



In₂S₃/CuS nanosheet composite: An excellent visible light photocatalyst for H₂ production from H₂S

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ABSTRACT

As hydrogen sulfide (H₂S) is a toxic chemical emitted in large quantities from both natural sources and industrial processes, resource utilization of H₂S has become a hotspot research in recent years. We report herein, synthesis and characterization of a highly active In₂S₃/CuS nanosheet composite photocatalyst via a facile one-pot solvothermal route. The as-obtained In₂S₃/CuS composite show a special hierarchical structure and remarkable visible light absorption ability with an absorption edge of 785 nm. Its remarkable light absorption ability enables it to fully absorb the visible light. The as-obtained In₂S₃/CuS composite exhibits a superior visible-light photocatalytic activity and long-term durability in H₂S splitting. As a result, a maximum H₂ production rate of 14950 μmol g⁻¹ h⁻¹ over In₂S₃/CuS composite has been achieved even without any noble metal co-catalysts, which is 404 and 87 fold higher than that of over bare β-In₂S₃ and Cu₉S₅, respectively. The corresponding apparent quantum yield (AQY) of In₂S₃/CuS at 420 nm is 9.3%. The excellent photocatalytic activity depends on the chemical structure, phase, optical nature and folded nanosheet like geometry of In₂S₃/CuS composite, which facilitated electron transfer between interfaces of β-In₂S₃ and CuS, and improved the separation of photo-generated electron-hole pairs. Therefore, In₂S₃/CuS composite could serve as an efficient and practical visible-light response photocatalyst for H₂ production from toxic and corrosive H₂S.

1. Introduction

Progress in clean energy technology requires terrific uprising in renewable energy research attributable to the global energy and environmental disasters. Innovations with new approaches are producing fuels alternatives. Hydrogen (H₂) is becoming one of the leading competitors for future fuel, which has the highest energy density (120–142 MJ/kg) in comparison to any other fuel without carbon trace [1–10]. Concerning the economic and environmental advantages, hydrogen sulfide (H₂S) has drawn more attention due to possess less decomposition energy ($\Delta G^\circ = 33.3$ kJ/mol), to convert into hydrogen and sulfur [11]. H₂S is a regular noxious waste generated during petroleum refining, gasification of coal and very little quantity in biochemical process [12]. An abundant availability in various natural and industrial resources reveals that it remains an ultimate foundation for the H₂ production with a great economic value. However, the inexpensive and conventional production of H₂ from toxic and corrosive H₂S is still a significant scientific confront. The traditional Claus process has been widely utilized in industry to realize the removal of H₂S via partial oxidation of H₂S into sulfur and water where H₂ is wasted, thus this

process has some economic and environmental drawbacks [12]. In 1975, Raymont recognized dry box process followed by oxide re-activation for decomposition of H₂S into hydrogen and elemental sulfur, although the equilibrium constant of thermolysis reaction did not favor to proceed [13]. On the other hand, after the successful research on photoelectrocatalytic water splitting by Fujishima and Honda in 1972, the hydrogen production by splitting H₂O or H₂S over various types of semiconductor photocatalysts such as metal oxide and metal sulfide has been studied [14–23,30–34]. A first successful application for decomposition of H₂S into hydrogen and sulfur was reported by Nick Serpone in 1984 via electron transfer from the conduction band of CdS to that of TiO₂ particles occurs in alkaline suspensions containing SH⁻ ions under visible light irradiation [36]. Subsequently, hydrogen production via photocatalytic H₂S splitting has become a clean, economical, and environmental friendly approach. In the past few decades, several active metal sulfide photocatalysts have been developed for H₂S splitting under solar energy irradiation, which elucidate better charge transfer processes and improve the efficiency to disintegrate H₂S [19–23,31–34,36]. Nevertheless an obvious regular improvement in activity and stability of photocatalyst along with better efficiency of

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hydrogen production via H_2S disintegrations is still a challenge for its practical applications. Hence, it is highly desirable to develop a highly efficient catalyst with elevated activity and stability under visible light illumination.

