation carried out for V-substituted ZnIn$_2$S$_4$. Total DOS in black; colored traces correspond to the partial DOS centered on each element. The vertical dashed line marks the Fermi energy.

Figure 6. (a) Decrease in the HCOOH concentration for the V-substituted ZnIn$_2$S$_4$ photocatalyst using different filters (the numbers indicate the wavelength utilized). (b) Comparison of the HCOOH photodegradation rate constants found for undoped and V-substituted ZnIn$_2$S$_4$, including also the absorption spectra of each material.

A caveat must be mentioned here. As shown in Ref. [26], in the photodegradation of aqueous HCOOH using undoped ZnIn$_2$S$_4$ (in well-aerated conditions), a significant photocorrosion of that sulphide took place. This has not been verified here for V-substituted ZnIn$_2$S$_4$, but a similar effect might happen as well since this latter material has more defects (as evidenced by its diffractogram); the increase in Madelung-type stability due to the smaller radius of the vanadium ion may compensate this only partially. However, this might not be the case when using this material for the photocatalytic generation of H$_2$, especially when utilizing a sacrificial reagent, as was the case in Refs. [7,8]. Therefore, the interest of the work presented here, having as main objective the extension to higher wavelengths of the photocatalytic response when using V-substituted ZnIn$_2$S$_4$, might be applied to the situations when photoproduction of H$_2$ with visible light is the main objective.
3.2.3. Likely Degradation Products and Reaction Mechanism

As stated in Ref. [36], the most likely degradation mechanism corresponds to reaction

$$\text{HCOOH} + \frac{1}{2}\text{O}_2 \rightarrow \text{CO}_2 + \text{H}_2\text{O} \quad (1)$$

Other degradations, like

$$\text{HCOOH} \rightarrow \text{CO}_2 + \text{H}_2 \quad (2)$$

or

$$2\text{HCOOH} \rightarrow (\text{HCOO})_2 + \text{H}_2 \quad (3)$$

are unlikely since such degradations usually require Pt or a similar metal to generate H\textsubscript{2}, and the only other alternative

$$\text{HCOOH} \rightarrow \text{CO} + \text{H}_2\text{O} \quad (4)$$

is also unlikely since such reaction requires usually a rather acidic catalyst, which is not the case here.

Concerning the reaction mechanism, there are two main possibilities: via OH or O\textsubscript{2}\textsuperscript{−} radicals. The former are likely to be present, since, as shown in Ref. [34], both V-substituted and V-free In\textsubscript{2}S\textsubscript{3} (sulphides very similar to that used here) generate OH radicals, as evidenced by the terephtalic acid test; these radicals are indeed very aggressive and reactive. The participation of superoxide (or a HO\textsubscript{2} radical, for that matter) is less clear; however, it cannot be discarded, since, as shown in Ref. [26], where the degradation mechanism of the rhodamine B dye was studied using In\textsubscript{2}S\textsubscript{3} as photocatalyst (again, a sulphide similar to that used here), there was a large difference between bubbling O\textsubscript{2} and bubbling N\textsubscript{2}: the last steps of rhodamine B degradation proceeded much more slowly when N\textsubscript{2} was bubbled. Therefore, both OH and O\textsubscript{2}\textsuperscript{−} radicals might participate in the mechanism of the final degradation, which should proceed according to the first reaction above.

Concerning singlet oxygen, it does not seem to play a large role in photocatalysis [42]; the present authors only know one reference in which it plays a significant role in photocatalysis including a visible light-active sulphide [43]. H\textsubscript{2}O\textsubscript{2}, on the other hand, is much less reactive than OH or O\textsubscript{2}\textsuperscript{−}/HO\textsubscript{2} radicals; it is not likely to have a significant role here.

3.2.4. General Discussion

It is evidenced that including vanadium in the solvothermal synthesis of ZnIn\textsubscript{2}S\textsubscript{4} leads to a noticeable extension in the visible light range of the photocatalytic response, at least for the HCOOH photodegradation; comparison of this result with that found in Ref. [26] (the only other case in which photocatalysis involving aqueous HCOOH and ZnIn\textsubscript{2}S\textsubscript{4} has been addressed) makes this rather clear. As said in the last paragraph of Section 3.2.3, in these conditions, ZnIn\textsubscript{2}S\textsubscript{4} (V-substituted or not) may suffer photocorrosion. In most cases, this photocorrosion effect can be avoided or reduced by combining with other materials [44–46]. However, it may be that as said above such photocorrosion does not occur when trying to photogenerate H\textsubscript{2} using a sacrificial reagent, as is the case not only of Refs. [7,8] (in the latter case, using photoelectrochemistry), which are the first ones that the present authors could detect; additionally, other more recent cases have appeared [24,47–50]. In fact, not only H\textsubscript{2} can be produced by ZnIn\textsubscript{2}S\textsubscript{4}; in recent years, it has also been found possible to photoreduce CO\textsubscript{2} or produce syngas, in some cases combining two semiconductors [51–54]. In many of these cases, stable and reproducible behavior was always observed.

