

Article

ZnO/ZnS-Polyvinyl Alcohol Hydrogel for Photocatalytic H₂-Generation

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Abstract: The separation of nanoparticles from a solution-based photocatalytic reaction is a significant problem in practical applications. To address the issue, we developed a new photocatalyst composite based on ZnO-ZnS heterojunction (ZnOS) embedded in polyvinyl alcohol (PVA) hydrogel, which showed satisfactory results for photocatalyst recycling. PVA-ZnOS composite hydrogel was fabricated by freezing-induced gelation, which enabled the encapsulation of ZnOS nanoparticles into polymeric matrices. PVA hydrogel served as a promising candidate in photocatalytic applications due to its excellent properties such as high transparency, porosity, hydrophilicity, and stability under ultraviolet (UV) light. PVA-ZnOS hydrogel showed worthy activity in H₂ generation from Na₂S/Na₂SO₃ aqueous solution under UV radiation with a production rate of 18.8 μmol·h⁻¹. PVA-ZnOS composite hydrogel is a separation-free photocatalyst, which is prospective in a solution-based photocatalytic reactor.

Keywords: ZnO-ZnS heterojunction; PVA hydrogel photocatalyst; H₂ generation; catalyst immobilization; photocatalytic recycling

1. Introduction

Climate change produced by the increasing levels of carbon dioxide (CO₂) release is considered a significant threat to life on earth; therefore, in 2015 the Paris Climate Accord agreed on providing feasible solutions by holding the global temperature rise below 2 °C by reducing CO₂ emissions to net 0 by 2050 [1]. Hydrogen (H₂) gas used in fuel cell technologies emits zero CO₂, contributing decisively to solving the environmental problem and securing the earth's energy future [2]. H₂ is considered a primary global business that demands the global market increase from 71.5 million tonnes per year in 2019 to 289 million tonnes per year in 2050 (IEA, 2020) [3]. Therefore, H₂ production is of great interest for the clean energy business. Hopefully, developing green hydrogen technology can offer a promising solution to environmental remediation.

Currently, H_2 is generated by thermal energy at high temperature through steam reforming via reacting fossil fuel with steam (e.g., $CH_4 + H_2O \rightarrow CO + 3H_2$) or by coal gasification via reacting fossil fuel in the presence of a controlled amount of oxygen and/or steam (e.g., $3C + O_2 + H_2O \rightarrow H_2 + 3CO$) [4]. However, these processes would require higher energy consumption and produce carbon oxide gases, amongst other released greenhouse gases. After discovering a water-splitting reaction enabled by a TiO_2 photocatalyst and photon light energy, photocatalytic H_2 -generation became a clean and encouraging method for scientists [5]. Many semiconductor photocatalysts and photocatalyst compounds have been developed for H_2 generation [6]. Among them, ZnS-ZnO heterojunction material exhibited excellent performance in H_2 generation under UV and visible light [7–10]. In addition, ZnS and ZnO are low-cost materials, of which synthesis methods of creating a heterojunction have been well studied. ZnS-ZnO photocatalyst can oxidize water to produce oxygen gas and simultaneously reduce water to form hydrogen gas [11,12]. We successfully developed ZnS-ZnO nanostructures for high-performance H_2 -generation reaction and Cr(VI) reduction [13,14].

The next step after the development of active photocatalysts is to explore material processing methods for H_2 -generation reaction to maximize the performance of catalysts and minimize operational costs. In particular, recovering catalysts for recycling is one of the major concerns in photocatalytic reactions performed by nanoparticles (NPs). Generally, NPs are immobilized onto supports such as polymers [15], carbons [16], stainless steel [17], and ceramics [16,18]. Recently, nanoparticle immobilization into three-dimensional (3D) network structures of hydrogels have gained popularity for photocatalytic applications with separation-free titles [19,20]. Hydrogel-based materials have strong absorption capabilities due to their 3D network structures, which provide good mass transfer channels. In addition, they have high thermal and mechanical stabilities, which are suitable for various applications. Jiang et al. prepared polyaniline (PANI)/ TiO_2 composites and utilized them for photocatalytic dye removal [19]. In a similar concept, Li et al. prepared polyethylene glycol (PEG)/ TiO_2 -graphene hydrogel for photocatalytic chromium (IV) reduction with enhanced charge separation capability [20]. Earlier, a new method was reported for anti-hydration application to synthesize polyvinyl alcohol hydrogel (PVA) with surface structures engineering [21]. Later, PVA-graphene hydrogel was fabricated as an effective solar evaporator, enabling rapid water evaporation at 92% energy efficiency under one sun condition (AM 1.5 G) [22]. Based on these experiences, we considered PVA hydrogel an excellent host matrix for photocatalytic H_2 -generation due to its transparent nature, porous structure, hydrophilicity, and good stability.

This study presents a new hydrogel photocatalyst composed of ZnO-ZnS (ZnOS) embedded into a PVA matrix for H_2 generation under UV light. PVA-ZnOS composite hydrogel showed noble performance and stability for H_2 generation under UV light from Na_2S/Na_2SO_3 solution. ZnS, ZnO, and PVA are low-cost materials suitable for producing large-scale amounts of PVA-ZnOS hydrogel composite for industrial purposes, thus becoming a promising photocatalyst for H_2 generation.

2. Results and Discussion

Different amounts of ZnOS nanoparticles were embedded into PVA hydrogel. Hydrogels with 100 mg, 150 mg, and 200 mg amounts of ZnOS NPs were named PVA-ZnOS100, PVA-ZnOS150, and PVA-ZnOS200, respectively. Morphological structures of ZnOS were investigated by scanning electron microscopy (SEM) in Supplementary Information (Figure S1). The specific surface area of ZnOS NPs, measured by Brunauer–Emmett–Teller (BET), was $36.8 \text{ m}^2 \cdot \text{g}^{-1}$. To ensure the homogeneous mixture of ZnOS NPs in PVA solution, ZnOS was predispersed into N-methyl pyrrolidone (NMP) solvent before adding PVA. After mixing at a temperature of 110°C for 60 min, a stable solution of PVA-ZnOS-NMP was obtained and cast in a Petri dish mold. During freezing-induced gelation, PVA polymer chains shrank and drew closer to each other, creating strong interactions with solvent-forming polymer–solvent complexes. At the same time, the hydroxyl groups on

the surface of ZnOS could also form hydrogen bonds with PVA [23,24], encapsulating NPs in the gel network (as shown in Figure 1). Finally, the hydrogel photocatalytic composite was obtained by solvent replacement with water.

