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Photochemical Decomposition of Hydrogen Sulfide

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Abstract

Hydrogen sulfide is an extremely toxic gas which is generated from both nature factors and human factors. A proper method for the efficient decomposition of hydrogen is of great importance. Using traditional Claus process, hydrogen sulfide could be decomposed into hydrogen oxide and sulfur. One drawback of this process is that the energy stored in hydrogen sulfide is partially wasted by the formation of hydrogen oxide. In fact, the energy could be utilized for the generation of hydrogen, a potential energy source in future, or other chemical products. Various methods that could possibly make better use of hydrogen sulfide have been studied in recent years, like thermal decomposition, plasma method, electrochemical method, and photochemical method. In particular, there have been high hopes in photochemical method due to the possible direct solar energy conversion into chemical energy. Unlike traditional photocatalytic water splitting, hydrogen sulfide decomposition is more accessible from the thermodynamic point of view. Photocatalytic hydrogen sulfide decomposition could occur in both gas phase and solution phase and various systems have been reported. Besides, the photoelectrochemical decomposition of hydrogen sulfide is also highlighted. In this chapter, we will simply introduce the current situation for photochemical decomposition of hydrogen sulfide.

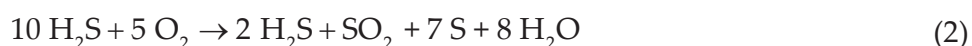
Keywords: photocatalysis, hydrogen sulfide

1. Introduction

Hydrogen sulfide (H_2S) is an extremely toxic and corrosive gas with an odor of rotten eggs. Usually, H_2S could be released due to nature factors like microbial metabolism in the absence of oxygen and volcanic eruptions. However, in modern society, the main source of H_2S should be more attributed to human activities like the refinery of crude oil (desulfurization) and the sweetening of natural gas. For example, due to the exhaustion of high-quality natural gas reservoirs and our continued growth in energy demand, people has to turn to some sour nature gas reservoirs with a large amount of H_2S . As a matter of fact, the H_2S content of sour natural

gas at some locations could be as high as 70–80% (like Harmatten, Alberta in Canada) that they are considered unusable [1]. A concentration of H_2S above 320 ppm in air could lead to pulmonary edema with the possibility of death [2], and H_2S must be carefully removed in related human activities.

Classically, the Claus process is the industrial standard to remove hydrogen sulfide. With this process, gaseous hydrogen sulfide could be decomposed into hydrogen oxide and sulfur (see Eq. (1)) with first thermal step at temperature above 850°C (Eq. (2)) and subsequently catalytic step (Eq. (3)) with activated aluminum(III), titanium (IV) oxide and so on [3].



Although this process is very mature and yields elemental sulfur as a by-product, one big drawback of it is that the energy stored in hydrogen sulfide is partially wasted by the formation of hydrogen oxide. In fact, the energy stored in H_2S could be utilized for the generation of hydrogen, a potential energy source in future, or other chemical products like H_2O_2 . Other disadvantages of Claus treatment include additional tail gas treatment and inflexibility to adjust to changes [4].

Various methods that could possibly make better use of hydrogen sulfide have been studied in recent years, like thermal decomposition, electrochemical method, plasmachemical method, and photochemical method [5]. For thermal decomposition, high temperature above 1000 K for significant conversion of H_2S is often required. Besides, high pressure and proper catalyst like molybdenum sulfide and other metal sulfide are commonly suggested, too. Interestingly, solar furnace was also suggested as the thermal source from the energy source point of view. Electrochemical method like direct electrolysis is often carried out in basic solutions where H_2S is absorbed. Anode poisoning by sulfur is a big challenge. In addition, chemical redox couples such as I^{3-}/I^- and $\text{Fe}^{3+}/\text{Fe}^{2+}$ are also introduced for indirect electrolysis of H_2S . The main problem of electrochemical method is the high electricity costs today. Plasma generated from microwave, ozonizer, and glow discharge was also reported to be an active species to induce the decomposition of H_2S into H_2 and S. In comparison, the plasma method is relatively clean and effective. However, similar to electrochemical method, the big obstacle of the plasma-chemical method is the use of electricity.

In contrast to others like thermal and electrochemical methods, the photodecomposition of H_2S is much less mature. Nevertheless, it is a very attracting method, as it offers us one possible approach to directly harness solar energy and convert them into chemical energy, in a period that we are under the pressure of both exhaustion of fossil fuel and increase in energy demand worldwide.

2. The principles for photochemical method

As early as 1912, photochemist Giacomo Ciamician has drawn us a picture of the future [6]:

“On the arid lands there will spring up industrial colonies without smoke and without smokestacks; forests of glass tubes will extend over the plains and glass buildings will rise everywhere; inside of these will take place the photochemical processes that hitherto have been the guarded secret of the plants, but that will have been mastered by human industry which will know how to make them bear even more abundant fruit than nature, for nature is not in a hurry and mankind is. And if in a distant future the supply of coal becomes completely exhausted, civilization will not be checked by that, for life and civilization will continue as long as the sun shines! If our black and nervous civilization, based on coal, shall be followed by a quieter civilization based on the utilization of solar energy, that will not be harmful to progress and to human happiness.”

However, even after 100 years later of this vision, human civilization is still “made use almost exclusively of fossil solar energy. Would it not be advantageous to make better use of radiant energy?”

In this chapter, we will mainly focus on photocatalysis (photochemical reaction carried out in the presence of catalyst), which has risen during the last half century. Ever since the discovery that TiO_2 could split water into hydrogen and oxygen with the assistance of light and electricity in 1972, photocatalysis has aroused great interest of people [7]. Usually, photocatalysis is a chemical process triggered by photogenerated electrons and holes from light-responsive materials. Like photosynthesis happening in nature, the light energy could be converted into chemical energy with photocatalysis. Therefore, some photocatalytic reaction like water splitting for hydrogen and oxygen evolution is called *artificial photosynthesis* and has given high hopes.

Both molecule and inorganic semiconductor systems could be constructed for photocatalysis. Typically, three processes are necessary to complete the photocatalysis (Figure 1): (1) absorption of photons and subsequent generation of free electrons and holes (see Eq. (4) and the enlarged section on the top right of Figure 1); (2) charge transfer and separation of photogenerated carriers (pathway C and D), accompanied with the competitive charge recombination processes (pathways A and B); (3) reduction of reaction substrates by electrons; and (4) oxidation of adsorbents by holes (Eq. (5)).



For molecular systems, these three steps are often occurred on different materials. Taken photocatalytic hydrogen evolution as an example, step 1 is often carried out by one kind

molecule (like ruthenium complexes), and step 3 is finished with the help of another molecule (such as recently popular cobalt and nickel complexes), while step 2 occurs both intra and intermolecularly. For semiconductor systems, all three steps could happen on one material (TiO_2 for instance), although sometimes cocatalyst (like Pt nanoparticles) is introduced for a higher light-to-chemical energy conversion. Molecular systems could be easily modified and could help us better observe the underlying catalytic mechanism from molecular level; nevertheless, such systems usually lack long-term stability and we will mainly focus on semiconductor-based photocatalytic systems in this chapter.

