

NANO EXPRESS

Open Access

Solar light-driven photocatalytic hydrogen evolution over ZnIn_2S_4 loaded with transition-metal sulfides

Shaohua Shen^{1,2}, Xiaobo Chen², Feng Ren², Coleman X Kronawitter², Samuel S Mao^{2*} and Liejin Guo^{1*}

Abstract

A series of Pt-loaded MS/ ZnIn_2S_4 (MS = transition-metal sulfide: Ag_2S , SnS, CoS, CuS, NiS, and MnS) photocatalysts was investigated to show various photocatalytic activities depending on different transition-metal sulfides. Thereinto, CoS, NiS, or MnS-loading lowered down the photocatalytic activity of ZnIn_2S_4 , while Ag_2S , SnS, or CuS loading enhanced the photocatalytic activity. After loading 1.0 wt.% CuS together with 1.0 wt.% Pt on ZnIn_2S_4 , the activity for H_2 evolution was increased by up to 1.6 times, compared to the ZnIn_2S_4 only loaded with 1.0 wt.% Pt. Here, transition-metal sulfides such as CuS, together with Pt, acted as the dual co-catalysts for the improved photocatalytic performance. This study indicated that the application of transition-metal sulfides as effective co-catalysts opened up a new way to design and prepare high-efficiency and low-cost photocatalysts for solar-hydrogen conversion.

Introduction

Since the discovery of photo-induced water splitting on TiO_2 electrodes [1], solar-driven photocatalytic hydrogen production from water using a semiconductor catalyst has attracted a tremendous amount of interest [2,3]. To efficiently utilize solar energy, numerous attempts have been made in recent years to realize different visible light-active photocatalysts [4-8]. Among them, sulfides, especially CdS-based photocatalysts with narrow band gaps, proved to be good candidates for photocatalytic hydrogen evolution from water under visible light irradiation [9-12]. However, CdS itself is not stable for water splitting, and Cd^{2+} is hazardous to environment and human health. A number of nontoxic multicomponent sulfides without Cd^{2+} ions have been developed to show comparable photocatalytic efficiency for hydrogen evolution [13-17]. In our previous work [18-22], hydrothermally synthesized ZnIn_2S_4 was found to have photocatalytic and photoelectrochemical properties that made it a good candidate for hydrogen production from water under visible light irradiation. On the other hand, a

solid co-catalyst, typically noble metal (e.g., Pt, Ru, Rh) [23] or transition-metal oxide (e.g., NiO [24], $\text{Rh}_2\text{-yCr}_y\text{O}_3$ [25], RuO_2 [26], IrO_2 [27]), loaded on the surface of the base photocatalyst can be beneficial to photocatalytic H_2 and/or O_2 evolution for water splitting [25]. Nevertheless, there have been only a limited number of studies in which metal sulfides acted as co-catalysts to enhance the activity of a semiconducting photocatalyst [28-30]. For instance, Li and co-workers observed that dual co-catalysts consisting of noble metals (Pt, Pd) and noble-metal sulfides (PdS , Ru_2S_3 , Rh_2S_3) played a crucial role in achieving very high efficiency for hydrogen evolution over CdS photocatalyst [29,30]. In this study, a series of transition-metal sulfides (MS: Ag_2S , SnS, CoS, CuS, NiS, and MnS) were deposited on hydrothermally synthesized ZnIn_2S_4 by a simple precipitation process. The photocatalytic activities for hydrogen evolution over these MS/ ZnIn_2S_4 products were investigated. We demonstrated that transition-metal sulfides, such as CuS, combined with Pt could act as dual co-catalysts for improving photocatalytic activity for hydrogen evolution from a $\text{Na}_2\text{SO}_3/\text{Na}_2\text{S}$ aqueous solution under simulated sunlight.

* Correspondence: ssmao@lbl.gov; lj-guo@mail.xjtu.edu.cn

¹State Key Laboratory of Multiphase Flow in Power Engineering, Xi'an Jiaotong University, Xi'an, Shaanxi 710049, China