4. Conclusions

The effects of substituting part of the In atoms by vanadium are evidenced here: once a proper solvent and source of sulfur are chosen, an in-gap band partially filled is formed that leads to an extension of the wavelength range of photocatalytic activity, even entering a bit
into the NIR range. The possibility of extending this effect to photocatalytic H₂ production would be the succeeding step to follow.

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**References**

1. Li, S.; Sun, J.; Guan, J. Strategies to improve electrocatalytic and photocatalytic performance of two-dimensional materials for hydrogen evolution reaction. *Chin. J. Catal.* 2021, 42, 511–556. [CrossRef]

2. Nasir, J.A.; ur Rehman, Z.; Ali Shah, S.N.; Khan, A.; Butler, I.S.; Catlow, C.R.A. Recent developments and perspectives in CdS based photocatalysts for water splitting. *J. Mater. Chem. A* 2020, 8, 20735–21342. [CrossRef]

3. Zhang, W.; Mohamed, A.R.; Ong, W.J. Z-Scheme Photocatalytic Systems for Carbon Dioxide Reduction: Where Are We Now? *Angew. Chem. Int. Ed.* 2020, 59, 2–24. [CrossRef] [PubMed]

4. Palchoudhury, S.; Ramasamy, K.; Gupta, A. Multinary copper-based chalcogenide nanocrystal systems from the perspective of device applications. *Nanoscale Adv.* 2020, 2, 3069–3082. [CrossRef]

5. Li, J.; Jiménez-Calvo, P.; Painneau, E.; Ghazzal, M.N. Metal Chalcogenides Based Heterojunctions and Novel Nanostructures for Photocatalytic Hydrogen Evolution. *Catalysts* 2020, 10, 89. [CrossRef]

6. Chandrasekaran, S.; Yao, L.; Deng, L.; Bowen, C.; Zhang, Y.; Chen, S.; Lin, Z.; Peng, F.; Zhang, P. Recent advances in metal sulfides: From controlled fabrication to electrocatalytic, photocatalytic and photoelectrochemical water splitting and beyond. *Chem. Soc. Rev.* 2019, 48, 4178–4280. [CrossRef]

7. Lei, Z.; You, W.; Liu, M.; Zhou, G.; Takata, T.; Hara, M.; Domen, K.; Li, C. Photocatalytic water reduction under visible light on a novel ZnIn₄S₄ catalyst synthesized by hydrothermal method. *Chem. Commun.* 2003, 17, 2142–2143. [CrossRef]

8. Li, M.; Su, J.; Guo, L. Preparation and characterization of ZnIn₄S₄ thin films deposited by spray pyrolysis for hydrogen production. *Int. J. Hydrogen Energy* 2008, 33, 2891–2896. [CrossRef]

9. Yu, H.; Quan, X.; Zhang, Y.; Ma, N.; Chen, S.; Zhao, H. Electrochemically Assisted Photocatalytic Inactivation of *Escherichia coli* under Visible Light Using a ZnIn₄S₄ Film Electrode. *Langmuir* 2008, 24, 7599–7604. [CrossRef]

10. Chen, Z.; Li, D.; Zhang, W.; Chen, C.; Li, W.; Sun, M.; He, Y.; Fu, X. Low-Temperature and Template-Free Synthesis of ZnIn₂S₄ Microphases. *Inorg. Chem.* 2008, 47, 9766–9772. [CrossRef]

11. Bai, Z.; Yan, X.; Kang, Z.; Hu, Y.; Zhang, X.; Zhang, Y. Photoelectrochemical performance enhancement of ZnO photoanodes from ZnIn₄S₄ nanosheets coating. *Nano Energy* 2015, 14, 392–400. [CrossRef]

12. Wei, N.; Wu, Y.; Wang, M.; Sun, W.; Li, Z.; Ding, L.; Cui, H. Construction of noble-metal-free TiO₂ nanobelt/ZnIn₂S₄ nanosheet heterojunction nanocomposite for highly efficient photocatalytic hydrogen evolution. *Nanotechnology* 2019, 30, 045701. [CrossRef] [PubMed]