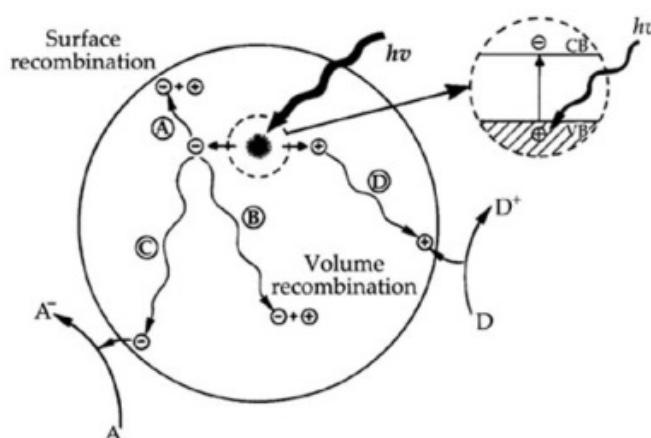


Figure 1. Schematic photoexcitation in a solid followed by deexcitation events. Adapted with permission from reference [8]. Copyright 1995 American Chemical Society.

Various kinds of semiconductors have been developed for photocatalysis. Due to its nontoxicity, low cost, and high stability, TiO_2 is the most studied semiconductor ever since its big sensation in 1972, and it is still very popular today. However, the crystal symmetry of TiO_2 allows only indirect interband transitions, and TiO_2 suffers from serious recombination of charge carriers [9]. Most importantly, the wide band gap of TiO_2 (3.2 eV for anatase and 3.0 eV for rutile) only makes it response to UV light (with wavelength below 398 nm for anatase and 413 nm for rutile), which only accounts for about 4% of the full solar spectrum [10]. Sensitization and doping are two common methods for modification of TiO_2 to increase its responsibility to visible light. Recently, it has been reported that with disorder engineering by hydrogenation, the onset of optical absorption of TiO_2 could be shifted to about 1200 nm (corresponding to 1.0 eV), and no obvious loss of photocatalytic activity of TiO_2 is observed [11].

In addition to TiO_2 , many other binary and ternary oxides are also studied, such as d^0 metal oxides (SrTiO_3 , ZrO_2 , Nb_2O_5 , Ta_2O_5 , $\text{Bi}_2\text{W}_2\text{O}_9$, etc.), d^{10} metal oxides (ZnO , In_2O_3 , etc.), and f^0 metal oxides (like CeO_2). Metal sulfides are another important category of photocatalysts. Among them, CdS has attracted large attentions. The main advantage of CdS is its responsibility to visible light (with a direct band gap of 2.4 eV), while one big disadvantage is its instability (mainly the oxidation of S^{2-} in the absence of hole scavenger) under light illumination. Other sulfides like ZnS , CuInS_2 , AgInS_2 , and their solid solution have also been well studied for photocatalysis [12]. In particular, carbon materials, like graphene carbon nitride

and carbon quantum dots, have lately aroused people's great interests due to their metal-free property and easy preparation [13,14]. Figure 2 shows the band gap and conduction and valence band levels of several typical semiconductors at pH 0. A more comprehensive presentation of the band structure of oxides and sulfide semiconductors was reported by Schoonen and Xu [15]. From the thermodynamic point of view, the conduction and valence band edge of semiconductors is an indication of their reducing and oxidizing ability, respectively. For instance, oxides often have deep valence band edge and hence strong oxidizing ability.

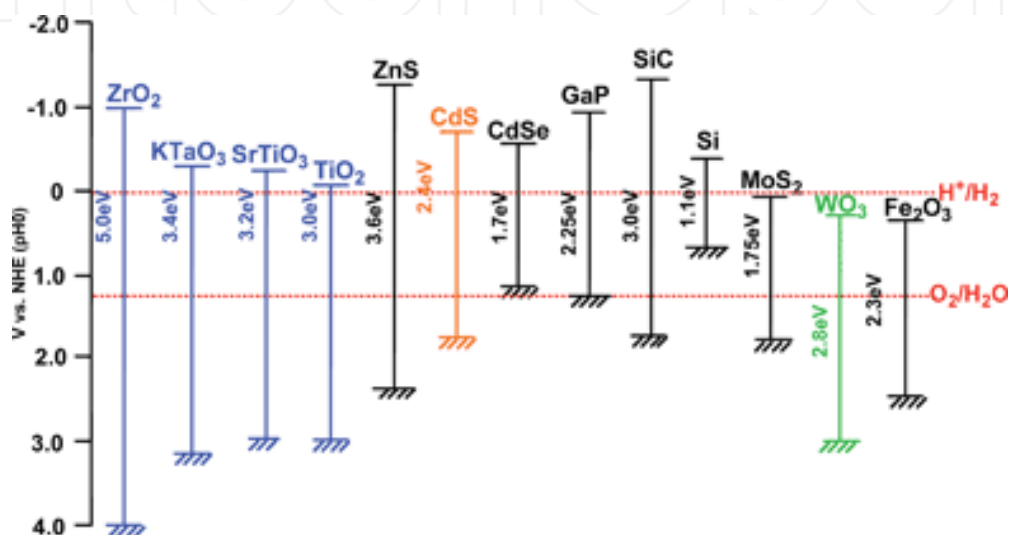


Figure 2. Relationship between band structure of semiconductor and redox potentials of water splitting. Reproduced by permission from the Royal Society of Chemistry from reference [12]. All rights reserved.

In all photocatalytic reactions were studied, water splitting is considered to be the Holy Grail of solar energy conversion. Over the last 40 years, scientists have been committed to find ideal photocatalytic systems that could turn water into hydrogen and oxygen by solar light. For a semiconductor qualified for water splitting, the conduction band edge should be more negative than the redox potential of H^+/H_2 (0 V vs NHE at pH 0), and the valence band edge should be more positive than the redox potential of $\text{O}_2/\text{H}_2\text{O}$ (1.23 V vs NHE at pH 0). Nevertheless, overpotential and large kinetic barriers are also needed to be considered in practice. Several semiconductor systems have been reported for the stoichiometry water splitting for hydrogen and oxygen evolution (with mole ration of 2:1), such as $\text{In}_{1-x}\text{Ni}_x\text{TaO}_4$ ($x = 0-0.2$) [16], NiO (0.2 wt%)/ $\text{NaTaO}_3\cdot\text{La}$ (2%) [17], and the lately reported visible light-responsive carbon dot/ C_3N_4 nanocomposite [14].