²Lawrence Berkeley National Laboratory, Berkeley, CA 94720, USA

Full list of author information is available at the end of the article

Experimental section

All chemicals are of analytical grade and used as received without further purification. ZnIn_2S_4 products were prepared by a cetyltrimethylammoniumbromide (CTAB)-assisted hydrothermal synthetic method as described in our previous studies [18,19]. For the synthesis of $\text{MS}/\text{ZnIn}_2\text{S}_4$ ($\text{MS} = \text{Ag}_2\text{S}$, SnS , CoS , CuS , NiS , and MnS), 0.1 g of prepared ZnIn_2S_4 was dispersed in 20 mL of distilled water and ultrasonicated for 20 min. Under stirring, a desired amount of 0.1 M AgNO_3 (J.T. Baker Chemical Co., Phillipsburg, NJ, USA), SnCl_2 (Sigma-Aldrich, Milwaukee, WI, USA), $\text{Co}(\text{NO}_3)_2$ (Aldrich), $\text{Cu}(\text{NO}_3)_2$ (Fluka Chemical Company, Buchs, Switzerland), $\text{Ni}(\text{NO}_3)_2$ (Fluka), or $\text{Mn}(\text{CH}_3\text{COO})_2$ (Alfa-Aesar, Ward Hill, MA, USA) aqueous solution was dropped into the above suspension, followed by a dropwise addition of 0.1 M $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$ (Sigma-Aldrich) aqueous solution, containing double excess of S^{2-} relative to the amount of metal ions. The resulting suspension was stirred for another 20 min, then the $\text{MS}/\text{ZnIn}_2\text{S}_4$ precipitate was collected by centrifugation and washed with distilled water for several times, and dried overnight at 65°C . The weight contents of transition-metal sulfides (MS) in these $\text{MS}/\text{ZnIn}_2\text{S}_4$ products were controlled at 0.5% to approximately 2.0%.

X-ray diffraction patterns were obtained from a PANalytical X'pert diffractometer (PANalytical, Almelo, The Netherlands) using Ni-filtered $\text{Cu K}\alpha$ irradiation (wavelength 1.5406 Å). UV-visible absorption spectra were determined with a Varian Cary 50 UV spectrophotometer (Varian Inc, Cary, NC, USA) with MgO as reference. Morphology inspection was performed with a high-resolution scanning electron microscope (SEM, Hitachi S-4300, Tokyo, Japan). Transmission electron microscopy (TEM) study was carried out on a JEOL JEM 2010 instrument (JEOL Ltd., Tokyo, Japan). The X-ray photoelectron spectroscopy (XPS) measurements were conducted on a Kratos spectrometer (AXIS Ultra DLD, Shimadzu/Kratos Analytical, Hadano, Kanagawa, Japan) with monochromatic $\text{Al K}\alpha$ radiation ($h\nu = 1,486.69$ eV) and with a concentric hemispherical analyzer. Elemental Analysis was conducted on the Bruker S4 PIONEER X-ray fluorescence spectrum (XRF, Bruker AXS GmbH, Karlsruhe, Germany) using Rh target and 4-kW-maximum power.

Photocatalytic hydrogen evolution was performed in a side-window reaction cell. A 300-W solar simulator (AM 1.5; Newport Corporation, Irvine, CA, USA) was used as the light source. The amount of hydrogen evolved was determined using a gas chromatograph (CP-4900 Micro-GC, thermal conductivity detector, Ar carrier; Varian Inc., Palo Alto, CA, USA). In all experiments, 100 mL of deionized water containing 0.05 g of catalyst and 0.25 M $\text{Na}_2\text{SO}_3/0.35$ M Na_2S mixed

sacrificial agent was added into the reaction cell. Here, sacrificial agent was used to scavenge photo-generated holes. Argon gas was purged through the reaction cell for 30 min before reaction to remove air. Pt (1.0 wt.%) as a co-catalyst for the promotion of hydrogen evolution was deposited in situ on the photocatalyst from the precursor of $\text{H}_2\text{PtCl}_6\cdot x\text{H}_2\text{O}$ (Aldrich; 99.9%). In all cases, the reproducibility of the measurements was within $\pm 10\%$. Control experiments showed no appreciable H_2 evolution without solar light irradiation or photocatalyst.

Results and discussion

The ZnIn_2S_4 products prepared by the CTAB-assisted hydrothermal method possessed a hexagonal structure and morphology of microspheres comprising of numerous petals, and showed an absorption edge at about 510 nm (Additional file 1, Figure S1-3). Compared to pure ZnIn_2S_4 , the obtained $\text{MS}/\text{ZnIn}_2\text{S}_4$ ($\text{MS} = \text{metal sulfide: Ag}_2\text{S}$, SnS , CoS , CuS , NiS , and MnS) displayed different absorption profiles (Additional file 1, Figure S4), with enhanced absorption in the visible light region from 550 to 800 nm. Such additional broad band ($\lambda > 550$ nm) can be assigned to the absorption of transition-metal sulfides.