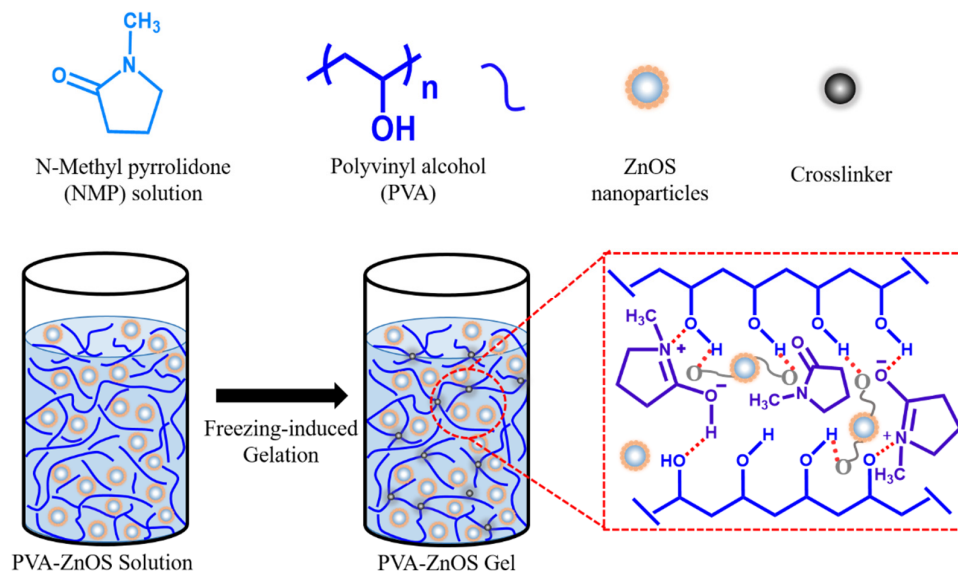


Figure 1. Fabrication process of ZnOS-PVA hydrogels.

Photographs in Figure 2a show that pure PVA hydrogel was highly transparent. The incorporation of ZnOS NPs into PVA gel turned its color from clear to white, the intensity of which was enhanced with increased ZnOS concentrations. SEM images of gel surfaces in Figure 2b–d indicate ZnOS nanoparticles (white spots) embedded well inside the gel surface. For further investigation inside the gel's matrix, PVA, PVA-ZnOS100, and PVA-ZnOS200 gel were cut into small pieces, and cross-sectional views of these fractions were observed by SEM (Figure 2e–g). It was observed that ZnOS particles were encapsulated inside the gel matrix. However, at high ZnOS concentration (PVA-ZnOS200), particles tended to aggregate with each other and the surface of the gel was rougher, whereas some parts appeared cracked (see white circles). EDS of the gels confirmed the Zn, O, and S elements in PVA-ZnOS, only informing the presence of ZnOS in composite gel (Figure S2a,b). XRD patterns showed crystal structures of PVA-ZnOS hydrogels composed of PVA, ZnO, and ZnS phases (Figure 3a). The intense peak at 20° belongs to polymers (PVA) [21,22] and is identified in both PVA and PVA-ZnOS hydrogels. Diffraction peaks at higher angles were fitted to cubic ZnS (JCPDS#04-016-6848) and wurtzite ZnO (JCPDS#04-016-6648).

The optical properties of gels were studied by UV-vis absorption spectra shown in Figure 3b. No noticeable absorption from UV to visible ranges was observed with pure PVA gel. Commonly, it was seen that ZnOS absorbed UV ranges (<400 nm), which resembled PVA-ZnOS. From the UV-absorption spectrum, bandgap energy was calculated based on a Tauc plot (Figure S3). It is seen that there were two absorption bands at 3.30 and 3.55 eV, which correspond to the bandgap energy of ZnO and ZnS, respectively. This evidenced that the synthesized sample was composed of ZnO and ZnS phases, which agreed with the XRD pattern. The characteristic absorption of ZnO/ZnS-PVA mainly originated from bandgap absorption of ZnO and ZnS semiconductors because pure PVA does not have such characteristic absorption. Fourier Transform Infrared (FTIR) spectroscopy of pure PVA and PVA-ZnOS showed the chemical bonding modes of the polymers' functional groups (Figure 3c). The broad peak at $3000\text{--}3600\text{ cm}^{-1}$ is attributed to an absorption peak of the OH functional group of PVA, originating from intermolecular and intramolecular hydrogen bonds in PVA. C–H stretching vibration was observed in $-\text{CH}_2-$ skeletons placed at $\sim 2920\text{ cm}^{-1}$. Peaks at 1716 and 1661 cm^{-1} belong to the stretching modes of C=C and C=O, respectively. Absorption peaks at 1423 and 1331 cm^{-1} were bending and wagging

vibrations of the CH_2 group. The lower absorption band at 1090 cm^{-1} was stretching vibration of the oxygen-contained functional group C–O in C–O–H groups [23]. Major absorption peaks of FTIR spectra were almost identical between pure PVA and PVA–ZnOS. However, these peak characteristics were not observed with ZnOS nanoparticles, which suggested that those peaks originated from PVA gel. The reaction induced between ZnO/ZnS and PVA matrix is attributed to hydrogen bonding between the –OH group of PVA and the sulfur of ZnS and oxygen of ZnO. The elongation of the O–H bond due to hydrogen bond formation with sulfur resulted in spectrum shift to high wavenumbers [23]. Because a small amount of ZnOS was embedded into the PVA, a slight shift of OH peak to a higher wavenumber with PVA–ZnOS film was observed.