As a matter of fact, the photocatalytic decomposition of H_2S is similar to that of water splitting. To some extent, the direct decomposition of H_2S into H_2 and elemental S is much easier than that of H_2O from the thermodynamic point of view: the energy needed for H_2O decomposition is about 237.2 kJ/mol [18], while that for H_2S is only 39.3 kJ/mol [4,10]. The reductive reaction that occurs in the decomposition process of H_2S is still hydrogen evolution from protons in most cases (with exception mentioned below), but the oxidative reaction changes from O_2

evolution to oxidation of S^{2-} . Therefore, for a semiconductor qualified for H_2S decomposition, the conduction band edge should still be more negative than the redox potential of H^+/H_2 , but the valance band edge only needs to be more positive than the redox potential of H_2S/S^{2-} (0.14 V vs NHE at pH 0). This means that for semiconductors that are capable of water splitting are all qualified for H_2S decomposition. Besides, for some semiconductor, even if they may be not proper for water splitting due to the less positive valance band edge, they still have the potential for H_2S decomposition. One example is silicon. As seen from Figure 2, the valence band edge of silicon is far more negative than the redox potential of H_2O/O_2 , which determines its inability for oxygen evolution. Nevertheless, it could be used in the system of H_2S decomposition (see below).

Like water splitting could occur in both gas phase (water vapor) and liquid phase, H_2S , as an acid gas, could be decomposed in gas phase directly and disposed in liquid phase indirectly after being absorbed by solution. Moreover, here we will have a review of these two cases, respectively.

3. Photocatalytic hydrogen sulfide decomposition by gas phase reaction

Jardim et al. studied the gas phase destruction of H_2S with a low concentration range of hundreds of ppm using TiO_2 as the catalyst and black light lamp as the light source [19]. In the existence of oxygen and water vapor, H_2S could be effectively decomposed (about 99% efficiency) and the main product is determined as SO_4^{2-} . The deactivation of TiO_2 would happen with a H_2S concentration larger than 600 ppm, and it was mainly caused by the adsorption of by-product on its surface. No elemental S was detected by the color change of TiO_2 from white to yellow, and hydrogen evolution was not considered in this study. Notably, if oxygen is absent in the system, H_2S could be barely removed.

In a similar experiment, with the assistance of in situ FT-IR, Anderson et al. confirmed that no other gaseous products like SO_2 or SO, and SO^{2-} adsorbed on TiO_2 may be one intermediate during the “eight electron transfer” process [20]. Furthermore, Sano et al. have found that the photodeposition of Ag on TiO_2 would promote the adsorption of H_2S on the sample, possibly due to the partially oxidized silver surface, and the deposited Ag could act as a cocatalyst for removal of H_2S . Both factors made Ag-deposited TiO_2 more efficient for H_2S degradation [21].

In addition, Sánchez et al. have tried glass “Raschig” ring, poly(ethylene terephthalate) (PET), and cellulose acetate (CA) as the supports to load TiO_2 for photocatalytic treatment of H_2S gas [22]. Glass rings supported TiO_2 (which has underwent fire treatment) outperforms PET and CA supported TiO_2 . For PET and CA supports with low temperature treatment, PET supports displayed the higher photocatalytic activity, and TiO_2 caused the degradation of CA supports under illumination. Different from reports before, although SO_4^{2-} is one main product of H_2S removal, SO_2 was detected from these systems.

The interaction of H_2S with the semiconductor surfaces has also been investigated. Two adsorption modes of H_2S with high defect density rutile TiO_2 (110) surfaces were suggested:

dissociative adsorption with both H and S atom attached to the Ti atom at low H₂S concentration and molecular adsorption at high H₂S concentration [23]. Moreover, the preadsorption of H₂S would significantly block O₂ adsorption on TiO₂ surfaces even in the presence of large Ti³⁺ cations. Using Langmuir isotherm, Sopyan further discovered that H₂S adsorbed more strongly on rutile (0.7 molecules / nm²) rather than anatase (0.4 molecules/nm²). This is in sharp contrast with other molecules like acetaldehyde and ammonia [24]. Consequently, photocatalytic activity of anatase film is only 1.5 times higher than that of rutile for degradation of H₂S.

In all the above systems, H₂S in gas phase is studied within low concentration (tens to hundreds of ppm) and people mainly concerns with the oxidation product of H₂S. Little attention is paid to the reductive reaction of H₂S. Nevertheless, the reduction of H₂S (which is often the conversion of H₂S into H₂) is more attractive from an energy point of view.

Early in 1990s, Naman has combined thermal and photocatalytic decomposition of H₂S together and studied the influence of light influx on the thermal decomposition of H₂S by V_xS_y on different substrates (TiO₂, Al₂O₃, and ZnO) [25]. Under light irradiation, the conversion of H₂S to H₂ was increased by 27.6%, 44.6%, and 16.5% at 500°C, respectively. The Arrhenius activation energy for H₂S decomposition has also calculated to be 50% of that in darkness. The author tentatively attributes this photoactivation effect on thermal decomposition to the photoexcitation of semiconductors (including V_xS_y) and the subsequent generated charge carriers.

In 2008, Li et al. have compared the activity of five typical semiconductors TiO₂, CdS, ZnS, ZnO, and ZnIn₂S₄ for the direct decomposition of H₂S in gaseous phase [26]. With illumination of Xe lamp and Pt loading (0.2 wt%), the efficiency of the decomposition of 5% H₂S in argon decreases as a sequence of ZnS > TiO₂ > ZnIn₂S₄ > ZnS > CdS under the gas flow rate of 6 ± 0.5 mL/min. Various noble metal loadings on ZnS have been compared, and it turns out that Ir is superior than others (Pd, Pt, Ru, Rh, and Au), which improves the hydrogen evolution efficiency from 1.2 to 4.5 μmol/h. Doping ZnS was also carried out, and transition metal Cu²⁺ doping (0.5% mol) could greatly promote the decomposition process and improve efficiency of the hydrogen evolution by about 20 times in contrast to blank ZnS. In addition, the absorption edge of ZnS shift from 400 to 450 nm after Cu doping, and this contributes to a photocatalytic H₂ production rate of 17 μmol/h under visible light irradiation (λ > 420 nm). Similarly, one limitation of this research is that only the reduction product, H₂, is detected in the system and the oxidative products are ignored.

Although systematic experimental studies of the photocatalytic decomposition of H₂S in gaseous phase are scarce, thermodynamic analysis of solar-based photocatalytic H₂S decomposition has recently been reported, which may be instructive for further studies on experiments [27]. Analysis indicates that energy efficiency of this process is not significantly affected by the intensity of solar irradiation. Exergy efficiency (the second law efficiency) will decrease with the increase of solar intensity, while the hydrogen yield will increase. Although the exergy efficiency value of current catalyst is calculated to be less than 1%, the author envisioned that an exergy efficiency of 10% could be achieved in the near future, and a maximum exergy efficiency of 27% may be obtained for a chemical conversion ratio of 0.6 if close to optimum cases of the quantum efficiency and the catalyst band gap can be obtained.