We investigated the photocatalytic activity for hydrogen evolution over $\text{MS}/\text{ZnIn}_2\text{S}_4$ ($\text{MS} = \text{metal sulfide: Ag}_2\text{S}$, SnS , CoS , CuS , NiS , and MnS). Photocatalytic activities for hydrogen evolution over $\text{MS}/\text{ZnIn}_2\text{S}_4$ were evaluated by loading 1 wt.% Pt as co-catalyst. Figure 1 shows the average rates of H_2 evolution over Pt-loaded $\text{MS}/\text{ZnIn}_2\text{S}_4$ photocatalysts under simulated solar irradiation in the initial 20-h period. The Pt- ZnIn_2S_4 showed a photocatalytic activity for H_2 production at the rate of $126.7 \mu\text{mol}\cdot\text{h}^{-1}$, which is comparable to

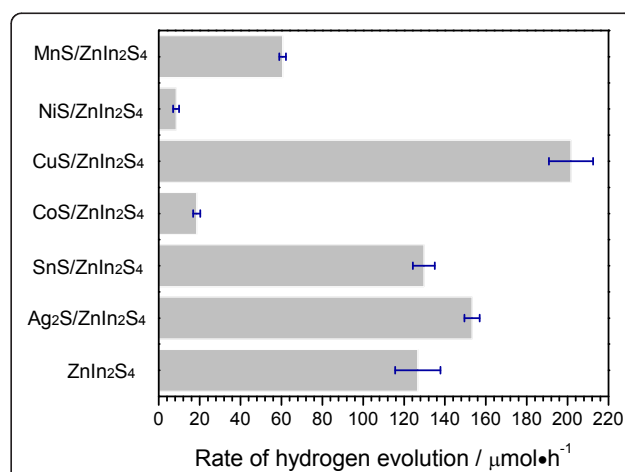
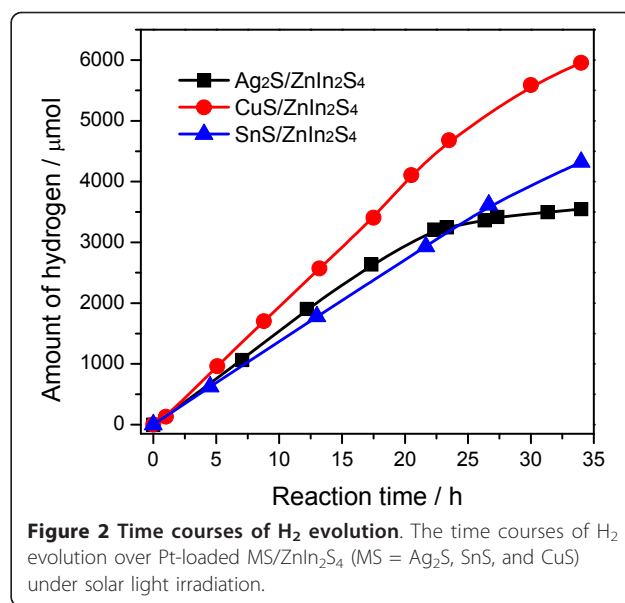


Figure 1 Average rates of H_2 evolution. The average rates of H_2 evolution over Pt-loaded $\text{MS}/\text{ZnIn}_2\text{S}_4$ ($\text{MS} = \text{metal sulfide: Ag}_2\text{S}$, SnS , CoS , CuS , NiS , and MnS) under solar light irradiation in the initial 20-h period.

