



# Article

# Synthesis of AgInS<sub>2</sub>-xAg<sub>2</sub>S-yZnS-zIn<sub>6</sub>S<sub>7</sub> (x, y, z = 0, or 1) Nanocomposites with Composition-Dependent Activity towards Solar Hydrogen Evolution

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**Abstract:** Metal sulfides-based nanomaterials have been used as a class of efficient solar driven photocatalysts. However, the H<sub>2</sub>-production rate observed over these photocatalysts remains problematic. Here, the AgInS<sub>2</sub>-*x*Ag<sub>2</sub>S-*y*ZnS-*z*In<sub>6</sub>S<sub>7</sub> (*x*, *y*, *z* = 0 or 1) nanocomposites with controlled compositions have been successfully prepared by a simple hydrothermal method with AgI polyhedrons as silver source. The obtained AgInS<sub>2</sub>-*x*Ag<sub>2</sub>S-*y*ZnS-*z*In<sub>6</sub>S<sub>7</sub> nanocomposites showed a composition-dependent activity for H<sub>2</sub> evolution from aqueous solution under simulated sun-light irradiation. The results showed that the optimized product of AgInS<sub>2</sub>-Ag<sub>2</sub>S-ZnS nanoparticles synthesized with the precursor ratio of Ag:Zn = 1:1 exhibited the highest H<sub>2</sub> evolution rate of 5.4 mmol· g<sup>-1</sup>· h<sup>-1</sup>. Furthermore, the catalyst can be used for 20 h without loss of activity, showing its high stability. It opens a new path to achieve highly efficient solar photocatalyst for H<sub>2</sub> evolution from water splitting.

Keywords: heterojunction; AgInS<sub>2</sub>-*x*Ag<sub>2</sub>S-*y*ZnS-*z*In<sub>6</sub>S<sub>7</sub>; photocatalysis; H<sub>2</sub> evolution

# 1. Introduction

Two major kinds of photocatalysts in terms of composition are mainly used to drive solar water-splitting [1]. One is single-component material possessing proper band structure aligned for hydrogen generation. The other is multi-component composite made of different photo-absorbers with the matched band alignments to split water. The bandgap of these materials should be relatively narrow, which can efficiently favor the absorption of solar light [2–4]. Additionally, the conduction band edge must be sufficiently more negative than the reduction potential of protons. Compared with single-component material, making a complex catalyst composite has several advantages. First, the potentials of the conduction and valence bands shift successively with composition. According to the band gap transition, the composite is able to absorb enough visible light. Second, photogenerated electrons and holes can move smoothly in the continuous valence and conduction bands, rather than in the discrete levels seen in the single photocatalyst. A series of ZnS-CuInS<sub>2</sub>-AgInS<sub>2</sub> with a different percentage of the components have been successfully prepared, whose absorption edges were shifted monotonically to longer wavelengths as the ratio of MInS<sub>2</sub> (M = Cu and Ag) to ZnS increases [5]. Moreover, optoelectronic materials with electronically coupled components usually possess interesting

and unique optical and electronic properties, *i.e.*, enlarged absorption region of the solar spectrum, facilitated charge transportation without increasing the rate of charge recombination, and enhanced charge collection efficiency [6,7]. These excellent properties make optoelectronic composites potential candidates for application in the fields of photocatalysis. The nanocomposite theoretically has the ability to provide a high photocatalytic water-splitting efficiency. The heterojunction with different energy levels may form an ideal system to cause a rapid photo-induced charge separation and decreased recombination chance of electron–hole pairs [8,9]. Therefore, under the irradiation of solar energy, a photoinduced electron would transfer efficiently in photochemically stable semiconductor nanocrystals by the synergetic effect of the multi-component system [10–13].