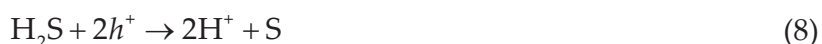
4. Photocatalytic hydrogen sulfide decomposition in solution

4.1. H₂S decomposition in aqueous solution

In comparison with solid gas phase photocatalysis, more often H₂S is first absorbed in solution. Under these circumstances, H₂S mainly participate in the photocatalytic reaction in the form of S²⁻ or HS⁻, depending on the pH of the system. (The dissociative constants for the first and the second dissociation of H₂S at 298 K are 1.02×10^{-7} and 1.3×10^{-12} , respectively.) Hydrogen (in most cases) is generated in these systems as a result of the proton reduction. H₂S has a high solubility in pure water (ca. 0.1 M at 298 K); however, due to the limited availability of S²⁻ and HS⁻, the hydrogen evolution efficiency is low [28]. More often, H₂S is absorbed by alkaline solution like NaOH and KOH solution, and sulfide solution is often used to replace the gaseous H₂S for photocatalytic H₂ evolution.

In 1976, Wrighton et al. reported that when using Na₂S as the sacrificial reagents in the presence of NaOH, the photocorrosion of CdS or CdSe photoelectrodes could be effectively inhibited [29]. The added S²⁻ in solution is oxidized, judging from the color change of the solution from transparent to yellow. H₂ was evolved at the Pt counter electrode. Later, Nozik proved that when the Schottky-type n-CdS/Pt photochemical diodes was suspended in the solution containing 1 M Na₂S and 1 M NaOH, hydrogen evolution could be observed with the illumination of simulated sunlight [30].

Early exhaustive studies of such work were conducted by Grätzel et al. [31]. When loaded with RuO₂ (0.1 wt%), CdS shows a high H₂ evolution rate of 0.128 mL g⁻¹ h⁻¹ in the presence of 0.1 M Na₂S (pH 3). With the S²⁻ ions present in the photocatalytic solution, a H₂S to H₂ conversion efficiency of 90% was calculated. Also, the concomitantly formed oxidation product S would not interfere with the water reduction (hydrogen evolution). The reaction mechanisms are shown in Eqs. (6–8):



Moreover, the overall reaction corresponds to H₂S splitting into H₂ and S with the assistance of two photons (Eq. (9)):



During the photocatalytic process, although oxygen reduction can compete with hydrogen reduction, the existence of O_2 has little effect on the system's efficiency. Furthermore, the study shows that a basic solution and a higher RuO_2 loading (but no more than 0.5 wt%) could obviously improve the efficiency, while increase of the concentration of S^{2-} in solution and Pt loading on CdS seems has no significant influence on hydrogen evolution. Under optimal conditions, a quantum yield of 0.35 is obtained. In a similar CdS involved photocatalytic system with S^{2-} as the electron donor, Reber et al. pointed out that in contrast to an acidic environment, only disulfide instead of elemental sulfur is formed in an alkaline medium [32].

Photocatalytic hydrogen evolution with in situ H_2S absorption in alkaline solution has been carried out with various kinds of semiconductor photocatalysts, too (Table 1). The mechanism of such systems is similar to that contains sulfide solution. One recent example with relatively high efficiency for hydrogen evolution was reported by Kale et al. with nanostructure Bi_2S_3 , which has a direct band gap of 1.3–1.7 eV [33]. Both nanorod and hierarchical nanoflower Bi_2S_3 were synthesized by hydrothermal method. With continuous H_2S bubbling into KOH solution, a hydrogen evolution efficiency of 8.88 and 7.08 mmol $g^{-1} h^{-1}$ was observed for nanoflower and nanorod, respectively, under solar irradiation (from 11:30 a.m. to 2:30 p.m.).

photocatalyst	light source	aqueous reaction solution	Cocatal./ H_2 activity ($\mu mol \cdot h^{-1} g^{-1}$)	Quantum yield (%)	Ref.
$CdIn_2S_4$	450-W Xe	$H_2S + KOH$	6960	17.1 (500 nm)	[40]
$ZnIn_2S_4$	300-W Xe	$H_2S + KOH$	10574	-	[41]
N-doped TiO_2	300-W Xe	$H_2S + KOH$	8800	-	[42]
N-doped ZnO	300-W Xe	$H_2S + KOH$	19785	-	[43]
Bi_2S_3	Sunlight	$H_2S + KOH$	8880	-	[33]
6,13-Pentacenequinone	450-W Xe, > 420 nm	$H_2S + KOH$	48480	-	[44]
$CdSe_{0.5}S_{0.5}$ in GeO_2 glass	450-W Xe, > 420 nm	$H_2S + KOH$	8165	26 (> 420 nm)	[45]
CdSe in GeO_2 glass	450-W Xe, > 420 nm	$H_2S + KOH$	7257	21 (> 420 nm)	[45]
CdS in GeO_2 glass	450-W Xe, > 420 nm	$H_2S + KOH$	7560	-	[46]
Bi QD in GeO_2 glass	450-W Xe, > 420 nm	$H_2S + KOH$	11541	-	[47]
$Cd_{0.1}Zn_{0.9}S$	450-W Xe, > 420 nm	$H_2S + KOH$	8320	-	[48]
$FeGaO_3$	450-W Xe,	$H_2S + KOH$	$NiO_x/5890$	9.3 (550 nm)	[49]

photocatalyst	light source	aqueous reaction solution	Cocatal./H ₂ activity (μmol·h ⁻¹ g ⁻¹)	Quantum yiled (%)	Ref.
	> 420 nm				
FeGaO ₃	450-W Xe, > 420 nm	H ₂ S + KOH	NiO _x /4730	7.5 (550 nm)	[49]
CuGa ₂ O ₄	450-W Xe, > 420 nm	H ₂ S + KOH	3212	5.3 (550 nm)	[50]
CuGa _{1.4} Fe _{0.6} O ₄	450-W Xe, > 420 nm	H ₂ S + KOH	RuO ₂ /9548	15.0 (550 nm)	[50]
CuGaO ₂	450-W Xe, > 420 nm	H ₂ S + KOH	7316	11.4 (550 nm)	[51]
CuGa _{0.065} In _{0.935} O ₂	450-W Xe, > 420 nm	H ₂ S + KOH	RuO ₂ /8656	13.6 (550 nm)	[51]
Nb ₂ Zr ₆ O _{17-x} N _x	450-W Xe, > 420 nm	H ₂ S + KOH	8566	13.5 (550 nm)	[52]
CdS-TiO ₂	500-W Hg, > 420 nm	H ₂ S + NaOH	Pt/9800	41 (> 420 nm)	[53]
CdS in HY zeolite	250-W Hg, > 400 nm	H ₂ S + NaOH / Na ₂ SO ₃	24000	-	[54]

Table 1. Photocatalytic systems directly using H₂S gas dissolved in alkaline solution for hydrogen evolution.