reported values in previous literatures [18-20]. The hydrogen production rates of Pt-MS/ZnIn₂S₄ photocatalysts varied with different kinds of loaded transition-metal sulfides. The Pt-MS/ZnIn₂S₄ (MS = Ag₂S, SnS, and CuS) photocatalysts displayed enhanced activities for hydrogen evolution under solar irradiation. In particular, the H₂ evolution rate greatly increased to 200 μmol·h⁻¹ after loading 1.0 wt.% of CuS on ZnIn₂S₄. In this CuS/ZnIn₂S₄ sample, the formation of CuS (copper monosulfide) could be evidenced by XPS analysis results shown in Figure S5 (Additional file 1). The survey scan spectrum (Figure S5A of Additional file 1) indicated the presence of Cu, Zn, In, and S in the sample [21,31]. The binding energies shown in Figure S5E (Additional file 1) for Cu 2p_{3/2} and Cu 2p_{1/2} were 952.5 and 932.5 eV, respectively, which are close to the reported value of Cu²⁺[31]. The actual molar ratio of Cu:Zn:In:S was 0.011:0.2:0.39:1.01 as confirmed by XRF analysis result, with weight content of CuS calculated to be 1.15 wt.%, which is quite close to the proposed stoichiometric ratio. The photocatalytic activities for hydrogen evolution over Pt-MS/ZnIn₂S₄ (MS = Ag₂S, SnS, and CuS) in the initial 20-h period were measured to increase in the order of SnS < Ag₂S < CuS. Generally, these transition-metal sulfides (SnS, Ag₂S, and CuS) alone are not photocatalytically active for H₂ evolution, as no H₂ was detected when they were used as the catalysts. Thus, the improvement of photocatalytic performances of Pt-MS/ZnIn₂S₄ (MS = Ag₂S, SnS, and CuS) can be related to the enhanced separation of photo-generated electrons and holes induced by the hybridization of MS with ZnIn₂S₄. In this photocatalysis system, transition-metal sulfides (MS = Ag₂S, SnS, and CuS) combined with noble-metal Pt acted as dual co-catalysts for photocatalytic hydrogen evolution. However, when transition-metal sulfides (MS = CoS, NiS, and MnS) were loaded on ZnIn₂S₄, the rates of H₂ evolution over Pt-MS/ZnIn₂S₄ (MS = CoS, NiS, and MnS) were sharply decreased. Instead of the role as effective co-catalysts, these transition-metal sulfides (i.e., CoS, NiS, and MnS) may work as the recombination center of photo-generated electron-hole pairs, which lowered the photocatalytic activity for hydrogen evolution over Pt-MS/ZnIn₂S₄ (MS = CoS, NiS, and MnS). Further investigation is needed and also under way to provide enough supporting information to evidence the negative effects of CoS, NiS, and MnS, although main attention has focused on the more effective co-catalysts such as Ag₂S, SnS, and CuS in the following discussion.

Figure 2 shows the reaction time depended H₂ evolution over Pt-loaded MS/ZnIn₂S₄ (MS = Ag₂S, SnS, and CuS) under solar irradiation. Pt-SnS/ZnIn₂S₄ and Pt-CuS/ZnIn₂S₄ exhibited stable activity in the period of 34-h experiment. However, the rate of H₂ production



over Pt-Ag₂S/ZnIn₂S₄ had a significant drop after irradiation for approximately 20 h. This deactivation may result from gradual reduction of Ag₂S particles loaded on the surface of ZnIn₂S₄ to metallic Ag by photo-generated electrons during the reaction. Similar deactivation of photocatalyst was previously observed for CdS modified with Ag₂S [32]. However, this result is quite different from our previous report on Pt-Ag₂S/CdS, in which the high dispersion of Ag₂S in the nanostructure of CdS contributed to stable photocatalytic activity for hydrogen evolution [33]. Taking into account the reduction potential (*vs.* normal hydrogen electrode (NHE)) of Ag⁺/Ag (0.80 V), Cu²⁺/Cu (0.34 V), and Sn²⁺/Sn (-0.14 V), reduction of Ag₂S by photo-generated electrons is easier than photoreduction of CuS and SnS. Therefore, Pt-MS/ZnIn₂S₄ (MS = SnS and CuS) turned to be more stable than Pt-Ag₂S/ZnIn₂S₄ during the photocatalytic reaction for hydrogen evolution.

Table 1 shows the dependence of photocatalytic activity for H₂ evolution over Pt-loaded MS/ZnIn₂S₄ (MS = SnS and CuS) on the loading amount of transition-metal sulfides. With the increase of SnS-loading from 0 to 2.0 wt.%, the rate of H₂ evolution over Pt-SnS/ZnIn₂S₄ does not show significant changes. In contrast, the photocatalytic performance of Pt-CuS/ZnIn₂S₄ depends strongly on the amount of CuS-loading, and the optimum loading amount of CuS is approximately 1.0 wt.%. The progressive regression of photocatalytic activity observed with the amount of CuS increasing from 1.0 to 2.0 wt.% may be due to the fact that excess CuS particles loaded on the surface of ZnIn₂S₄ could act as the optical filter or charge recombination center instead of co-catalyst for charge separation [19,32].