As is the case with metal oxide semiconductors, e.g., TiO<sub>2</sub> and ZnO, I-III-VI<sub>2</sub> (e.g., (Cu)AgInS<sub>2</sub>) [14–18] and II-VI (e.g., Zn(Cd)S) [19–22], groups have been developed as a new platform for photocatalytic applications. With the rapid growth of research in this area, synthesis strategies such as alloying, doping, and solid solution nanomaterials have attracted much attention with regard to band gap and electronic wave function engineering [23,24]. For example, Kudo and Peng synthesized  $(AgIn)_x Zn_{2(1-x)}S_2$  and  $(CuIn)_x Zn_{2(1-x)}S_2$  solid solutions with the capacity to reduce water to H<sub>2</sub> under visible light [14,17]. Mao et al. investigated the tunable light absorption and photoluminescence properties of AgInS<sub>2</sub>/ZnS nanocrystals [25]. Michalska et al. synthesized core/shell CuInS<sub>2</sub>/ZnS quantum dots and studied the optical features and structure in detail [26]. However, there are no obvious heterointerfaces in solid solutions and the doping system, and it is difficult to achieve the morphology and size control. In semiconductor nanocomposites, alloying of the heterojunction interface can reduce the lattice mismatch between different components, where the mixed compositions allow for gradual strain release with improved optical properties [27,28]. The reaction chemistry of the AgInS<sub>2</sub>-ZnS system is complicated and very intriguing. It can favor the design of photocatalysts with widely tunable properties. However, it is still not well understood how to control the structure of the multi-component, and to tune the photochemistry properties of alloying semiconductors.

Herein, we have developed a facile hydrothermal method to prepare  $AgInS_2-xAg_2S-yZnS-zIn_6S_7$ (x, y, z = 0 or 1) nanocomposites. The compositions of the resulting nanocomposites can be controlled through varying the ratios of feeding stocks, which are the main factors in determining their activities towards solar hydrogen evolution. The experimental results demonstrated that the heterojunction structures exhibited much higher photocatalytic activity than single  $AgInS_2$  and  $AgInS_2-Ag_2S$  for solar  $H_2$  evolution.

# 2. Results and Discussion

In order to obtain an optimized efficient solar photocatalyst for H<sub>2</sub> production, the multi-component nanocomposites were synthesized at various molar ratios of Ag<sup>+</sup> to Zn<sup>2+</sup> ions. Figure 1 shows XRD patterns of the as-synthesized AgInS<sub>2</sub>-*x*Ag<sub>2</sub>S-*y*ZnS-*z*In<sub>6</sub>S<sub>7</sub> nanoheterojunctions produced at different Ag:Zn ratios. It shows that only single orthorhombic phase of AgInS<sub>2</sub> is obtained when the starting molar ratio of Ag:Zn is 5:1 (Figure 1A). Compared with tetragonal AgInS<sub>2</sub>, the orthorhombic AgInS<sub>2</sub> can be obtained under a mild condition (180 °C), which may be due to the proper chemical environment and conditions used for the materials preparation. With decreasing the ratio to 2:1, monoclinic Ag<sub>2</sub>S appears in the product (Figure 1B). Further increasing the dosage of Zn<sup>2+</sup> (Ag:Zn = 1:1), as shown in Figure 1C, the characteristic peak of hexagonal ZnS appears, meaning that AgInS<sub>2</sub>-Ag<sub>2</sub>S-ZnS nanocomposite formed. However, as shown in Figure 1D,E, further increasing of the amount of Zn<sup>2+</sup> ions it results in the formation of In<sub>6</sub>S<sub>7</sub>, and the product thus switches to AgInS<sub>2</sub>-Ag<sub>2</sub>S-ZnS-In<sub>6</sub>S<sub>7</sub>. It is clear that no other characteristic peaks for external impurities are observed, indicating that the phase composition of the final products can be controlled through varying the addition of Zn<sup>2+</sup> ions.



**Figure 1.** X-ray diffraction patterns of the as-synthesized AgInS<sub>2</sub>-*x*Ag<sub>2</sub>S-*y*ZnS-*z*In<sub>6</sub>S<sub>7</sub> nanojunctions with different molar ratios of Ag to Zn. AgInS<sub>2</sub>: JCPDS 25-1328, Ag<sub>2</sub>S JCPDS 14-0072, ZnS: JCPDS 36-1450, In<sub>6</sub>S<sub>7</sub>: JCPDS 19-0587.