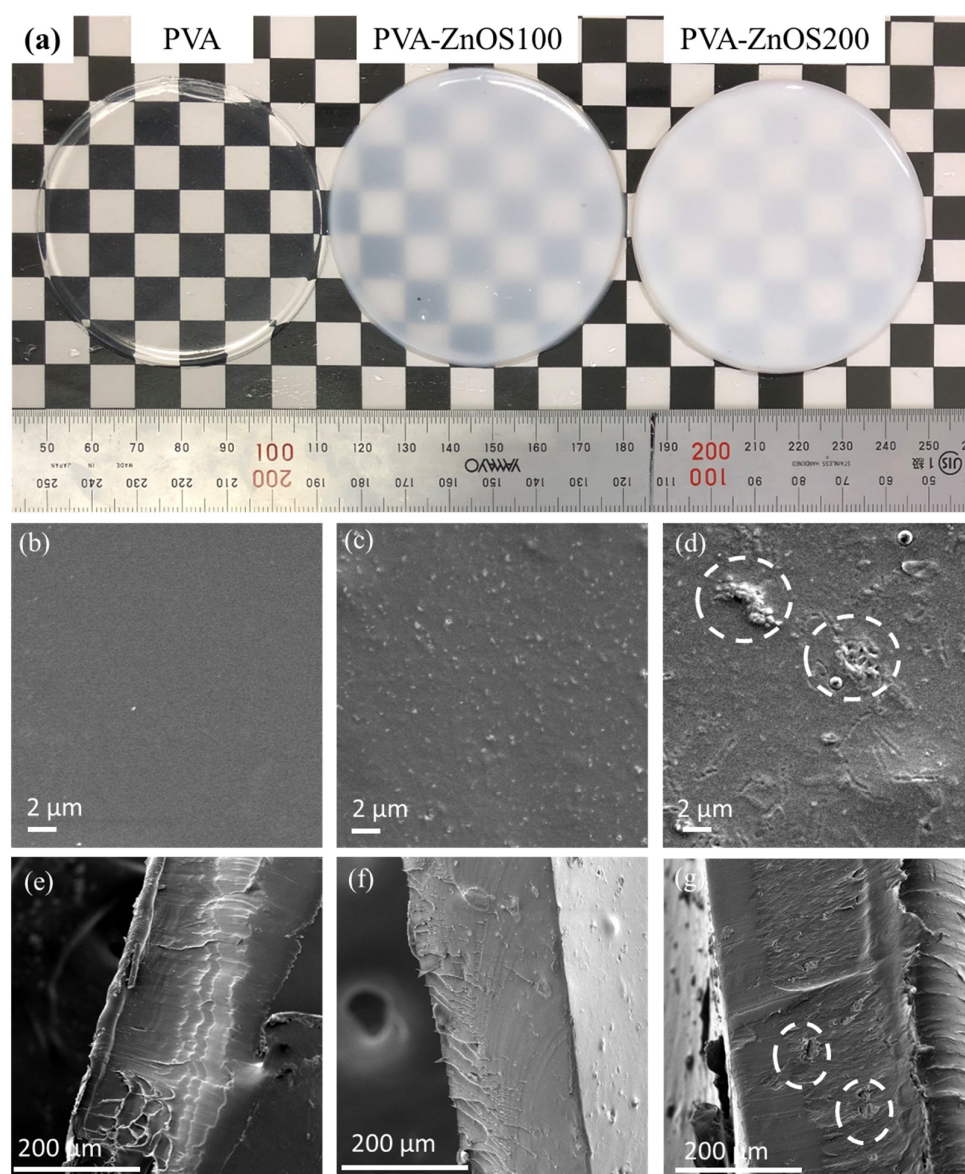


Figure 2. (a) photographs of PVA, PVA–ZnOS100, and PVA–ZnOS200; SEM images of surfaces (b–d) and cross-section (e–g) of PVA, PVA–ZnOS100, and PVA–ZnOS200.

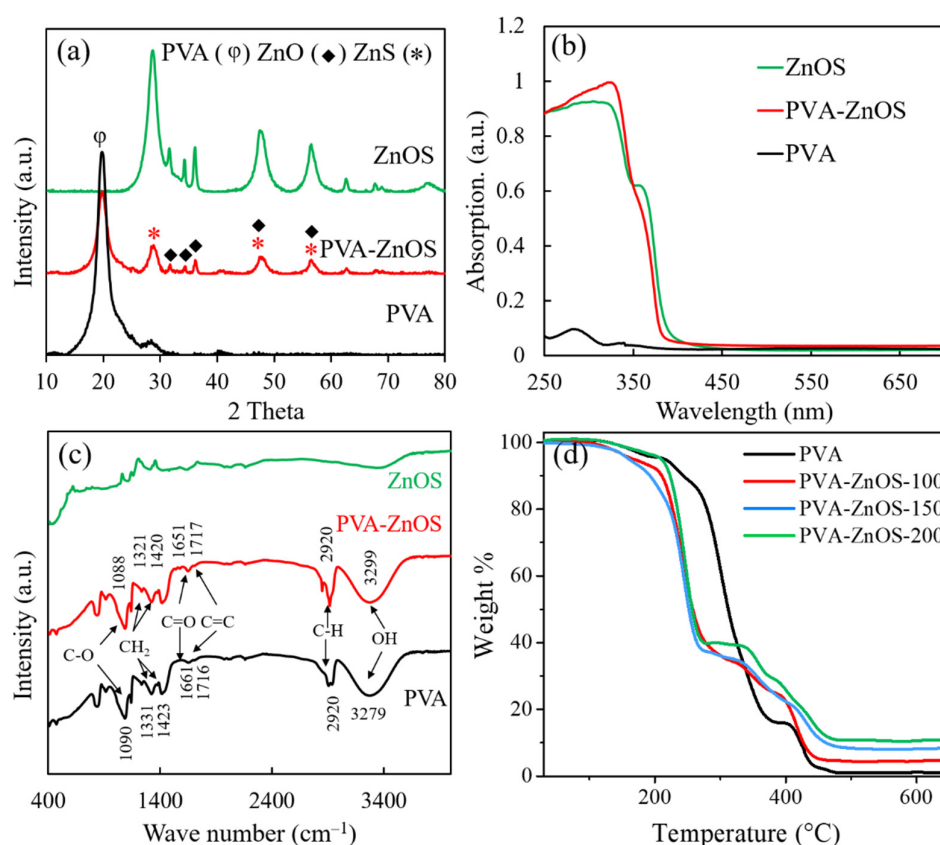


Figure 3. (a) XRD pattern of pure PVA, ZnOS, and PVA-ZnOS100; (b) UV-vis absorption spectra of PVA, ZnOS, and PVA-ZnOS100; (c) FTIR spectra of PVA, ZnOS, and PVA-ZnOS100; and (d) TGA analysis of PVA and PVA with different ZnO-ZnS contents.

Thermal analysis was conducted for both pure PVA and PVA/ZnO-ZnS composites in a dry state (PVA-ZnOS100, PVA-ZnOS150, and PVA-ZnOS-200). All samples' thermogravimetric analysis (TGA) spectra showed three critical decomposition phases. Weight loss at temperatures lower than 212 °C was due to moisture removal, accounting for ~5 wt.% of weight loss (see Table S1). The second weight loss at 159–371 °C was attributed to the decomposition of polymeric side chains in PVA. This weight loss was around 55–79%. The last decomposition stage, observed at 345 °C and above, was cleavage of C–C bonding in polymers with weight loss of 15–30%. At temperatures greater than 450 °C, PVA polymers were fully decomposed. It is differentiated that weight loss of pure PVA was 79% of the second stage, while weight loss of composite films was 63, 56, and 55% for PVA-ZnOS100, ZnOS150, and ZnOS200, respectively. Although the second stage decomposition of composite hydrogels took place at a lower temperature than that of pure PVA due to a decreased crystallinity of crosslinking [25], the lower weight loss suggests the thermal stability of composite films. It was widely known that networks formed by the interaction between inorganic nanoparticles and polymers restricted the mobility of polymer chains, resulting in enhanced heat capacity. A similar result was reported with nanoparticles/PVA composite [23,24]. From TGA analysis, NP contents in the dry gels were 3.93, 7.52, and 9.83 wt.% in PVA-ZnOS100, PVA-ZnOS150, and PVA-ZnOS200, respectively. From ICP analysis, the detected zinc metallic quantity of wet PVA-ZnOS200 hydrogel was 515×10 ppm.