Table 1 Average rates of H₂ evolution over Pt-loaded MS/ZnIn₂S₄

Photocatalyst MS/ZnIn ₂ S ₄	Content of MS	Rate of hydrogen evolution μmol/h
ZnIn ₂ S ₄	0	126.7
SnS/ZnIn ₂ S ₄	0.5%	115.4
SnS/ZnIn ₂ S ₄	1.0%	129.7
SnS/ZnIn ₂ S ₄	2.0%	127.1
CuS/ZnIn ₂ S ₄	0.5%	181.4
CuS/ZnIn ₂ S ₄	1.0%	201.7
CuS/ZnIn ₂ S ₄	2.0%	139.4

The average rates of H₂ evolution over Pt-loaded MS/ZnIn₂S₄ (MS = metal sulfide: SnS and CuS) under solar light irradiation in the initial 20-h period.

To visualize hybridization of CuS with ZnIn₂S₄, ZnIn₂S₄, and CuS/ZnIn₂S₄ photocatalysts were investigated by TEM. A representative TEM image of ZnIn₂S₄ is shown in Figure 3A, which shows the formation of microspheres, 1-2 μm in diameter and comprised of a circle of micro-petals. The ED pattern (inset of Figure 3A) substantiates that the ZnIn₂S₄ microsphere is of a hexagonal phase. The TEM image in Figure 3B shows that some nanoparticles are loaded on the surface of ZnIn₂S₄ microspheres. Such nanoparticles were confirmed by the ED pattern (inset in Figure 3B) to be CuS with typical orthorhombic structure. Thus, nanosized CuS particles dispersed on the ZnIn₂S₄ surface would act as the charge-transfer co-catalyst, together with photodeposited Pt particles. The Pt-CuS dual co-catalysts improved the charge separation and therefore increased the photocatalytic activity.

Figure 4 illustrates the process of photo-generated charge transfer for photocatalytic hydrogen evolution over Pt-CuS/ZnIn₂S₄ in an aqueous solution containing Na₂SO₃/Na₂S under simulated sunlight. Band gap excitation produces electron-hole pairs in ZnIn₂S₄ particles. The excited electrons are subsequently channeled to Pt sites, which reduce protons to generate hydrogen. On the other hand, the valence band potential of ZnIn₂S₄, deduced from the conduction band potential (0.29 V vs. NHE) [22] and the band gap energy (2.43 eV), is about 2.72 V vs. NHE, which is more positive than the OH⁻/O₂ redox potential [4]. The valence band potential of CuS is less positive than the OH⁻/O₂ redox potential [34]. Such a difference of valence band potentials makes it possible for the excited holes to transfer from ZnIn₂S₄ to CuS to react with Na₂S/Na₂SO₃ electron donor in the solution. Therefore, Pt and CuS are supposed to act as the reduction and oxidation co-catalyst, respectively, which leads to more efficient charge separation, thus improves photocatalytic activity of Pt-CuS/ZnIn₂S₄. Similar benefits of dual co-catalysts on photocatalytic activity have been observed for CdS loaded with noble metals as reduction catalysts and noble-metal sulfides as oxidation catalysts [29,30]. It is noteworthy that replacing