Figure 2 shows a series of SEM images of the as-synthesized samples and a comparison of their solar hydrogen evolution property correspondingly. As revealed in Figure 2A-E, different molar ratios of Ag:Zn result in the formation of products with diverse compositions and morphologies. The obtained AgInS<sub>2</sub> nanoparticles with molar ratio of Ag:Zn at 5:1 display regular flowers with the size of 810 nm and are assembled by many nanosheets (Figure 2A). With the ratio decreased to 2:1, the produced  $AgInS_2-Ag_2S$  is mainly composed of nanoplates with a length of 300–400 nm and thickness of several tens of nanometer (Figure 2B). However, further increasing the dosage of zinc ions, *i.e.*, Ag:Zn = 1:1, as shown in Figure 2C, the as-obtained AgInS<sub>2</sub>-Ag<sub>2</sub>S-ZnS shows aggregation of the nanoplates. When the mole number of Zn is higher than that of Ag, the product contains AgInS<sub>2</sub>-Ag<sub>2</sub>S-ZnS-In<sub>6</sub>S<sub>7</sub>. The particles reveal irregular and aggregated morphology (Figure 2D,E). Figure S1 shows diffuse reflectance spectra (DRS) of the prepared composites. Obviously, when the amount of Zn added in the preparation is higher than that of Ag (Ag:Zn = 1:5 or 1:2), the DRS spectra exhibit intense absorption bands with steep edges, which mainly depends on the UV absorption band of ZnS. With the decrease in the dosage of  $Zn(Ac)_2$ , the composites have absorptions in the range of visible light ( $\lambda > 450$  nm), whereas ZnS has little absorption in this range. The presence of AgInS<sub>2</sub> and Ag<sub>2</sub>S contributes to the increased visible-light absorption. Notably, the absorption spectrum of  $AgInS_2-xAg_2S-yZnS-zIn_6S_7$  composite photocatalysts can be easily controlled by modifying the dosage of  $Zn(Ac)_2$  continuously. The complexity of the composite in both structure and chemical composition may endow the materials with exceptional optical properties.

Figure 2F shows the photocatalytic activities of the photocatalysts. The hydrogen production mainly depends on the compositions regardless of their morphology. The AgInS<sub>2</sub>-Ag<sub>2</sub>S-ZnS with

the feed ratio of Ag:Zn at 1:1 exhibits the highest activity with a hydrogen evolution rate of 5.4 mmol·g<sup>-1</sup>·h<sup>-1</sup>, which is higher than that of previous reported AgInS<sub>2</sub>, Ag<sub>2</sub>S, ZnS composite photoctalysts (comparison results is shown in Table S1). Moreover, the photocatalyst presents good stability even after 20 h duration (Supplementary Materials, Figure S2). The pristine AgInS<sub>2</sub> nanoparticles possessed very weak photo-activity towards H<sub>2</sub> evolution. Of course, Pt salt added in the photocatalytic reaction played an important role in promoting the photocatalytic activity. Without cocatalyst of Pt salt, the catalyst itself also achieved a comparable activity towards solar hydrogen evolution of a rate of 1.8 mmol·g<sup>-1</sup>·h<sup>-1</sup> (Supplementary Materials, Figure S3). Figure S4 reveals the surface area of the samples, suggesting that surface characteristics do not dominate the photocatalytic activity for H<sub>2</sub> evolution. In other words, activities of the nanocomposites are mainly determined by their compositions.



**Figure 2.** SEM images of AgInS<sub>2</sub>-*x*Ag<sub>2</sub>S-*y*ZnS-*z*In<sub>6</sub>S<sub>7</sub> composite nanoparticles with different molar ratios of Ag:Zn (**A**) 5:1; (**B**) 2:1; (**C**) 1:1; (**D**) 1:2; (**E**) 1:5 (The scale bars are all 400 nm); and a corresponding comparison chart of the photocatalytic H<sub>2</sub> production in a reaction period of 12 h (**F**).