XPS spectrum analysis of dried PVA-ZnOS200 indicated that the sample contained major elements of Zn, O, S, and C (Figure 4). Spin-orbit coupling in the XPS spectrum of Zn 2p was observed at 1021 (2p_{3/2}) and 1044 eV (2p_{1/2}). The O1s peak showed the strongest intensity of broad binding energy from 529 to 535 eV compared with other elements. The broad peak composed of oxygen lattice of ZnO (~530 eV) and hydroxyl group (~532 eV) originated from surface defects of ZnOS (e.g., vacancies) and the OH group of PVA [26,27].

Because PVA contained a large number of $-OH$ groups [28], the intensity of O1s was the highest. S2p peaks were observed at ~ 161 and 163 eV, identified as $S2p_{3/2}$ and $2p_{1/2}$ of the S^{2-} oxidation state of the sulfur lattice of ZnS [13,29,30]. XPS analysis confirmed that PVA-ZnOS contained both ZnS and ZnO, corresponding well to XRD spectra.

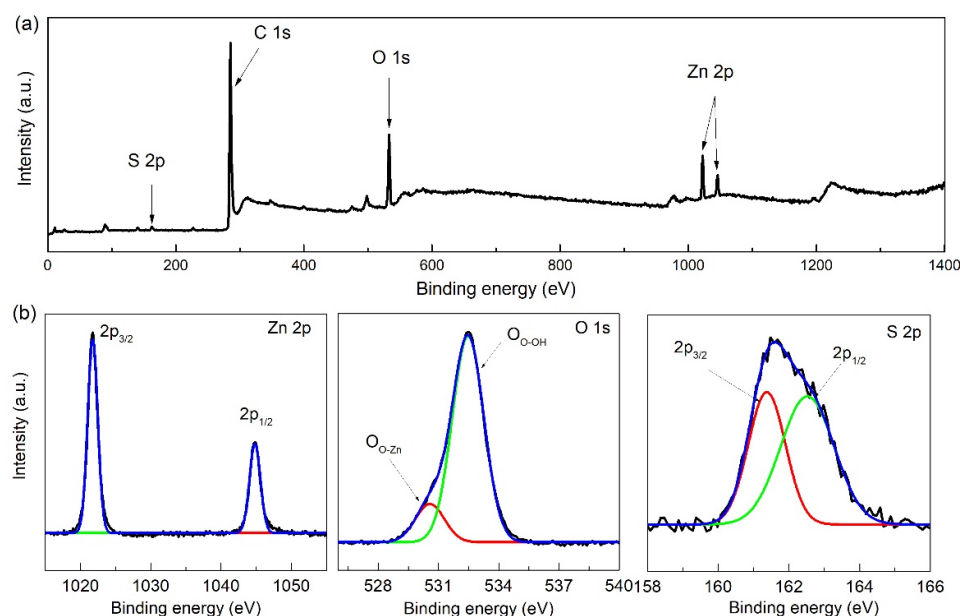


Figure 4. XPS spectra of dried PVA-ZnOS200: (a) survey spectrum and (b) deconvoluting high-resolution spectra of Zn2p, S2p, and O1s, respectively.

Photocatalytic activity of both pure PVA and PVA-ZnOS hydrogels was evaluated by H_2 generation from Na_2S/Na_2SO_3 solution under UV light irradiation. Figure 5a shows a photograph of a photocatalytic reactor containing PVA-ZnOS submerged into Na_2S/Na_2SO_3 solution under UV radiation. H_2 started being produced with composite hydrogels, whereas no H_2 generation was detected from pure PVA hydrogel. Total H_2 production from PVA-ZnOS100 was $63 \mu\text{mol}$ for a 4-h reaction. The increase of ZnOS amount from 100 to 150 and 200 mg yielded higher H_2 generation, increasing from $63 \mu\text{mol}$ to $67 \mu\text{mol}$ and $75 \mu\text{mol}$, corresponding to ZnOS100, ZnOS150, and ZnOS200, respectively. Average H_2 -production rates obtained from 4-h reactions were 15.8 , 16.9 , and $18.8 \mu\text{mol}\cdot\text{h}^{-1}$ from PVA-ZnOS100, PVA-ZnOS150, and PVA-ZnOS200, respectively. Incorporating a larger amount of NPs was not beneficial to enhance photocatalytic activities (PVA-ZnOS100 vs. PVA-ZnOS200). The amount of NPs was increased twice, but H_2 -production was increased by only $\sim 19\%$. At a higher concentrations of ZnOS, NPs tend to aggregate in a polymeric matrix, reducing the active sites for photocatalysis [15]. For comparison, we conducted the H_2 production under the same conditions for ZnO, ZnS, and ZnO/ZnS nanoparticles, where 50 mg nanoparticles were used in a 50 ml Na_2S/Na_2SO_3 solution under UV light irradiation (see Figure S4). Total H_2 production from ZnO/ZnS nanoparticles was much higher than our composite hydrogel due to the suspension of nanoparticles being better-dispersed in the solution than in gel. However, nanoparticles might not be appropriate to use for H_2 production due to the difficulties in the recycling process as well as the utilization of powder catalyst waste that is produced after reaction, thereby restraining their practical application. On the contrary, the recyclability of PVA-ZnO/ZnS hydrogel should be more promising.