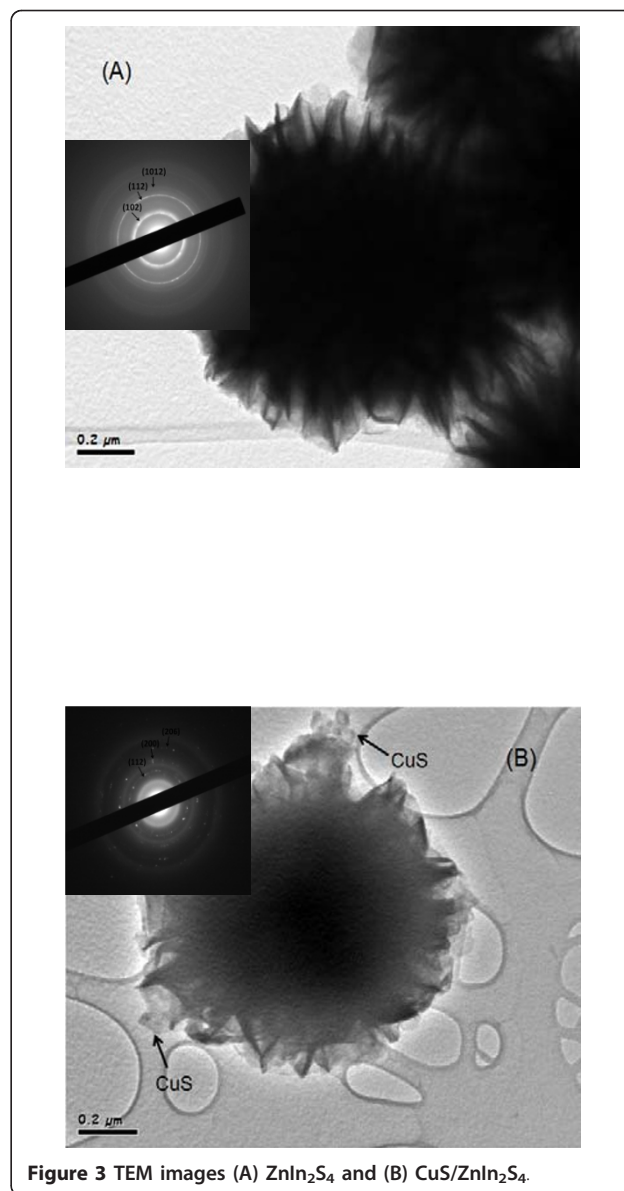


Figure 3 TEM images (A) ZnIn₂S₄ and (B) CuS/ZnIn₂S₄.

noble-metal sulfides (such as PdS) by transition-metal sulfides (such as CuS) as the co-catalysts would help lower the cost of photocatalysts for solar-hydrogen production. Moreover, seeking effective co-catalyst candidates could be expanded to other transition-metal sulfides such as FeS and SnS₂, etc. Detailed research on this subject is still an ongoing progress in our group.

Conclusions

In summary, a series of Pt-loaded MS/ZnIn₂S₄ (MS = transition-metal sulfides: Ag₂S, SnS, CoS, CuS, NiS, and MnS) photocatalysts were developed. It is found that Ag₂S, SnS, and CuS could enhance the photocatalytic activity of hydrogen evolution over ZnIn₂S₄ to varying degrees, while SnS, CoS, and NiS would reduce the

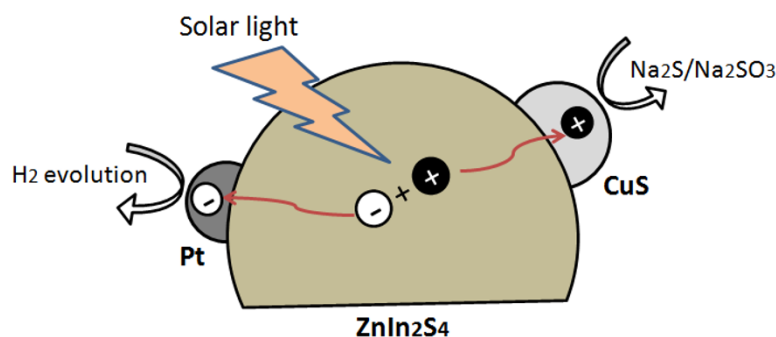


Figure 4 Schematic illustration of photo-generated charge-transfer process for photocatalytic hydrogen evolution over Pt-CuS/ ZnIn_2S_4 . From an aqueous solution containing $\text{Na}_2\text{SO}_3/\text{Na}_2\text{S}$ under simulated solar light.

activity. Among them, the Pt-CuS/ ZnIn_2S_4 photocatalyst exhibited the most efficient and stable activity for hydrogen evolution. This can be attributed to the fact that the dual co-catalysts of Pt and CuS entrapped photo-induced electrons and holes for reduction and oxidation reaction, respectively, improving charge separation and hence the photocatalytic activity. Application of transition-metal sulfides as co-catalysts opens up an opportunity toward realizing high-efficiency, low-cost photocatalysts for solar-hydrogen conversion.

Additional material

Additional file 1: Figures S1, S2, S3, S4 and S5.

Acknowledgements

The authors acknowledge the support by the National Basic Research Program of China (No. 2009CB220000), Natural Science Foundation of China (No. 50821064 and No. 90610022), and the U.S. Department of Energy. One of the authors (SS) was also supported by China Scholarship Council and the Fundamental Research Funds for the Central Universities (No. 08142004 and No. 08143019).

Author details

¹State Key Laboratory of Multiphase Flow in Power Engineering, Xi'an Jiaotong University, Xi'an, Shaanxi 710049, China ²Lawrence Berkeley National Laboratory, Berkeley, CA 94720, USA

Authors' contributions

SS carried out experiments except SEM and TEM characterization, and drafted the manuscript. XC participated in the design of the study. FR performed the TEM characterization. CXK performed the SEM characterization and improved English writing. SSM provide financial support and participated in the design and coordination of this study. LG conceived of the study, and participated in its design and coordination. All authors read and approved the final manuscript.