Typically, we further investigated the detailed structures of  $AgInS_2-Ag_2S-ZnS$  with the maximum activity by HRTEM measurement. Figure 3 clearly shows that the  $AgInS_2-Ag_2S-ZnS$  nanocomposite has clear interconnecting lattice fringes with interplaner spacing distance of 0.319, 0.285, and 0.295 nm, which correspond to (121) and (002) planes for orthorhombic  $AgInS_2$ , (-112) plane for monoclinic  $Ag_2S$ , and (101) plane for hexagonal ZnS, respectively. The results demonstrate that the photocatalyst composites have been successfully prepared through the simple hydrothermal method.



**Figure 3.** Transmission electron micrograph (TEM) (**A**) and HRTEM (**B**) images of the AgInS<sub>2</sub>-Ag<sub>2</sub>S-ZnS composite nanoparticles.

The photocurrent response is also used to compare the photo-activity on the as-synthesized samples. As shown in Figure 4, all the samples can be excited to produce photo-carriers under simulated sunlight illumination. The electrons transport from the photocatalysts to ITO glass surface and then external circuit to produce photocurrent [29]. Prompt and reproducible current responses during repeating on-off illumination cycles are observed from each electrode of the five samples. When the illumination stops, the photocurrent drops to zero immediately. The photocurrent density increases with the increase of ratio of Ag:Zn. For AgInS<sub>2</sub>-Ag<sub>2</sub>S-ZnS-In<sub>6</sub>S<sub>7</sub> (Ag:Zn = 1:5), the photocurrent response is very weak. The result can be ascribed to the increased content of ZnS bearing a wide bandgap (3.55 eV), leading to the low utilization ratio of solar photons. In contrast, the AgInS<sub>2</sub>-Ag<sub>2</sub>S-ZnS-In<sub>6</sub>S<sub>7</sub> produced at Ag:Zn = 1:2 exhibits an improved photocurrent. For the AgInS<sub>2</sub>-Ag<sub>2</sub>S-ZnS obtained at Ag:Zn = 1:1, a photocurrent peak was observed at the initial irradiation stage, followed by a slow decrease before reaching a constant value. It suggests that recombination of photo-generated electrons and holes occur in the process [30]. Meanwhile, the photocurrent of the other two samples obtained with Ag:Zn = 2:1 and Ag:Zn = 5:1, *i.e.*, AgInS<sub>2</sub>-ZnS and AgInS<sub>2</sub>, are significantly higher than the above samples. Nevertheless, the current decreases along with the irradiation time, indicating the easy excitation and fast recombination of photo-generated carriers. The results are in accordance with previous reports [31], which suggest that the production of photocurrent is primarily determined by the transporting speed of excited electrons from semiconductor to ITO and the recombination at the electrolyte/film interface. Considering the photo-activity of photocurrent production and  $H_2$  evolution, it is deduced that the photocatalysts with stable and high photocurrent are favorable for the H<sub>2</sub> generation. Therefore, the production and transfer rate of photo-generated electrons for the samples obtained with Ag:Zn of 1:1, 1:2, 1:5 are consisted with their hydrogen

evolution activity. For the AgInS<sub>2</sub> and AgInS<sub>2</sub>-ZnS nanoparticles obtained from Ag:Zn of 5:1 and 2:1, the hydrogen evolution rates are lower although their photocurrents are higher than the others.



**Figure 4.** Photocurrent-density responses (I-t) of the samples synthesized with different ratios of Ag:Zn in 0.5 M Na<sub>2</sub>SO<sub>3</sub> solution under simulated sunlight illumination.