13. Ben Assaker, I.; Gannouni, M.; Ben Naceur, J.; Almessiere, M.A.; Al-Otaibi, A.L.; Ghrib, T.; Shen, S.; Chtourou, R. Electodeposited ZnIn₄S₄ onto TiO₂ thin films for semiconductor-sensitized photocatalytic and photoelectrochemical applications. *Appl. Surf. Sci.* 2015, 351, 927–934. [CrossRef]

14. Yang, C.; Li, Q.; Xia, Y.; Lv, K.; Li, M. Enhanced visible-light photocatalytic CO₂ reduction performance of ZnIn₂S₄ microphases by using CoO₂ as cocatalyst. *Appl. Surf. Sci.* 2019, 464, 388–395. [CrossRef]

15. Yuan, D.; Sun, M.; Tang, S.; Zhang, Y.; Wang, Z.; Qi, J.; Rao, Y.; Zhang, Q. All-solid-state BiVO₄/ZnIn₂S₄ Z-scheme composite with efficient charge separations for improved visible light photocatalytic organics degradation. *Chin. Chem. Lett.* 2020, 31, 547–550. [CrossRef]

16. Wei, L.; Chen, Y.; Zhao, J.; Li, Z. Preparation of NiS/ZnIn₂S₄ as a superior photocatalyst for hydrogen evolution under visible light irradiation. *Beilstein J. Nanotech.* 2013, 4, 949–955. [CrossRef]

17. Hou, J.; Yang, C.; Cheng, H.; Wang, Z.; Jiao, S.; Zhu, H. Ternary 3D architectures of CdS QDs/graphene/ZnIn₂S₄ heterostructures for efficient photocatalytic H₂ production. *Phys. Chem. Chem. Phys.* 2013, 15, 15660–15668. [CrossRef]

18. Guo, X.; Peng, Y.; Liu, G.; Xie, G.; Guo, Y.; Zhang, Y.; Yu, J. An Efficient ZnIn₂S₄@CuInS₄ Core-Shell p-n Heterojunction to Boost Visible-Light Photocatalytic Hydrogen Evolution. *J. Phys. Chem. C* 2020, 124, 5934–5943. [CrossRef]
19. Pan, J.; Guan, Z.; Yang, J.; Li, Q. Facile fabrication of ZnIn$_2$S$_4$/SnS$_2$ 3D heterostructure for efficient visible-light photocatalytic reduction of Cr(VI). *Chin. J. Catal.* 2020, 41, 200–208. [CrossRef]

20. Liu, H.; Jin, Z.; Xu, Z.; Zhang, Z.; Ao, D. Fabrication of ZnIn$_2$S$_4$–g-C$_3$N$_4$ sheet-on-sheet nanocomposites for efficient visible-light photocatalytic H$_2$-evolution and degradation of organic pollutants. *RSC Adv.* 2015, 5, 97951–97961. [CrossRef]

21. Li, X.; Wang, X.; Zhu, J.; Li, Y.; Zhao, J.; Li, F. Fabrication of two-dimensional Ni$_2$P/ZnIn$_2$S$_4$ heterostructures for enhanced photocatalytic hydrogen evolution. *Chem. Eng. J.* 2018, 353, 15–24. [CrossRef]

22. Pan, Y.; Yuan, X.; Jiang, L.; Yu, H.; Zhang, J.; Guan, R.; Zhao, J. Recent advances in synthesis, modification and photocatalytic applications of micro/nano-structured zinc indium sulphide. *Chem. Eng. J.* 2018, 354, 407–431. [CrossRef]

23. Li, Y.; Gao, C.; Long, R.; Xiong, Y. Photocatalyst design based on two-dimensional materials. *Mater. Today Chem.* 2019, 11, 197–216. [CrossRef]

24. Mao, S.S.; Shena, S.; Guo, L. Nanomaterials for hydrogen production, storage and utilization. *Progr. Nat. Sci. Mater. Intern.* 2012, 22, 522–534. [CrossRef]

25. Yao, J.; Lu, H. Recent Advances in Liquid-phase Heterogeneous Photocatalysis for Organic Synthesis by Selective Oxidation. *Curr. Org. Chem.* 2014, 18, 1365–1372.

26. Lucena, R.; Conesa, J.C. Photocatalysis with octahedral sulfides. In *Current Developments in Photocatalysis and Photocatalytic Materials—New Horizons in Photocatalysis*; Wang, D., Anpo, M., Fu, X., Eds.; Elsevier: Amsterdam, The Netherlands, 2020; ISBN 978-0-12-819000-5.