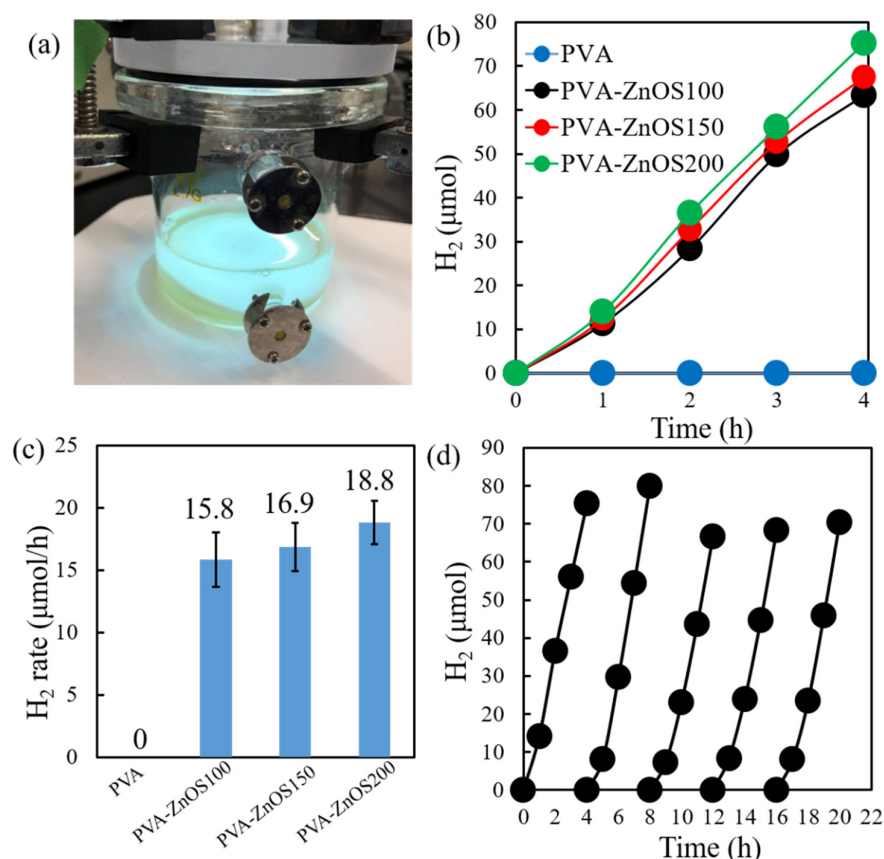


Figure 5. (a) Photograph of photocatalytic-reactor-contained PVA-ZnOS gel under UV radiation; (b) H₂ generation as a function of radiation time from pure PVA and PVA-ZnOS; (c) average production rate of H₂ of all samples; (d) Recycling test performed with PVA-ZnOS200.

A recycling test was performed to study the stability of composite gels. PVA-ZnOS200 was selected due to its highest H₂ production rate. After each cycle, the hydrogel was placed into deionized water for 30 min, then placed into a new reaction solution (Na₂S/Na₂SO₃) for running the next experiment cycle. After a 5-cycle test with a total radiation time of 20 h, H₂ production was still stable. The hydrogel's stability was investigated with FTIR analysis of PVA-ZnOS200 before and after the 20-h reaction (Figure 6). The same absorption characteristics of its FTIR spectra were observed, suggesting the unchanged chemical compositions and structures of hydrogel before and after the reaction. Since the same material (ZnOS nanoparticles) was used for all hydrogels, but in different weight percentages, the recycling trend for PVA-ZnOS100 and PVA-ZnOS200 should be the same as for PVA-ZnOS200. We also calculated the production rates proportionally to 1 g of catalyst used and summarized in Figure S5. These production rates were compared to those of the recent works related to hydrogel photocatalysts (Table S2). Although our hydrogel catalysts showed lower hydrogen production rates than those of recent reports, these composite hydrogels were composed of low-cost and non-toxic elements and are easier to recycle due to their cylindrical shape, as shown in Figure 2a, whereas most other catalysts are in a powdery form which requires filtration or centrifugation. We performed the leaching study by ICP-OES of the Na₂S/Na₂SO₃ solution that remained after photocatalytic hydrogen production with PVA-ZnOS200. The determined zinc metallic content of the solution was 0 ppm within the zinc detection limit of 0.5 ppm.

According to our observation, catalysts played a significant role in H₂ generation, while PVA polymers acted as frameworks to detain catalyst particles. Drawbacks due to light blocking by PVA were not accounted for because PVA is highly transparent. Reaction mechanisms of H₂ evolution from scavenger Na₂S/Na₂SO₃ solutions containing S^{2−},

SO_3^{2-} , or $\text{S}_2\text{O}_3^{2-}$ with PVA-ZnOS hydrogel are proposed in Figure 7. The valence band maximum (VBM) and conduction band minimum (CBM) of ZnO and ZnS were widely reported in the literature [7–14], where the VB of ZnO is lower than that of ZnS and the CB of ZnS is higher than that of ZnO, allowing maximum redox capability of the ZnO/ZnS interface. The presence of $\text{Na}_2\text{S}/\text{Na}_2\text{SO}_3$ solution stimulates the H_2 evolution by scavenging photogenerated holes, suppressing the formation of S_2^{2-} from Na_2S by SO_3^{2-} from Na_2SO_3 [31]. When UV light was radiated, ZnO/ZnS photocatalyst was activated by Z-scheme heterojunction, where excited electrons at the CB of ZnO recombined with holes at the VB of ZnS [8,11,14]. The accumulation of holes at the VB of ZnO and electrons at the CB of ZnS reduced the recombination between electrons and holes, enhancing the photocatalytic reaction [13,14]. Reactions of holes and electrons in scavenger solution to generate H_2 were performed as follows [31–33]:

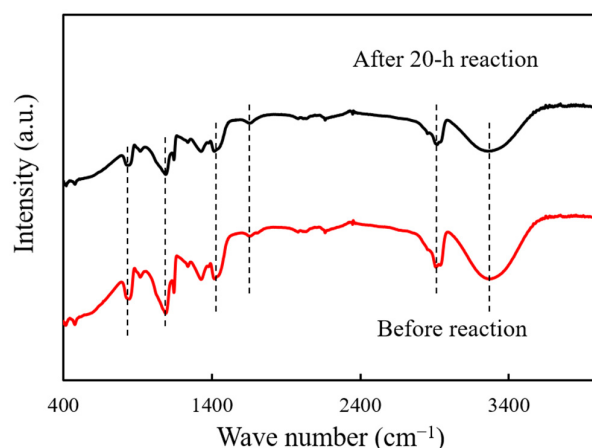
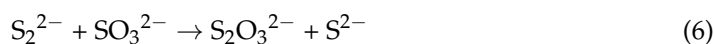
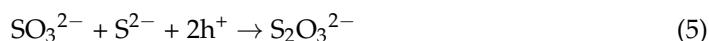
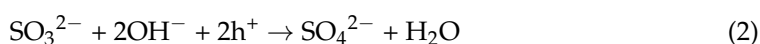


Figure 6. FTIR spectra of PVA-ZnOS200 before and after 20 h photoreaction.

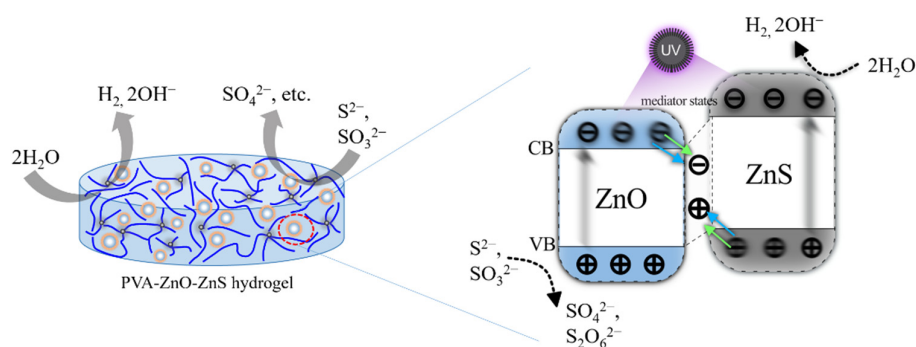


Figure 7. Schematic representation of photocatalytic H_2 -generation by PVA-ZnOS hydrogel from $\text{Na}_2\text{S}/\text{Na}_2\text{SO}_3$ solution.