Electrochemical impedance spectroscopy (EIS) is also a powerful technology to probe the charge transfer process at an electrode interface [32,33]. The semicircle at high frequencies represents the capacitance and the resistance of the solid-state interface layer, which is formed at highly charged states and results from the passivation reaction between the electrolyte and the surface of the electrode [33]. As shown in Figure 5, the semicircle diameters of AgInS<sub>2</sub>-Ag<sub>2</sub>S-ZnS (Ag:Zn = 1:1) and AgInS<sub>2</sub>-Ag<sub>2</sub>S-ZnS-In<sub>6</sub>S<sub>7</sub> (Ag:Zn = 1:2) are smaller than those of the other samples, The higher hydrogen evolution activities would be attributed to faster interfacial electron transfer. The moderate amounts of ZnS and In<sub>6</sub>S<sub>7</sub> added into AgInS<sub>2</sub>-Ag<sub>2</sub>S benefit the charge transfer and lower the recombination probability of photogenerated charges. Consequently, the ZnS and In<sub>6</sub>S<sub>7</sub> nanoparticles can work as electron acceptors and transporters in the obtained composite, which significantly enhances the photocatalytic activity for H<sub>2</sub> production.



**Figure 5.** Nyquist plots of electrochemical impedance spectra (EIS) of the as-prepared samples (AgInS<sub>2</sub>-xAg<sub>2</sub>S-yZnS-zIn<sub>6</sub>S<sub>7</sub>). The EIS measurements were performed in the presence of a 2.5 mM K<sub>3</sub>[Fe(CN)<sub>6</sub>]/K<sub>4</sub>[Fe(CN)<sub>6</sub>] (1:1) mixture as a red-ox probe in 0.5 M Na<sub>2</sub>SO<sub>4</sub> aqueous solution.

It is known that  $Ag_2S$  is a narrow band gap semiconductor and may have an extended absorption range, thus it can be easily excited to generate  $h^+$ - $e^-$  pairs and produce intense photo-current [34,35]. However, these generated electrons are unstable to reduce  $H_2O$  into  $H_2$  due to their lower conduction band potential than  $H^+/H_2$  pair. As shown in Figure 6, AgInS<sub>2</sub> has an appropriate band structure for water splitting to evolve  $H_2$  [36]. Since the conduction band level is negative enough for a reduction potential of  $H_2O/H_2$ , ZnS with a wide bandgap (3.73 eV) is an ideal photocatalyst from the viewpoint of preeminent ability to generate  $H_2$  [37]. Herein, photocatalyst of AgInS<sub>2</sub>-Ag<sub>2</sub>S-ZnS possesses the best photocatalytic activity among the as-obtained samples with various ratios of Ag:Zn and excessive quantity of ZnS is unfavorable for solar light absorption to produce  $H_2$ . However, regarding the feasible point of modifying by In<sub>6</sub>S<sub>7</sub>, more experimental and theoretical evidence is needed to clarify this in the future.



Figure 6. A diagrammatic scheme of energetic band structure of AgInS<sub>2</sub>-Ag<sub>2</sub>S-ZnS (Ag:Zn = 1:1).

# 3. Materials and Methods

#### 3.1. Materials

Silver acetate (AgAc), zinc acetate (Zn(Ac)<sub>2</sub>), potassium iodide (KI), polyvinylpyrrolidone (PVP) and ethylenediamine (En) were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Indium trichloride (InCl<sub>3</sub>·4H<sub>2</sub>O), sodium diethyldithiocarbamate trihydrate ((C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>NCSSNa·3H<sub>2</sub>O, Na(DDTC)), polyethylene glycol (PEG, molecular weight = 10,000 g·mol<sup>-1</sup>) were purchased from Shanghai SSS Reagent Co., Ltd. (Shanghai, China). All the reagents were analytical grade and used as received without further purification.

# 3.2. Synthesis of AgI Polyhedrons

In a typical procedure, 0.05 g of PVP and 0.06 g of AgAc were dissolved in a mixture of 10 mL of deionized water and 1 mL of En under magnetic stirring at 60 °C. After they were totally dissolved, 5 mL of KI aqueous solution (0.084 mol/L) was introduced at a rate of 1 mL/min to the above solution with a syringe pump and the resulting mixture was stirred continuously for 10 min. SEM image of the obtained AgI precursor is given in Supplementary Materials, Figure S5.