27. Luque, A.; Martí, A. Increasing the efficiency of ideal solar cells by photon induced transitions at intermediate levels. *Phys. Rev. Lett.* 1997, 78, 5014–5017. [CrossRef]

28. Palacios, P.; Fernández, J.J.; Sánchez, K.; Conesa, J.C.; Wahnón, P. First-principles investigation of isolated band formation in half-metal Ti$_x$Ga$_{1-x}$P compound at different dilutions. *Phys. Rev. B* 2006, 73, 085206. [CrossRef]

29. Palacios, P.; Sánchez, K.; Wahnón, P.; Conesa, J.C. Characterization by Ab-initio Calculations of an Intermediate Band Material Based on Chalcopyrite Semiconductors Substituted by Several Transition Metals. *J. Sol. Energy Eng.* 2007, 129, 314–318. [CrossRef]

30. Palacios, P.; Aguilera, I.; Sánchez, K.; Conesa, J.C.; Wahnón, P. Transition Metal Substituted Indium Thiospinels as Novel Intermediate Band Materials: Prediction and Understanding of their Electronic Properties. *Phys. Rev. Lett.* 2008, 101, 046403. [CrossRef]

31. Wahnón, P.; Conesa, J.C.; Palacios, P.; Lucena, R.; Aguilera, I.; Seminovski, Y.; Fresno, F. V-doped SnS$_2$: A new intermediate band material for a better use of the solar spectrum. *Phys. Chem. Chem. Phys.* 2011, 13, 20401–20407. [CrossRef]

32. García, G.; Palacios, P.; Menéndez-Prupin, E.; Montero-Alejo, A.L.; Conesa, J.C.; Wahnón, P. Influence of chromium hyperdoping on the electronic structure of CH$_3$NH$_3$PbI$_3$ perovskite: A first-principles insight. *Sci. Rep.* 2018, 8, 2511. [CrossRef] [PubMed]

33. Sánchez-Palencia, P.; García, G.; Conesa, J.C.; Wahnón, P.; Palacios, P. Spinel-Type Nitride Compounds with improved features as Solar Cell Absorbers. *Acta Mater.* 2020, 197, 316–329. [CrossRef]

34. Lucena, R.; Conesa, J.C.; Aguilera, I.; Palacios, P.; Wahnón, P. V-substituted In$_2$S$_3$: An intermediate band material with photocatalytic activity in the whole visible light range. *J. Mater. Chem. A* 2014, 2, 8236–8245. [CrossRef]

35. Serrano-Sánchez, F.; Conesa, J.C.; Rodríguez, J.E.; Marini, C.; Martínez, J.L.; Alonso, J.A. Divalent chromium in the octahedral positions of the novel hybrid perovskites CH$_3$NH$_3$Pb$_{1-x}$Cr$_x$(Br$_2$Cl)$_3$ (x = 0.25, 0.5): Induction of narrow bands inside the bandgap. *J. Alloys Comp.* 2020, 821, 153414. [CrossRef]

36. Lucena, R.; Fresno, F.; Conesa, J.C. Spectral response and stability of In$_2$S$_3$ as visible light active photocatalyst. *Catal. Commun.* 2012, 20, 1–5. [CrossRef]

37. Lucena, R.; Fresno, F.; Conesa, J.C. Hydrothermally synthesized nanocrystalline tin disulphide as visible light-active photocatalyst: Spectral response and stability. *Appl. Catal. A Gen.* 2012, 415, 111–117. [CrossRef]

38. Lucena, R.; Aguilera, I.; Palacios, P.; Wahnón, P.; Conesa, J.C. Synthesis and Spectral Properties of Nanocrystalline V-Substituted In$_2$S$_3$, a Novel Material for More Efficient Use of Solar Radiation. *Chem. Mater.* 2008, 20, 5125–5127. [CrossRef]

39. Kresse, G.; Hafner, J. Abinitio molecular-dynamics for liquid-metals. *Phys. Rev. B* 1993, 47, 558–561. [CrossRef] [PubMed]

40. Kresse, G.; Joubert, D. From ultrasoft pseudopotentials to the projector augmented-wave method. *Phys. Rev. B* 1999, 59, 1758–1775. [CrossRef]

41. Bucko, T.; Lebegue, S.; Angyan, J.G.; Hafner, J. Extending the applicability of the Tkatchenko-Scheffler dispersion correction via iterative Hirshfeld partitioning. *J. Chem. Phys.* 2014, 141, 034114. [CrossRef] [PubMed]

42. Rangarajan, G.; Yan, N.; Farnood, R. High-performance photocatalysts for the selective oxidation of alcohols to carboxyl compounds. *Can. J. Chem. Eng.* 2020, 98, 2259–2293. [CrossRef]