Competing interests

The authors declare that they have no competing interests.

Received: 6 October 2010 Accepted: 5 April 2011 Published: 5 April 2011

References

1. Fujishima A, Honda K: Electrochemical photolysis of water at a semiconductor electrode. *Nature (London)* 1972, **238**:37.

2. Mao SS, Chen X: Selected nanotechnologies for renewable energy applications. *Int J Energy Res* 2007, **31**:619.
3. Chen X, Mao SS: Titanium dioxide nanomaterials: synthesis, properties, modifications, and applications. In *Chem Rev. Volume 107*. Washington, D. C.; 2007:2891.
4. Kudo A, Miseki Y: Heterogeneous photocatalyst materials for water splitting. *Chem Soc Rev* 2009, **38**:253.
5. Chen X, Shen S, Guo L, Mao SS: Semiconductor-based photocatalytic hydrogen generation. In *Chem Rev. Volume 110*. Washington, D.C.; 2010:6503.
6. Zou ZG, Ye JH, Sayama K, Arakawa H: Direct splitting of water under visible light irradiation with an oxide semiconductor photocatalyst. *Nature (London)* 2001, **414**:625.
7. Maeda K, Teramura K, Lu D, Takata T, Saito N, Inoue Y, Domen K: Photocatalyst releasing hydrogen from water. *Nature (London)* 2006, **440**:295.
8. Maeda K, Domen K: New non-oxide photocatalysts designed for overall water splitting under visible light. *J Phys Chem C* 2007, **111**:7851.
9. Xing C, Zhang Y, Yan W, Guo L: Band structure-controlled solid solution of $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ photocatalyst for hydrogen production by water splitting. *Int J Hydrogen Energy* 2006, **31**:2018.
10. Jing D, Guo L: A novel method for the preparation of a highly stable and active CdS photocatalyst with a special surface nanostructure. *J Phys Chem B* 2006, **110**:11139.
11. Shen S, Guo L: Growth of quantum-confined CdS nanoparticles inside Ti-MCM-41 as a visible light photocatalyst. *Mater Res Bull* 2008, **43**:437.
12. Bao N, Shen L, Takata T, Domen K: Self-templated synthesis of nanoporous CdS nanostructures for highly efficient photocatalytic hydrogen production under visible light. *Chem Mater* 2008, **20**:110.
13. Kaga H, Saito K, Kudo A: Solar hydrogen production over novel metal sulfide photocatalysts of $\text{AGa}_2\text{In}_3\text{S}_8$ (A = Cu or Ag) with layered structures. *Chem Commun* 2010, **46**:3779.
14. Jang JS, Choi SH, Shin N, Yu C, Lee JS: AgGaS_2 -type photocatalysts for hydrogen production under visible light: Effects of post-synthetic H_2S treatment. *J Solid State Chem* 2007, **180**:1110.
15. Tsuji I, Shimodaira Y, Kato H, Kobayashi H, Kudo A: Novel stannite-type complex sulfide photocatalysts $\text{A}^{\text{I}}_2\text{-Zn-A}^{\text{IV}}\text{-S}_4$ (A^{I} = Cu and Ag; A^{IV} = Sn and Ge) for hydrogen evolution under visible-light irradiation. *Chem Mater* 2010, **22**:1402.
16. Tsuji I, Kato H, Kobayashi H, Kudo A: Photocatalytic H_2 evolution reaction from aqueous solutions over band structure-controlled $(\text{AgIn})_x\text{Zn}_{2(1-x)}\text{S}_2$ solid solution photocatalysts with visible-light response and their surface nanostructures. *J Am Chem Soc* 2004, **126**:13406.
17. Tsuji I, Kato H, Kudo A: Photocatalytic hydrogen evolution on $\text{ZnS-CuInS}_2\text{-AgInS}_2$ solid solution photocatalysts with wide visible light absorption bands. *Chem Mater* 2006, **18**:1969.
18. Shen S, Zhao L, Guo L: Cetyltrimethylammoniumbromide (CTAB)-assisted hydrothermal synthesis of ZnIn_2S_4 as an efficient visible-light-driven photocatalyst for hydrogen production. *Int J Hydrogen Energy* 2008, **33**:4501.
19. Shen S, Zhao L, Zhou Z, Guo L: Enhanced photocatalytic hydrogen evolution over Cu-doped ZnIn_2S_4 under visible light irradiation. *J Phys Chem C* 2008, **112**:16148.