4.2. H₂S decomposition through S²⁻/SO₃²⁻ solution

One challenge often encounters with alkaline sulfide solution for photocatalytic hydrogen evolution is the interference of by-product. Disulfide and polysulfide ions usually form in alkaline sulfide solution by reaction between S²⁻ and elemental S immediately after the photooxidation (see Eqs. (10–12)). These ions are yellow and can act as an optical filter, which reduces the absorption of photocatalyst. In addition, polysulfide would compete with protons for reduction. Therefore, with the accumulation of disulfide, the hydrogen evolution efficiency of related systems is slowed down. A common solution for this is the addition of SO₃²⁻ into the system. The additional sulfite could react with sulfur and avoid the generation of polysulfide; meanwhile, colorless thiosulfate is formed, which is thermodynamically less easily reduced than protons:

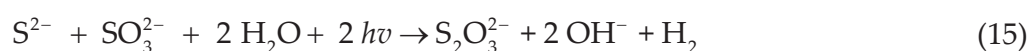




Then the net oxidative reaction that occurs in such a photocatalytic system is



and the whole photocatalytic hydrogen evolution reaction corresponds to



Photocatalytic hydrogen evolution systems based on $\text{S}^{2-}/\text{SO}_3^{2-}$ solution is widely reported, and some typical reports are given in Table 2 [10]. As a matter of fact, the $\text{S}^{2-}/\text{SO}_3^{2-}$ solution is one of the most famous sacrificial donors for photocatalytic hydrogen evolution under basic environment; this is especially true for metal sulfide photocatalysts. CdS, ZnS, CuInS₂, ZnInS₂, and their solid solution are all well studied for photocatalytic hydrogen evolution with such system. Metal sulfide often suffers from instability in photocatalytic processes as a result of the self-oxidation of sulfide with other sacrificial donors, but this could be effectively inhibited in the presence of sulfide in solution. This may be one important reason for the wide use of $\text{S}^{2-}/\text{SO}_3^{2-}$ solution in photocatalysis. In contrast, metal oxide is less popular in such system, probably due to their small response in the visible light region.

Using $\text{S}^{2-}/\text{SO}_3^{2-}$ solution, Kudo et al. have developed a series of visible light-responsive ZnS–CuInS₂–AgInS₂ solid solution photocatalysts for hydrogen evolution under irradiation from the solar simulator [34]. With increasing the proportion of CuInS₂ and AgInS₂ in the solid solution, the absorption spectrum of the photocatalyst could be extended to near-infrared region; however, hydrogen evolution was only observed with light absorption of wavelength less than 650 nm. When loaded with 0.75 wt% Ru, the initial hydrogen rate of 8.2 L m⁻² h⁻¹ and a quantum yield of 7.4% (at both 480 and 520 nm) could be observed with irradiation of solar simulator. Furthermore, they have demonstrated that with this photocatalytic system, a solar hydrogen evolution rate of about 2 L m⁻² h⁻¹ could be obtained for a reactor of 1 m² in November in Tokyo [12]. In addition, CdS loaded with RuO₂ (0.25 wt%) is also evaluated for its potential for commercial application. When the CdS–RuO₂ concentration is 2.0 mg mL⁻¹ in 500 mL solution of 0.1 M Na₂S and 0.1 M Na₂SO₃ (with a surface area of 112 cm²), a hydrogen generation rate of 28 mL h⁻¹ could be achieved under solar light irradiation [35].

photocatalyst	light source	Cocatalyst / H ₂ activity ($\mu\text{mol}\cdot\text{h}^{-1}\text{ g}^{-1}$)	Quantum yield (%)
CdS	300-W Xe, > 420 nm	Pt-PdS/29 233	93 (420 nm)
CdS/ZnS	350-W Xe, > 430 nm	900	10.2 (420 nm)
CdS/TiO ₂	350-W Hg, > 420 nm	Pt/6400	-
CdS/ZnO	300-W Xe	Pt/3870	3.2 (300-600 nm)
CdS/LaMnO ₃	300-W Xe, > 420 nm	375	-
c-CdS/Pt/hex-CdS	500-W Hg-Xe, > 420 nm	13 360	-
CdS/Na ₂ Ti ₂ O ₄ (OH) ₂	300-W Xe, > 420 nm	Pt/2680	43.4 (420 nm)
CdS/Zr _{0.25} Ti _{0.75} PO ₄	300-W Xe, > 430 nm	Pt/2300	27.2 (420 nm)
CdS/AgGaS ₂	450-W Hg, > 420 nm	Pt/4730	19.7 (> 420 nm)
CdS:Ag	900-W Xe	Pt/33480	~25 (450 nm)
CdS-ZnS:Ag	900-W Xe	Pt/40957.5	37 (450 nm)
CdS:In/Cu	300-W W-H, > 420 nm	Pt/2456	26.5 (420 nm)
CdS:Mn	500-W Xe, > 420 nm	RuO _x /1935	7 (> 420 nm)
Cd _{0.1} Zn _{0.9} S:Ni	350-W Xe, > 420 nm	Pt/585.5	15.9 (420 nm)
(Zn _{0.95} Cu _{0.05}) _{0.67} Cd _{0.33} S	300-W Xe, > 420 nm	Pt/3633.3	31.8 (420 nm)
ZnS:C	500-W Hg, > 420 nm	Pt/~90	-
ZnS:Ni	300-W Xe, > 420 nm	160	1.3 (420 nm)
ZnS:Pb/Cl	300-W Xe, > 420 nm	93	-
CdSe	700-W Hg, > 400 nm	436	13.4 (> 400 nm)
In ₂ S ₃	300-W Xe, > 400 nm	Pd/960.2	2.1 (430 nm)
CuInS ₂	500-W Xe, > 420 nm	Pt/84	-
ZnIn ₂ S ₄	300-W Xe, > 430 nm	Pt/562	18.4 (420 nm)
ZnIn ₂ S ₄ :Cu	300-W Xe, > 430 nm	Pt/757.5	14.2 (420 nm)
AgGaS ₂	500-W Hg, > 420 nm	Pt/2960	12.4 (> 420 nm)
CuGa ₃ S ₅	300-W Xe, > 420 nm	NiS/~2800	1.3 (420-520 nm)
AgIn ₅ S ₈	300-W Xe, > 420 nm	Pt/200	5.3 (411.2 nm)
Ag ₂ ZnSnS ₄	300-W Xe, > 420 nm	Ru/1607	3 (500 nm)
Cu ₂ ZnGeS ₄	300-W Xe, > 420 nm	Ru/1233	-
CuGa ₂ In ₃ S ₈	300-W Xe, > 420 nm	Rh/10667	15 (560 nm)
AgGa ₂ In ₃ S ₈	300-W Xe, > 420 nm	Rh/3433	15 (490 nm)
AgInZn ₇ S ₉	300-W Xe, > 420 nm	Pt/3164.7	20 (420 nm)
ZnS-In ₂ S ₃ -CuS	300-W Xe, > 400 nm	360 000	22.6 (420 nm)