3. Materials and Methods

3.1. ZnOS Nanoparticles (NP) Synthesis

ZnO was obtained by the precipitation method using a 1:2 molar ratio of ZnCl₂ (98%, Sigma Aldrich Inc., St. Louis, MO, USA) and NaOH (Granule, 97%, Daejung Chemicals, Siheung-si, Gyeonggi-do, Korea) in an ethanolic solution. Then, ZnO was mixed with 0.07 M Na₂S aqueous solution and stirred under UV light (UV-B lamp, 352 nm, G15T8E, Sankyodenki, Kanagawa, Japan) for 4 h. The resulting particles were separated by centrifugation and washed with water and ethyl alcohol several times. Finally, the white powder was dried at 60 °C in the oven for 24 h before use.

3.2. Fabrication of PVA-ZnOS Hydrogels

Figure 1 shows the fabrication process of PVA-ZnOS hydrogels. Different ZnOS powder amounts (100 mg, 150 mg, 200 mg) were dispersed into 30 mL N-methyl pyrrolidone (NMP) by 10 min sonication followed by 10 min stirring under ambient conditions. Then, 1.5 g of polyvinyl alcohol (PVA) (MW 130,000, 99%, hydrolyzed, Sigma Aldrich Inc., St. Louis, MO, USA) was added into the above mixture in a round-bottom flask and submerged into a 110 °C oil bath for 60 min to achieve complete dissolution of PVA polymers. Next, 10 g of the hot milky solution was poured into a Petri dish (85 mm diameter) and kept in a refrigerator at −10 °C overnight. Obtained hydrogels were submerged into the deionized (DI) water for another 24 h with frequent changes of DI water to remove NMP solvent from gels [22].

3.3. Characterizations

Morphological structures of ZnOS NPs and hydrogels were analyzed by an Inspect F scanning electron microscope (SEM) (F-SEM, FEI Company, Hillsboro, OR, USA). Energy dispersive X-ray spectroscopy (EDS) was analyzed by an EDS system combined with FE-SEM (JSM-7600F, JEOL, Tokyo, Japan). Crystal structures were analyzed by using X-ray diffraction (XRD; Ultima IV, Rigaku, Tokyo, Japan). Optical properties were studied using UV-vis absorption spectroscopy (V-670, Jasco, Tokyo, Japan). Fourier Transform Infrared (FTIR) spectra were obtained by an attenuated total reflectance (ATR) mode (Platinum ATR, Bruker Corp., Billerica, MA, USA). Elemental composition was analyzed by X-ray photoelectron spectroscopy (XPS, BELSORP-max TPDpro, BEL Japan Inc., Aoyama, Japan) under sputtering conduction. Thermal stability of hydrogels was measured by thermogravimetric analysis in the atmosphere at a scanning speed of 10 °C·min^{−1} (TGA/DSC1, METTLER TOLEDO, Columbus, OH, USA). The specific surface area of ZnOS NPs was measured by BET (Brunauer–Emmett–Teller) at 77 K with BELSORP-mini (BEL JAPAN INC., Osaka, Japan) after degassing at 150 °C for 3 h. Inductively coupled plasma-optical emission spectrometry (ICP-OES, Thermo Fisher Scientific, Waltham, MA, USA) was conducted to identify the metallic quantity in PVA-ZnOS-200 wet hydrogel and to determine Zn ions in Na₂S/Na₂SO₃ solution after the photocatalytic experiment.

3.4. Photocatalysis

The photocatalytic activity was evaluated by H₂ generation from a 0.1 M Na₂S and 0.1 M Na₂SO₃ aqueous solution under UV light (Hg-Xe lamp, MX3040, 200 W, Hayashi-Repic, Tokyo, Japan; wavelength: >200 nm; intensity = 146 mW·cm^{−2} at wavelength of 200–400 nm) (see radiation spectrum in Figure S6) [13]. A piece of hydrogel (cylindrical shape, 65 mm of diameter) was placed into a 300 mL glass-cell (top diameter of cell = 6.5 cm) contained 50 mL of 0.1 M Na₂S and 0.1 M Na₂SO₃ solution (pH~12.92). Then, the cell was covered with a quartz window and bubbled with N₂ gas for 20 min to remove oxygen contamination. The light was then radiated onto the top of the cell at a ca. 14 cm distance from the light source. The photocatalytic reaction was performed under ambient conditions. A total of 1 mL of gas was sampled every hour with a gas syringe and analyzed using gas chromatography (GC; GC-2014AT, Shimadzu, Kyoto, Japan; thermal conductivity detector, Ar carrier gas, molecular sieve 5Å column) to quantify the gas composition.

4. Conclusions

We successfully synthesized a new hydrogel-based photocatalyst composed of ZnOS nanoparticles embedded into the PVA polymeric matrix. PVA hydrogel provided a suitable framework support for photocatalytic H₂-generation due to high transparency, porous structures of 3D networks comprised of interlink between polymer chains, and hydrophilic nature, which delivered good water transport and light penetration channels. As a result, PVA-nanoparticle hydrogels exhibited good performance of photocatalytic H₂-generation and feasible recyclability. Average H₂-production rates under UV light were 18.8 $\mu\text{mol}\cdot\text{h}^{-1}$ from PVA-ZnOS. This work provides a guideline on hydrogel-based photocatalyst development, acknowledging the PVA hydrogel materials as a general framework for immobilization of not only ZnOS but other photocatalyst compounds.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/catal12030272/s1>, Figure S1: SEM images of ZnOS nanoparticles at (a) low resolution and (b) high resolution. Figure S2: EDS spectra of (a) pure PVA and (b) PVA-ZnOS100 composite. Figure S3: Bandgap energy from Tauc plot obtained from UV-vis absorption spectrum of ZnOS. Table S1. Decomposition temperature and weight loss (W.L.) obtained from TGA analysis. Figure S4: H₂ generation as a function of radiation time from ZnS, ZnO/ZnS, and ZnO nanoparticles; (b) average production rate of H₂ of all samples under the UV light irradiation. Figure S5: Hydrogen production rates in $\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$. Figure S6. Radiation spectrum of Xe-Hg lamp used in this experiment. Table S2: Photocatalytic activities for H₂ generation with previous reports (for comparison, production rates were normalized per gram catalyst) [34–38].