# 3.3. Synthesis of $In(DDTC)_3$

Fifty millilitres of ethanol solution of 0.1 mol/L of  $InCl_3 \cdot 4H_2O$  and 0.3 mol/L of Na(DDTC) were mixed under vigorous magnetic stirring for ~30 min. The obtained white product was rinsed with de-ionized water 3 times and collected via vacuum filtration.

#### 3.4. Synthesis of AgInS<sub>2</sub>-Ag<sub>2</sub>S-ZnS Heterojunction Nanostructures

The various nanocomposites were synthesized by a simple hydrothermal method through varying the ratios of starting materials. Briefly, the freshly synthesized AgI polyhedrons (0.12 g), 0.3 g of

In(DDTC)<sub>3</sub>, 0.08 g of Zn(Ac)<sub>2</sub> (molar ratio of Ag:Zn = 1:1) and 25 mL of deionized water were sequentially transferred into a Teflon-lined autoclave with the capacity of 45 mL. The autoclave was sealed tightly and heated at 180 °C for 24 h. The product was washed with de-ionized water 3 times and collected by centrifugation.

For comparison, other samples with different compositions were also synthesized by simply changing the addition quantity of  $Zn(Ac)_2$  to 0.16 g (molar ratio of Ag:Zn = 1:2), 0.4 g (molar ratio of Ag:Zn = 1:5), 0.04 g (molar ratio of Ag:Zn = 2:1) and 0.016 g (molar ratio of Ag:Zn = 5:1).

### 3.5. Characterization

The crystalline phases of the samples were analyzed by X-ray powder diffraction (XRD) (PANalytical B.V., Almelo, The Netherlands) on a Philips X'Pert diffractometer with Cu K $\alpha$  radiation ( $\lambda = 0.15418$  nm). The morphologies and sizes were observed with a Hitachi S-4800 field emission scanning electronic microscopy (FESEM) (Tokyo, Japan). Transmission electron micrographs (TEM) were obtained using a JEM-2100UHR transmission microscope (JEOL, Tokyo, Japan). The optical absorption spectra were measured on a UV-vis spectrometer (Shimadu UV2600, Kyoto, Japan) over a range of 200 to1000 nm.

# 3.6. Evaluation of Photo-Electrochemical Performance

For photo-electrochemical measurements,  $AgInS_2-xAg_2S-yZnS-zIn_6S_7$  heterojunctions were fabricated as the film electrodes. Typically, a glass substrate (ITO, 15  $\Omega/m^2$ ) was ultrasonically treated in a mixture of H<sub>2</sub>O, isopropanol, and acetone for 30 min. Then 30 mg of the as-synthesized samples and PEG aqueous solution (150 mg/mL) were mixed homogeneously. The obtained paste was spread onto the conducting glass substrate with a blade. Adhesive tapes were used as spacers. Finally, the resulted films with ~1 cm<sup>2</sup> active area were annealed at 30 °C for 30 min under N<sub>2</sub> atmosphere in order to achieve intimate contact between particles.

Photoelectrical response and electrochemical impedance spectroscopy (EIS) were measured on an electrochemical workstation (CHI 660E, CH Instruments, Chenhua, Shanghai, China) with a three-electrode cell. A Pt plate and saturated calomel electrode were used as the counter and reference electrodes, respectively. The as-prepared samples were employed as the working electrode with an active area of  $1 \times 1$  cm<sup>2</sup>. The photocurrents were measured with the same three-electrode system under irradiation of a 300 W Xe lamp in 0.5 mol/L Na<sub>2</sub>SO<sub>4</sub> aqueous solution. EIS was carried out with an open circuit potential (0.228 eV) from 1000 KHz–0.01 Hz in 0.50 M Na<sub>2</sub>SO<sub>4</sub> containing equimolar [Fe(CN)<sub>6</sub>]<sup>3–</sup> and [Fe(CN)<sub>6</sub>]<sup>4–</sup> (2.5/2.5 mM) solution.