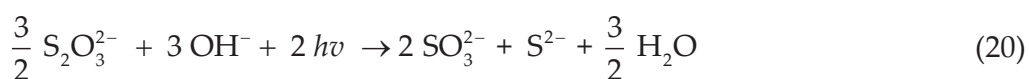
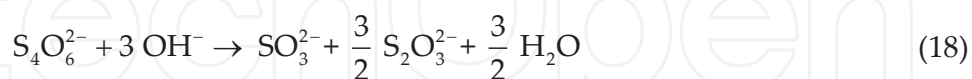
photocatalyst	light source	Cocatalyst / H ₂ activity (μmol·h ⁻¹ g ⁻¹)	Quantum yield (%)
ZnS-In ₂ S ₃ -Ag ₂ S	300-W Xe, > 400 nm	220 000	19.8 (420 nm)
Cu _{0.25} Ag _{0.25} In _{0.5} ZnS ₂	300-W Xe, > 420 nm	Ru/7666.7	7.4 (520 nm)
In(OH) ₃ :S/Zn	300-W Xe, > 420 nm	Pt/223.3	0.59 (420 nm)
ZnS _{1-x-0.5y} O _x (OH) _y	400-W Hg, > 420 nm	~460	3.0 (400-700 nm)
AgGaS ₂ /TiO ₂	450-W Hg, > 420 nm	Pt/4200	17.5 (> 420 nm)
TiO _{2-x} N _x /WO ₃	300-W Hg, > 400 nm	Pd/1005	0.45 (> 400 nm)
Cr ₂ O ₃ /Na ₂ Ti ₂ O ₄ (OH) ₂	350-W Xe, > 400 nm	36.4	-

Adapted with permission from reference [10]. Copyright 2010 American Chemical Society.

Table 2. Photocatalysts for hydrogen evolution using S²⁻/SO₃²⁻ related solution as the sacrificial donor under visible-light irradiation.

4.3. Thiosulfate cycle for H₂S decomposition

To make more efficient use of solution with mixed sulfide and sulfite for photocatalytic hydrogen evolution, Grätzel et al. further propose the concept “thiosulfate cycle” [36]. Under light illumination, S₂O₃²⁻ could be disproportionated into S²⁻ and SO₃²⁻ with the assistance of TiO₂ (see specific reaction in Eqs. (16–19) and overall reaction in Eq. (20)). Oxidation products like SO₄²⁻ and S₂O₆²⁻ are excluded from the system, and the 1:2 stoichiometric ratio of S²⁻ and SO₃²⁻ is maintained during the whole irradiation time:



Therefore, if a system contains both photocatalytic hydrogen generation (Eq. (15)) and sulfite generation (Eq. (20)) compartments and one coordinates to the other well, three molecules of

H₂ would be produced with the oxidation of one mol of S²⁻ into SO₃²⁻ through the thiosulfate cycle (Eq. (21)):



With such a cycle, no sulfur or thiosulfate would accumulate in such system. Figure 3 shows such a possible two-compartment system composed of CdS and TiO₂. Ideally, for the generation of 1 mol of H₂, 2 mol and 4/3 mol photons are needed to be absorbed by CdS and TiO₂, respectively. However, whether the efficiency of the two half cycles could match each other effectively is one important question unveiled to us, and there is no further clear report of this system till now.

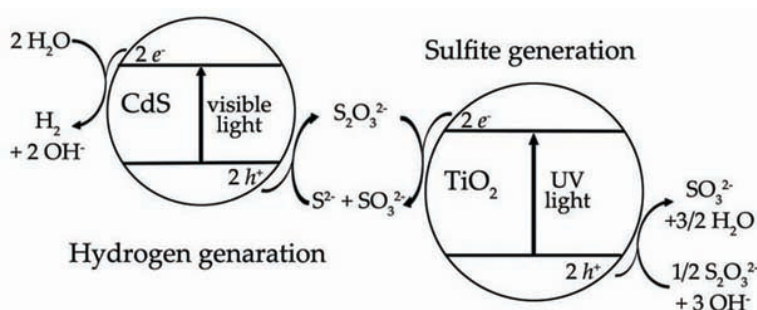


Figure 3. Schematic illustration of H₂S decomposition by two photosystems, linked through the S₂O₃²⁻/S²⁻/SO₃²⁻ redox system.

4.4. H₂S decomposition in ethanolamine solution

In addition to hydroxide alkaline solution, some other additives are introduced to promote the absorption of H₂S in solution. For example, ethanolamine solution is frequently used in gas sweetening industry. Naman and Grätzel have dissolved H₂S in aqueous solution of alkanolamines (including monoethanolamine (MEA), diethanolamine (DEA), and triethanolamine (TEA)) and studied the photocatalytic efficiency of such system with vanadium sulfide as the photocatalyst [37]. Taking monoethanolamine for instance, one monoethanolamine was able to dissolve one molecule of H₂S (see Eqs. (22 and 23)). However, one big disadvantage of this method is that ethanolamines themselves could be decomposed under light illumination and the amount of ammonia detected from the photocatalytic system could even be higher than that of H₂:



Furthermore, Li et al. used anhydrous ethanolamine solution to absorb H₂S [38]. Different from early report that system containing aqueous MEA outperforms that contains DEA and TEA, nonaqueous DEA solution is best for H₂S decomposition with CdS-based photocatalyst. Such a system is also better than system with NaOH-Na₂S solution from both the point of lifetime and rate for photocatalytic hydrogen evolution. In addition, the reduction of polysulfide in H₂S-DEM system is effectively depressed and could hardly compete with the proton reduction, which commonly occurs in NaOH-Na₂S system.

4.5. Extraction of elemental sulfur

Although numerous kinds of catalysts have been reported for the decomposition of H₂S through the above-mentioned method and hydrogen indeed evolves from solution, one problem is that S²⁻ often transforms into polysulfide, thiosulfate, or sulfite. How to deal with these by-products is another big challenge for us. Elemental S is more favored as the by-product; nevertheless, it could not be recovered from such photocatalytic system. To obtain pure sulfur, people have developed several ideas.