43. Ali, M.M.; Sandhya, K.N.Y. One-step solvothermal synthesis of carbon doped TiO$_2$–MoO$_2$ heterostructure composites with improved visible light catalytic activity. *New J. Chem.* 2016, 40, 8123–8130. [CrossRef]

44. Chen, J.; Zhang, H.; Liu, P.; Li, Y.; Liu, X.; Li, G.; Wong, P.K.; An, T.; Zhao, H. Cross-linked ZnIn$_2$S$_4$/rGO composite photocatalyst for sunlight-driven photocatalytic degradation of 4-nitrophenol. *Appl. Catal. B Environ.* 2015, 168, 266–273. [CrossRef]

45. Tian, Q.; Wu, W.; Liu, J.; Wu, Z.; Yao, W.; Ding, J.; Jiang, C. Dimensional heterostructures of 1D CdS/2D ZnIn$_2$S$_4$ composites with 2D graphene: Designed synthesis and superior photocatalytic performance. *Dalton Trans.* 2017, 46, 2770–2777. [CrossRef] [PubMed]

46. Li, L.; Che, H.; Yan, Y.; Liu, C.; Dong, H. Z-scheme AgVO$_3$/ZnIn$_2$S$_4$ photocatalysts: “One Stone and Two Birds” strategy to solve photocorrosion and improve the photocatalytic activity and stability. *Chem. Eng. J.* 2020, 398, 125523. [CrossRef]
47. Fan, W.-J.; Zhou, Z.-F.; Xu, W.-B.; Shi, Z.-F.; Ren, F.-M.; Ma, H.-H.; Huang, S.-W. Preparation of ZnIn$_2$S$_4$/fluoropolymer fiber composites and its photocatalytic H$_2$ evolution from splitting of water using Xe lamp irradiation. *Int. J. Hydrogen Energy* 2010, 35, 6525–6530. [CrossRef]

48. Shen, S.; Chen, X.; Ren, F.; Kronawitter, C.X.; Mao, S.S.; Guo, L. Solar light-driven photocatalytic hydrogen evolution over ZnIn$_2$S$_4$ loaded with transition-metal sulfides. *Nanoscale Res. Lett.* 2011, 6, 290. [CrossRef]

49. An, H.; Li, M.; Liu, R.; Gao, Z.; Yin, Z. Design of Ag$_x$Au$_{1-x}$ alloy/ZnIn$_2$S$_4$ system with tunable spectral response and Schottky barrier height for visible-light-driven hydrogen evolution. *Chem. Eng. J.* 2020, 382, 122953. [CrossRef]

50. Hu, J.; Chen, C.; Zheng, Y.; Zhang, G.; Guo, C.; Li, C.M. Spatially Separating Redox Centers on Z-Scheme ZnIn$_2$S$_4$/BiVO$_4$ Hierarchical Heterostructure for Highly Efficient Photocatalytic Hydrogen Evolution. *Small* 2020, 16, 2002988. [CrossRef]

51. Zhou, M.; Wang, S.; Yang, P.; Luo, Z.; Yuan, R.; Asiri, A.M.; Wakeel, M.; Wang, X. Layered Heterostructures of Ultrathin Polymeric Carbon Nitride and ZnIn$_2$S$_4$ Nanosheets for Photocatalytic CO$_2$ Reduction. *Chem. Eur. J.* 2018, 24, 18529–18534. [CrossRef]

52. Gao, W.; Wang, L.; Gao, C.; Liu, J.; Yang, Y.; Yang, L.; Shen, Q.; Wu, C.; Zhou, Y.; Zou, Z. Exquisite design of porous carbon microtubule-scaffolding hierarchical In$_2$O$_3$-ZnIn$_2$S$_4$ heterostructures toward efficient photocatalytic conversion of CO$_2$ into CO. *Nanoscale* 2020, 12, 14676–14681. [CrossRef] [PubMed]

53. Zhu, Z.; Li, X.; Qu, Y.; Zhou, F.; Wang, Z.; Wang, W.; Zhao, C.; Wang, H.; Li, L.; Yao, Y.; et al. A hierarchical heterostructure of CdS QDs confined on 3D ZnIn$_2$S$_4$ with boosted charge transfer for photocatalytic CO$_2$ reduction. *NanoResearch* 2021, 14, 81–90. [CrossRef]

54. Wang, X.; Chen, J.; Li, Q.; Li, L.; Zhuang, Z.; Chen, F.-F.; Yu, Y. Light-Driven Syngas Production over Defective ZnIn$_2$S$_4$ Nanosheets. *Chem. Eur. J.* 2020. [CrossRef]