# 3.7. Evaluation of Photocatalytic Performance

The photocatalytic activity of the as-synthesized AgInS<sub>2</sub>-xAg<sub>2</sub>S-yZnS-zIn<sub>6</sub>S<sub>7</sub> nanocomposites was evaluated by the photocatalytic reduction of water to produce H<sub>2</sub> under simulated sunlight irradiation. The H<sub>2</sub> evolution test was performed on a LabSolar-III AG reaction cell (Beijing Perfect Light Company, Beijing, China). In a typical experiment, 20 mg of AgInS<sub>2</sub>-xAg<sub>2</sub>S-yZnS-zIn<sub>6</sub>S<sub>7</sub> nanoparticles were dispersed in an 60 mL of aqueous solution containing 2.6 g of Na<sub>2</sub>SO<sub>3</sub> (0.33 mol·L<sup>-1</sup>), 3.6 g of Na<sub>2</sub>S (0.74 mol·L<sup>-1</sup>) as sacrificial reagents and 5 mL of 1 mg/mL Pt(NH<sub>4</sub>)<sub>2</sub>Cl<sub>6</sub> as promoter. The aqueous solution was irradiated by a 300 W Xe arc lamp (PLS-SEX300/300UV, Beijing Perfect Light Company) to produce H<sub>2</sub>. The yield of H<sub>2</sub> was determined with an on-line gas chromatograph (GC7900, Techcomp, Shanghai, China), which equipped with a molecular sieve 5A column and a thermal conductivity detector. N<sub>2</sub> was used as the carrier gas.

# 4. Conclusions

In summary, we have synthesized a class of efficient solar-driven nanophotocatalysts made of AgInS<sub>2</sub>-xAg<sub>2</sub>S-yZnS-zIn<sub>6</sub>S<sub>7</sub> composite, where the compositions can be controlled by varying the feed ratio of Ag<sup>+</sup> to Zn<sup>2+</sup> ions. The solar hydrogen evolution tests show that the as-synthesized AgInS<sub>2</sub>-Ag<sub>2</sub>S-ZnS obtained with Ag<sup>+</sup>:Zn<sup>2+</sup> of 1:1 exhibits the highest activity with a rate of 5.4 mmol  $h^{-1} \cdot g^{-1}$ . Compared with the pristine AgInS<sub>2</sub>, AgInS<sub>2</sub>-Ag<sub>2</sub>S-ZnS shows a significantly enhanced photocatalytic H<sub>2</sub> production performance by a factor of 14 and even higher than AgInS<sub>2</sub>-Ag<sub>2</sub>S-ZnS-In<sub>6</sub>S<sub>7</sub> under the same conditions. The results demonstrate that AgInS<sub>2</sub> nanoparticles integrated with appropriate proportion of Ag<sub>2</sub>S and ZnS can be used as a promising photocatalyst for H<sub>2</sub> production.

**Supplementary Materials:** The following are available online at www.mdpi.com/1996-1944/9/5/329/s1. Figure S1: Diffuse reflectance spectra of the as-prepared composite photocatalyhst with different ratio of Ag:Zn. Figure S2: The H<sub>2</sub> evolved from water under solar light over AgInS<sub>2</sub>-Ag<sub>2</sub>S-ZnS obtained with Ag:Zn = 1:1. Figure S3: Photocatalytic H<sub>2</sub> evolution under solar-light irradiation with the same sample as in Figure S2. It is showing that the addition of (NH<sub>4</sub>)<sub>2</sub>PtCl<sub>6</sub> improved the production rate of H<sub>2</sub> though the original catalyst also shows the good activity towards H<sub>2</sub> evolution. Figure S4: BET surface area and H<sub>2</sub> production of AgInS<sub>2</sub>-*x*Ag<sub>2</sub>S-*y*ZnS-*z*In<sub>6</sub>S<sub>7</sub> with different molar ratios of Ag<sup>+</sup> to Zn<sup>2+</sup> ions. Figure S5: An SEM image of the AgI precursor.

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**Author Contributions:** Zhaojie Wang organized the project as the head of the working group; Shutao Wang and Junxue Liu performed prepared and characterized the photocatalysts; Wen Jiang wrote the paper; Yan Zhou contributed analysis tool of electrochemical workstation; Changhua An and Jun Zhang analyzed the data and the enhancement mechanism.

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