One simple method is to take advantage of the limited acid stability of complex sulfur species. Both polysulfide and thiosulfate would produce S when the pH value of the system decreases to a certain extent. That is, if the outlet reaction solution after photocatalysis (containing polysulfide or thiosulfate) encounters the inlet acidic gas H₂S, elemental S could possibly be precipitated from the system with a proper drop of pH:



In this regard, Linkous et al. have designed a circulating photoreactor for H₂S decomposition (Figure 4) [39]. The feasibility of this system was conducted. In the photoreactor, hydroxide would be generated along with H₂ evolution, and the pH of the solution would increase. Nevertheless, when this solution flows into the scrubber tower, pH would decrease due to the input H₂S gas. For the fresh reaction solution constituted of both S²⁻ and SO₃²⁻, S₂O₃²⁻ would be generated after photocatalysis, and pH must be lowered to 4.2 (by neutralization with H₂S) for sulfur release from S₂O₃²⁻. Then S could be collected as precipitates and the remaining solution (enriched with HS⁻ and HSO₃⁻) would be sent back to the photoreactor for another round of photocatalysis, with a low pH (≤ 4.2). For fresh reaction solution only constituted of S²⁻, polysulfide would be generated and the pH of the solution need to be lower than 10 for precipitation of sulfur. Normally, the photocatalytic systems using S²⁻ or SO₃²⁻ as the electron donor are more efficient for hydrogen evolution under basic conditions (pH ≥ 10); in some cases, the system could not even work under a relatively acidic environment (like pH 4). This urges us to reconsider the effect of SO₃²⁻ under such circumstances: as described above, SO₃²⁻ are widely used in S²⁻ involved hydrogen evolution system to avoid the generation of polysulfide

(which competes not only with catalyst from light absorption but also with protons for reduction by electrons), but the acidity necessary for the release of S from the obtained thiosulfate would greatly reduce the photocatalytic activity of the catalysts. In their study, Linkous pointed out that if the depth of reaction solution in photoreactor is less than 1 cm, in order to reduce the light absorption of polysulfide, S^{2-} alone as the electron donor for photocatalytic hydrogen evolution is probably more suitable for the cyclic sulfur release in a CdS/Pt involved system. Additionally, another problem of this design is that if the commonly studied suspension system is used for photoreaction, photocatalyst could not be easily separated with the solution. Therefore, catalyst may need to be immobilized for circulating.

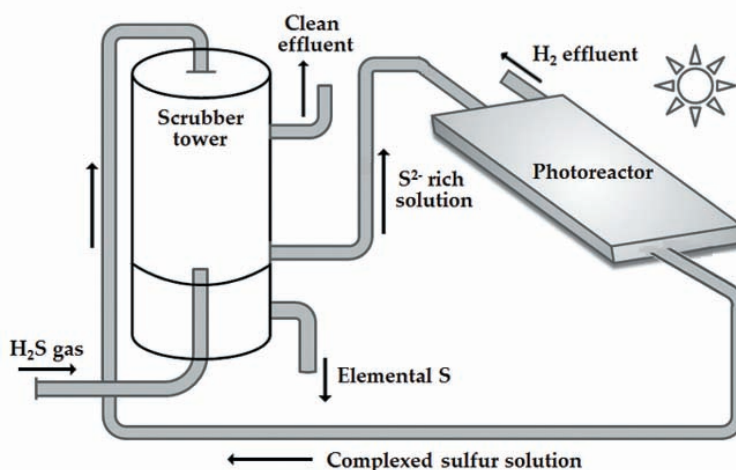


Figure 4. Generalized scheme for light-driven H_2S decomposition using an immobilized photocatalyst. Reprinted from reference [39], Copyright (1995), with permission from Elsevier.

5. Photoelectrochemical decomposition of hydrogen sulfide

In addition to the photocatalytic decomposition of H_2S alone, sometimes photochemical method is combined with electrochemical method for the decomposition of H_2S , that is, the photoelectron-chemical (PEC cell) decomposition of H_2S . Actually, the colloidal semiconductor photocatalyst system mentioned above could also be seen as some kind of short-circuit PEC cell, in which both anodic and cathodic reaction occurs on the surface of semiconductors at the same time (similar to the “photochemical diodes” developed by Nozik [30]). In this section, traditional PEC cells (with separated anode and cathode connected by wires) would be mainly focused. These cells could not only decompose hydrogen sulfide but also generate electricity. In addition, voltage bias could be applied to the cells if the drive force of light is not enough for hydrogen sulfide decomposition.

In 1987, Kainthla and Bockris reported a PEC cell for the decomposition of H_2S based on CdSe anode and Pt cathode [55]. CdSe film was directly grown on Ti substrate. Using polysulfide (prepared by H_2S dissolution in NaOH and subsequent addition of sulfur) as the electrolyte,

an open circuit voltage of 0.62 V and short circuit current of 8.82 mA cm⁻² could be achieved. H₂ bubbles could be observed to leave the Pt cathode when photocurrent flows through the cell and a Faraday efficiency of 0.97 is calculated. With the gradual accumulation of polysulfide during the reaction, elemental sulfur would precipitates from the solution when polysulfide reaches its solubility limit. Stability of the cell is also tested and short circuit drops less than 10% with continuous illumination of 2 weeks. The total cell conversion efficiency (ϵ) given as the ratio of the recoverable energy to the input energy is calculated based on Eq. (26):

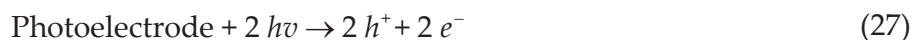
$$\epsilon(\%) = (0.171I + IV_{\text{cell}}) \times 100 / W_{\text{light}} \quad (26)$$

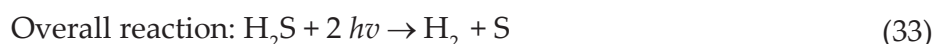
where 0.171I is the chemical energy storage for H₂S decomposition into H₂ and S, IV_{cell} is the electrical energy generated from the cell, and W_{light} is the intensity of light. Maximum light to chemical energy storage, light to electrical energy, and total cell conversion efficiency occurs at cell voltage of 0, 0.3, and 0.275 V, with the corresponding efficiency to be 1.5%, 1.8%, and 2.85%, respectively. In this regard, the PEC cell can be operated in a manner that electrical energy or chemical energy can be selectively collected.

It is noteworthy that for eliminating the competition of polysulfide with proton for reduction in this cell, which is also a big problem in suspension systems, anode and cathode are placed in two compartments, and Nafion membrane is used to prevent the contact of polysulfide with cathode. If there is no Nafion membrane, only polysulfide is reduced into sulfide, and no H₂ could be detected from the system. Under this circumstance, no net chemical reaction happens in the cell, and light energy could only be converted into electrical energy.