20. Shen S, Zhao L, Guo L: Crystallite, optical and photocatalytic properties of visible-light-driven ZnIn_2S_4 photocatalysts synthesized via a surfactant-assisted hydrothermal method. *Mater Res Bull* 2009, **44**:100.
21. Shen S, Zhao L, Guo L: Morphology, structure and photocatalytic performance of ZnIn_2S_4 synthesized via a solvothermal/hydrothermal route in different solvents. *J Phys Chem Solids* **69**:2426.
22. Li M, Su J, Guo L: Preparation and characterization of ZnIn_2S_4 thin films deposited by spray pyrolysis for hydrogen production. *Int J Hydrogen Energy* 2008, **33**:2891.
23. Sasaki Y, Iwase A, Kato H, Kudo A: The effect of co-catalyst for Z-scheme photocatalysis systems with an $\text{Fe}^{3+}/\text{Fe}^{2+}$ electron mediator on overall water splitting under visible light irradiation. *J Catal* 2008, **259**:133.
24. Tian M, Shangguan W, Yuan J, Jiang L, Chen M, Shi J, Ouyang Z, Wang S: $\text{K}_4\text{Ce}_2\text{M}_{10}\text{O}_{30}$ (M = Ta, Nb) as visible light-driven photocatalysts for hydrogen evolution from water decomposition. *Appl Catal A: Gen* 2006, **309**:76.
25. Maeda K, Teramura K, Domen K: Development of cocatalysts for photocatalytic overall water splitting on $(\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)$ solid solution. *Catal Surv Asia* 2007, **11**:145.
26. Yuan Y, Lv J, Jiang X, Li Z, Yu T, Zou Z, Ye J: Large impact of strontium substitution on photocatalytic water splitting activity of BaSnO_3 . *Appl Phys Lett* 2007, **91**:094107.
27. Hara M, Waraksa CC, Lean JT, Lewis BA, Mallouk TE: photocatalytic water oxidation in a buffered Tris(2,2'-bipyridyl)ruthenium complex-colloidal IrO_2 system. *J Phys Chem A* 2000, **104**:5275.
28. Zong X, Yan H, Wu G, Ma G, Wen F, Wang L, Li C: Enhancement of photocatalytic H_2 evolution on CdS by loading MoS_2 as cocatalyst under visible light irradiation. *J Am Chem Soc* 2008, **130**:7176.
29. Ma G, Yan H, Shi J, Zong X, Lei Z, Li C: Direct splitting of H_2S into H_2 and S on CdS-based photocatalyst under visible light irradiation. *J Catal* 2008, **260**:134.
30. Yan H, Yang J, Ma G, Wu G, Zong X, Lei Z, Shi J, Li C: Visible-light-driven hydrogen production with extremely high quantum efficiency on Pt-PdS/CdS photocatalyst. *J Catal* 2009, **266**:165.
31. Li Y, Chen G, Wang Q, Wang X, Zhou A, Shen Z: Hierarchical ZnS- In_2S_3 -CuS nanospheres with nanoporous structure: facile synthesis, growth mechanism, and excellent photocatalytic activity. *Adv Funct Mater* 2010, **20**:3390.
32. Reber JF, Rusek M: Photochemical hydrogen production with platinized suspensions of cadmium sulfide and cadmium zinc sulfide modified by silver sulfide. *J Phys Chem* 1986, **90**:824.
33. Shen S, Guo L, Chen X, Ren F, Mao SS: Effect of Ag_2S on solar-driven photocatalytic hydrogen evolution of nanostructured CdS. *Int J Hydrogen Energy* 2010, **35**:7110.
34. Xu Y, Schoonen MAA: The absolute energy positions of conduction and valence bands of selected semiconducting minerals. *Am Mineral* 2000, **85**:543.

doi:10.1186/1556-276X-6-290

Cite this article as: Shen et al.: Solar light-driven photocatalytic hydrogen evolution over ZnIn_2S_4 loaded with transition-metal sulfides. *Nanoscale Research Letters* 2011 **6**:290.

Submit your manuscript to a SpringerOpen[®] journal and benefit from:

- Convenient online submission
- Rigorous peer review
- Immediate publication on acceptance
- Open access: articles freely available online
- High visibility within the field
- Retaining the copyright to your article

Submit your next manuscript at ► springeropen.com