Author Contributions: V.P.: Investigation, data curation, experiment, analysis, visualization, writing—original draft, review and editing, and revision. W.L.: Investigation, data curation, experiment, analysis, visualization, writing—original draft, review and editing, and revision. S.K.: Investigation, data curation, experiment, analysis, visualization, writing—original draft, review and editing, and revision. E.L.T.: Formal analysis, data curation, and supervision. N.S.: Formal analysis, data curation, and supervision. C.T.: Formal analysis, data curation, and supervision. A.F.: Formal analysis, data curation, and supervision. K.-I.K.: Funding acquisition, conceptualization, supervision, manuscript reviewing and editing, and revision. S.-H.C.: Funding acquisition, conceptualization, supervision, manuscript reviewing and editing, and revision. All authors have read and agreed to the published version of the manuscript.

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References

1. United Nation, Paris Agreement, (2015, December). In Report of the Conference of the Parties to the United Nations Framework Convention on Climate Change (21st Session, 2015: Paris). Retrived December (Vol. 4, 2017). Available online: <https://unfccc.int/resource/docs/2015/cop21/eng/l09r01.pdf> (accessed on 11 November 2021).
2. Garland, N.L.; Papageorgopoulos, D.C.; Stanford, J.M. Hydrogen and fuel cell technology: Progress, challenges, and future directions. *Energy Procedia* **2012**, *28*, 2–11. [CrossRef]
3. International Energy Agency (IEA). Global Hydrogen Demand by Sector in the Sustainable Development Scenario, 2019–2070, Paris. 2020. Available online: <https://www.iea.org/data-and-statistics/charts/global-hydrogen-demand-by-sector-in-the-sustainable-development-scenario-2019-2070> (accessed on 11 November 2021).
4. Haryanto, A.; Fernando, S.; Murali, N.; Adhikari, S. Current status of hydrogen production techniques by steam reforming of ethanol: A review. *Energy Fuel* **2005**, *19*, 2098–2106. [CrossRef]
5. Fujishima, A.; Honda, K. Electrochemical photolysis of water at a semiconductor electrode. *Nature* **1972**, *238*, 37–38. [CrossRef] [PubMed]

6. Tee, S.Y.; Win, K.Y.; Teo, W.S.; Koh, L.-D.; Liu, S.; Teng, C.P.; Han, M.-Y. Recent progress in energy-driven water splitting. *Adv. Sci.* **2017**, *4*, 1600337. [[CrossRef](#)]
7. Zhang, X.; Zhou, Y.-Z.; Wu, D.-Y.; Liu, X.-H.; Zhang, R.; Liu, H.; Dong, C.-K.; Yang, J.; Kulinich, S.A.; Du, X.-W. ZnO nanosheets with atomically thin ZnS overlayers for photocatalytic water splitting. *J. Mater. Chem. A* **2018**, *6*, 9057–9063. [[CrossRef](#)]
8. Piña-Pérez, Y.; Aguilar-Martínez, O.; Acevedo-Peña, P.; Santolalla-Vargas, C.E.; Oros-Ruiz, S.; Galindo-Hernández, F.; Gómez, R.; Tzompantzi, F. Novel ZnS-ZnO composite synthesized by the solvothermal method through the partial sulfidation of ZnO for H₂ production without sacrificial agent. *Appl. Catal. B-Environ.* **2018**, *230*, 125–134. [[CrossRef](#)]
9. Sang, H.X.; Wang, X.T.; Fan, C.C.; Wang, F. Enhanced photocatalytic H₂ production from glycerol solution over ZnO/ZnS core/shell nanorods prepared by a low temperature route. *Int. J. Hydrogen Energy* **2012**, *37*, 1348–1355. [[CrossRef](#)]
10. Huang, H.-B.; Yu, K.; Wang, J.-T.; Zhou, J.-R.; Li, H.-F.; Lü, J.; Cao, R. Controlled growth of ZnS/ZnO heterojunctions on porous biomass carbons via one-step carbothermal reduction enables visible-light-driven photocatalytic H₂ production. *Inorg. Chem. Front.* **2019**, *6*, 2035–2042. [[CrossRef](#)]
11. Luan, Q.; Chen, Q.; Zheng, J.; Guan, R.; Fang, Y.; Hu, X. Construction of 2D-ZnS@ZnO Z-scheme heterostructured nanosheets with a highly ordered ZnO core and disordered ZnS shell for enhancing photocatalytic hydrogen evolution. *ChemNanoMat* **2020**, *6*, 470–479. [[CrossRef](#)]
12. Wang, X.; Cao, Z.; Zhang, Y.; Xu, H.; Cao, S.; Zhang, R. All-solid-state Z-scheme Pt/ZnS-ZnO heterostructure sheets for photocatalytic simultaneous evolution of H₂ and O₂. *Chem. Eng. J.* **2020**, *385*, 123782. [[CrossRef](#)]
13. Khan, S.; Je, M.; Ton, N.; Lei, W.; Taniike, T.; Yanagida, S.; Ogawa, D.; Suzuki, N.; Terashima, C.; Fujishima, A.; et al. C-doped ZnS-ZnO/Rh nanosheets as multijunctioned photocatalysts for effective H₂ generation from pure water under solar simulating light. *Appl. Catal. B-Environ.* **2021**, *297*, 120473. [[CrossRef](#)]
14. Poliukhova, V.; Khan, S.; Zhu, Q.; Zhang, J.; Kim, D.; Kim, S.; Cho, S.H. ZnS/ZnO nanosheets obtained by thermal treatment of ZnS/ethylenediamine as a Z-scheme photocatalyst for H₂ generation and Cr(VI) reduction. *Appl. Surf. Sci.* **2022**, *575*, 151773. [[CrossRef](#)]
15. Guo, J.; Khan, S.; Cho, S.-H.; Kim, J. Preparation and immobilization of zinc sulfide (ZnS) nanoparticles on polyvinylidene fluoride pellets for photocatalytic degradation of methylene blue in wastewater. *Appl. Surf. Sci.* **2019**, *473*, 425–432. [[CrossRef](#)]
16. Chen, J.; Li, G.; Huang, Y.; Zhang, H.; Zhao, H.; An, T. Optimization synthesis of carbon nanotubes-anatase TiO₂ composite photocatalyst by response surface methodology for photocatalytic degradation of gaseous styrene. *Appl. Catal. B-Environ.* **2012**, *123–124*, 69–77. [[CrossRef](#)]
17. Ramasundaram, S.; Yoo, H.N.; Song, K.G.; Lee, J.; Choi, K.J.; Hong, S.W. Titanium dioxide nanofibers integrated stainless steel filter for photocatalytic degradation of pharmaceutical compounds. *J. Hazard. Mater.* **2013**, *258–259*, 124–132. [[CrossRef](#)] [[PubMed](#)]
18. Miranda-García, N.; Suárez, S.; Sánchez, B.; Coronado, J.; Malato, S.; Maldonado, M.I. Photocatalytic degradation of emerging contaminants in municipal wastewater treatment plant effluents using immobilized TiO₂ in a solar pilot plant. *Appl. Catal. B-Environ.* **2011**, *103*, 294–301. [[CrossRef](#)]
19. Jiang, W.; Liu, Y.; Wang, J.; Zhang, M.; Luo, W.; Zhu, Y. Separation-free polyaniline/TiO₂ 3D hydrogel with high photocatalytic activity. *Adv. Mater. Interface.* **2016**, *3*, 1500502. [[CrossRef](#)]
20. Li, Y.; Cui, W.; Liu, L.; Zong, R.; Yao, W.; Liang, Y.; Zhu, Y. Removal of Cr(VI) by 3D TiO₂-graphene hydrogel via adsorption enriched with photocatalytic reduction. *Appl. Catal. B-Environ.* **2016**, *199*, 412–423. [[CrossRef](#)]
21. Lei, W.; Qi, S.; Rong, Q.; Huang, J.; Xu, Y.; Fang, R.; Liu, K.; Jiang, L.; Liu, M. Diffusion-freezing-induced microphase separation for constructing large-area multiscale structures on hydrogel surfaces. *Adv. Mater.* **2019**, *31*, 1808217. [[CrossRef](#)]
22. Lei, W.; Khan, S.; Chen, L.; Suzuki, N.; Terashima, C.; Liu, K.; Fujishima, A.; Liu, M. Hierarchical structures hydrogel evaporator and superhydrophilic water collect device for efficient solar steam evaporation. *Nano Res.* **2021**, *14*, 1135–1140. [[CrossRef](#)]
23. Rahman Khan, M.M.; Pal, S.; Hoque, M.M.; Alam, M.R.; Younus, M.; Kobayashi, H. Simple Fabrication of PVA-ZnS Composite Films with Superior Photocatalytic Performance: Enhanced Luminescence Property, Morphology, and Thermal Stability. *ACS Omega* **2019**, *4*, 6144–6153. [[CrossRef](#)] [[PubMed](#)]
24. Rahman Khan, M.M.; Akter, M.; Amin, M.; Younus, M.; Chakraborty, N. Synthesis, Luminescence and thermal properties of PVA-ZnO-Al₂O₃ composite films: Towards fabrication of sunlight-induced catalyst for organic dye removal. *J. Polym. Environ.* **2018**, *26*, 3371–3381. [[CrossRef](#)]
25. Chen, M.; Gong, G.; Zhou, L.; Zhang, F. Facile fabrication of a magnetic self-healing poly (vinyl alcohol) composite hydrogel. *RSC Adv.* **2017**, *7*, 21476–21483. [[CrossRef](#)]
26. Ranjith, K.S.; Senthamizhan, A.; Balusamy, B.; Uyar, T. Nanograined surface shell wall controlled ZnO-ZnS core-shell nanofibers and their shell wall thickness dependent visible photocatalytic properties. *Catal. Sci. Technol.* **2017**, *7*, 1167–1180. [[CrossRef](#)]
27. Khan, S.; Cho, H.; Kim, D.; Han, S.S.; Lee, K.H.; Cho, S.H.; Choi, H. Defect engineering toward strong photocatalysis of Nb-doped anatase TiO₂: Computational predictions and experimental verifications. *Appl. Catal. B-Environ.* **2017**, *206*, 520–530. [[CrossRef](#)]
28. Liao, J.; Liu, Z.; Wang, J.; Ye, Z. Cost-effective water-soluble poly(vinyl alcohol) as a functional binder for high-sulfur-loading cathodes in lithium-sulfur batteries. *ACS Omega* **2020**, *5*, 8272–8282. [[CrossRef](#)] [[PubMed](#)]
29. Laursen, A.B.; Kegnaes, S.; Dahl, S.; Chorkendorff, I. Molybdenum sulfides—Efficient and viable materials for electro- and photoelectrocatalytic hydrogen evolution. *Energy Environ. Sci.* **2012**, *5*, 5577–5591. [[CrossRef](#)]
30. Deng, H.; Xu, F.; Cheng, B.; Yu, J.; Ho, W. Photocatalytic CO₂ reduction of C/ZnO nanofibers enhanced by an Ni-NiS cocatalyst. *Nanoscale* **2020**, *12*, 7206–7213. [[CrossRef](#)]