Another advantage for PEC cells is that some strategies for the electrochemical decomposition of H₂S could be extended to PEC cell. One strategy is the indirect decomposition of H₂S with the assistance of redox couple like I⁻/I₃⁻ (or I⁻/IO₃⁻) and Fe³⁺/Fe²⁺, in which the electrical energy or solar energy is first stored in the redox intermediate species, and then the intermediate could drive the following chemical reactions. Although indirect strategy may consume more additional energy for H₂S decomposition from a thermodynamical point of view, it is kinetically more favored and is beneficial for the extraction of elemental sulfur from the system.

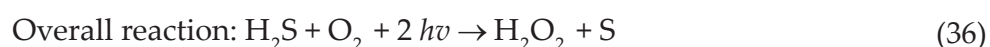
Lately, Li and Wang et al. have adopted this strategy in PEC cells for H₂S decomposition and achieved good results. PEC cell with p-type Si deposited with protective TiO₂/Ti n+ doping layer and H₂ evolution cocatalyst Pt (Pt/TiO₂/Ti/n+p-Si) as the photocathode and Pt plates as anode was reported for the decomposition of H₂S [56]. In a two-compartment cell separated by Nafion membrane, freshly prepared 0.2 M of FeSO₄ (or KI) in 0.5 M of H₂SO₄ solution and 0.5 M of H₂SO₄ was used as the anodic and cathodic electrolyte, respectively. After H₂S bubbling into the anode compartment, S and H₂ could be separately produced from the anode and the cathode under light illumination at an applied potential of 0.2 V vs RHE. In this system, the chemical redox couple is significant for the conversion of H₂S into H₂ and S (Eqs. (27–33)):





Control experiment shows that if there is no existence of Fe^{2+} or I^- in the electrolyte, such experiment is unsuccessful due to the low solubility of H_2S in acidic solution. Besides, n-type Si coated with 3,4-ethylenedioxythiophene (PEDOT) as the anode was also tested in this system, and it turns out that Fe^{2+} and I^- could be easily oxidized on it. Nevertheless, due to the low stability of the n-type Si anode, further study in this report is unclear.

Notably, they further developed this indirect strategy in PEC cell and have made H_2O_2 and S from H_2S in the presence of oxygen [57]. This is quite novel because most study related to H_2S decomposition is limited to H_2 as the only reduced product now. In addition to the redox couple I^-/I_3^- in the anode compartment of the cell for S production, another redox couple anthraquinone/anthrahydroquinone ($\text{AQ}/\text{H}_2\text{AQ}$) was introduced to the cathode cell for H_2O_2 production. In fact, AQ is also an important reaction substrate in Hysulf process, one indirect strategy related to the thermal decomposition of H_2S . The anode reaction is still the same as Eqs. (30 and 31), but the cathode reaction and the overall reaction change as follows (Eqs. (34–36)):



At zero bias, Pt/p+ n Si photoanode and Pt cathode can simultaneously oxidize I^- to I_3^- and reduce AQ to H_2AQ , respectively. Solar to chemical conversion efficiency was estimated to be 1.1%. If Pt cathode is replaced with carbon plate, a higher photocurrent could be observed.

6. Conclusion

In general, H_2S is a highly polluted gas that must be carefully handled and removed. The traditional Claus process suffers from high-energy consumption and waste of potential energy, H_2 . The photochemical decomposition of H_2S , which emerges with the rise of photocatalysis in the last century, could be one improved method for H_2S disposal. Lots of progress in the field of the photochemical decomposition of H_2S has been made in both gaseous phase and liquid phase. The mechanism of such reaction has been studied, and the efficiency of these systems has been calculated. Most often, the photochemical decomposition of H_2S is indirectly carried out in the form of photocatalytic H_2 production from aqueous sulfide solution. Details of the photochemical decomposition of H_2S , such as extraction of elemental sulfur from reaction system and the cyclic operation, were also of preliminary consideration. In addition, photochemistry was combined with electrochemistry for H_2S conversion: photoelectrochemical cells were built to extract H_2 (or H_2O_2) and S from H_2S with the assistance of redox couples.

In 2009, Li et al. reported CdS loaded with PdS and Pt dual cocatalyst can effectively generate H_2 , with a quantum yield of 93% at 420 nm in the presence of $\text{S}^{2-}/\text{SO}_3^{2-}$ solution and no deactivation was observed within illumination of 100 h for H_2 generation [58]. This is probably the most efficiency system reported relevant to the photocatalytic decomposition of H_2S till now. However, a lot of scientific problems are still unsolved, and there is a long, long way to go for the real application of the photocatalytic decomposition of H_2S in large scale chemical processing. In present, problems below may be considered in priority:

In gaseous phase systems, the concentration studied for H_2S decomposition is often low (with a volume concentration on ppm level); they are not practical in real industrial process. Also, people tend to focus on half of the reaction (oxidation of S^{2-} to SO_4^{2-} or H_2 generation). This is especially true in solution phase system with $\text{S}^{2-}/\text{SO}_3^{2-}$ or S^{2-} as the electron donor: most reports only consider how to improve the efficiency of hydrogen evolution. Without the thorough consideration of both oxidizing and reducing reactions, the photochemical decomposition of H_2S is not persuasive. Moreover, in solution phase system for H_2S decomposition, along with H_2 evolution, the simultaneously generated polysulfide or thiosulfate is also a pollutant to environment; subsequent processing of such reaction solution should be cared for meaningful utilization of H_2S . Although systems have been designed for sulfur generation from polysulfide or thiosulfate solution, successful trials are limited and the subsequent separation of sulfur from solution is also a challenge.

Current catalysts with high efficiency of photochemical H_2S decomposition are mainly metal sulfide loading with noble metal cocatalyst like Pt, RuO_2 , and so on. Although CdS is considered one of the most efficient photocatalyst for H_2 generation under visible light, the high toxicity of CdS should be taken seriously. New materials are needed to be exploited, and carbon materials may be alternative photocatalysts in consideration of cost, stability, and toxicity. Besides, noble metal poisoning by sulfide is another problem could happen sometimes and new earth abundant (low cost) cocatalyst resistive to sulfide poisoning is necessary. Transition metals like Fe, Co, and Ni and their compounds could be promising from the current available data. Similar in PEC cells for H_2S decomposition, stability and cost could be big problems, too.

To conclude, the photochemical decomposition of H_2S is still in a relatively early stage. New photocatalytic H_2S decomposition systems with low cost, high quantum efficiency, and long stability should be further developed, especially those responsive to the visible light region, which account for 43% in the full solar spectra. (Taking similar photocatalytic water spitting as a reference, a quantum yield of 30% at 600 nm is the starting point for practical application, which corresponds to about 5% solar energy conversion.) This may be fulfilled with optimized structure design, including chemical composition, electron and band structure, crystal structure and crystallinity, surface state, morphology, and so on, which is currently highlighted in nanoscience and technology. Moreover, people should keep in mind that oxidation and reduction of H_2S is equally important for H_2S decomposition if we want to handle H_2S in a really green way.

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