31. Chunxiang, L.; Hu, P.; Meng, H.; Jiang, Z. Role of sulfites in the water splitting reaction. *J. Solut. Chem.* **2016**, *45*, 67–80.
32. Nasir, A.; Ur Rehman, Z.; Shah, S.N.A.; 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*, 20752–20780. [[CrossRef](#)]
33. Reber, J.F.; Meier, K. Photochemical production of hydrogen with zinc sulfide suspensions. *J. Phys. Chem.* **1984**, *88*, 5903–5913. [[CrossRef](#)]
34. Li, F.; Yang, J.; Gao, J.; Liu, Y.; Gong, Y. Enhanced photocatalytic hydrogen production of CdS embedded in cationic hydrogel. *Int. J. Hydrogen Energy* **2020**, *45*, 1969–1980. [[CrossRef](#)]
35. Lu, J.; Zhang, X.; Gao, H.; Cui, W. Three-dimensional structure of PANI/CdS NRs-SiO₂ hydrogel for photocatalytic hydrogen evolution with high activity and stability. *Nanomaterials* **2019**, *9*, 427. [[CrossRef](#)]
36. Lei, L.; Wang, W.; Wang, C.; Fan, H.; Yadav, A.K.; Hu, N.; Zhong, Q.; Buschbaum, P.M. hydrogel-supported graphitic carbon nitride nanosheets loaded with Pt atoms as a novel water-storage photocatalyst for H₂ evolution. *J. Mater. Chem. A* **2020**, *8*, 23812–23819. [[CrossRef](#)]
37. Wang, J.; Cong, J.; Xu, H.; Wang, J.; Liu, H.; Liang, M.; Gao, J.; Ni, Q.; Yao, J. Facile gel-based morphological control of Ag/g-C₃N₄ porous nanofibers for photocatalytic hydrogen generation. *ACS Sustain. Chem. Eng.* **2017**, *5*, 10633–10639. [[CrossRef](#)]
38. Madhusudan, P.; Wang, Y.; Chandrashekar, B.N.; Wang, W.; Wang, J.; Miao, J.; Shi, R.; Liang, Y.; Mi, G.; Cheng, C. Nature inspired ZnO/ZnS nanobranched-like composites, decorated with Cu (OH)₂ clusters for enhanced visible-light photocatalytic hydrogen evolution. *Appl. Catal. B Environ.* **2019**, *253*, 379–390. [[CrossRef](#)]