For this purpose, metal sulfide systems have attracted great attentions due to their unique properties like appropriate band gap, crystalline structure and catalytic functions [16–18,23,31–34]. Among these metal sulfides, In_2S_3 with a narrow band gap of 2.0–2.2 eV existing in three different crystalline forms like defect cubic, defect spinel and layered structures [37]. However, quick recombination of photo-generated electron-hole pairs resulted in low efficient, which is still a confrontation to improve the photocatalytic efficiency of In_2S_3 . Consequently, various researches have been emerged for the enhancement of photocatalytic efficiency of In_2S_3 via different strategies, such as the modification of In_2S_3 morphologies, integrating with doping of metal and carbon materials, use of cocatalyst and composite formation between approximate similar band structure semiconductors [23,38–42]. Among them, the construction of composite is a promising strategy to enhance the photocatalytic performance of bulk In_2S_3 . Over the past decade, various In_2S_3 -based composites such as $\text{MnS}/\text{In}_2\text{S}_3$ [23], $\text{In}_2\text{S}_3/\text{ZnS}$ [24,25], $\text{In}_2\text{S}_3/\text{CdS}$ [26,27], $\text{ZnO}/\text{In}_2\text{S}_3$ [28] and $\text{In}_2\text{S}_3/\text{g-C}_3\text{N}_4$ [29] have been explored as appropriate photocatalyst with a relatively high performance for respective photocatalytic reaction. Meanwhile, copper sulfides (CuS), as one of the narrow band gap semiconductor, have aroused significant interests in the photocatalysis due to their variable stoichiometric composition, valence states, crystal morphologies and different unique properties [43,44,48–54]. Therefore, In_2S_3 accompanied to copper sulfide, could be a promising active photocatalyst through utilizing band gap engineering and matching crystal lattices for photocatalytic H_2 production from H_2S . However, to the best of our knowledge, there is no report on the photocatalytic H_2 production from H_2S over $\text{In}_2\text{S}_3/\text{CuS}$ composite.

Herein, the $\text{In}_2\text{S}_3/\text{CuS}$ nanosheet composite was successfully fabricated by one-pot solvothermal method. The composite exhibits superior visible light absorption ability. The photocatalytic H_2 evolution has been studied under visible light irradiation over $\text{In}_2\text{S}_3/\text{CuS}$ composite from H_2S decomposition using $\text{S}^{2-}/\text{SO}_3^{2-}$ as reaction medium, corresponding to H_2 evolution rate of $14590 \mu\text{mol g}^{-1} \text{h}^{-1}$, which is approximately 404 times higher than of pristine $\beta\text{-In}_2\text{S}_3$ ($37 \mu\text{mol g}^{-1} \text{h}^{-1}$) and 87 times higher than that of over bare Cu_9S_5 ($171 \mu\text{mol g}^{-1} \text{h}^{-1}$). The corresponding apparent quantum yield (AQY) of $\text{In}_2\text{S}_3/\text{CuS}$ at 420 nm is 9.3%. The superior visible light photocatalytic activity can be ascribed to the excellent electron-hole separation activity and the synergy effects of the $\beta\text{-In}_2\text{S}_3$ and CuS. Simultaneously, the introduction of CuS within composite material generates appropriate chemical structure, band gap energy in favor of facile transportation of photo-carriers, which is also favorable to enhance the photocatalytic activity. Furthermore, the role of reaction medium ($\text{S}^{2-}/\text{SO}_3^{2-}$) was also discussed. Finally, the photocatalytic H_2 production process over $\text{In}_2\text{S}_3/\text{CuS}$ composite is discussed.

2. Experimental

2.1. Synthesis of $\text{In}_2\text{S}_3/\text{CuS}$ composite

For the synthesis of composite, two solutions were prepared; $\text{InCl}_3 \cdot 2\text{H}_2\text{O}$ (100-x mmol) was dissolved in 1 pH of aqueous HCl. An appropriate amount of Na_2S solution was gradually added to the solution, with continuous stirring, to obtain a homogeneous yellow sol (the mol ratio of $\text{In}/\text{S} = 1/2$) as solution A. And copper acetate (x mmol) was dissolved in ethylenediamine with suitable amount of thioacetamide (TAA) by using a magnetic stirrer obtains another dark brown homogeneous sol as solution B. For expediency, the $\text{In}_2\text{S}_3/\text{CuS}$ composites were designated as $\text{In}_2\text{S}_3/\text{CuS}$ -80, $\text{In}_2\text{S}_3/\text{CuS}$ -60, $\text{In}_2\text{S}_3/\text{CuS}$ -40 and $\text{In}_2\text{S}_3/\text{CuS}$ -20 corresponding to the (100-x) value of 80, 60, 40 and 20 respectively. The solution A was dropwise added into the solution B

using a magnetic stirrer followed by adding diluted HCl to fix the pH of solution at 3 and immediately transferred into a Teflon-lined stainless steel autoclave with 50 mL inner volume. And then the autoclave was maintained at 180°C for 24 h. After the autoclave was cooled to room temperature naturally, the obtained orange red precipitate was centrifuged and washed with ethanol and water several times. Finally, $\text{In}_2\text{S}_3/\text{CuS}$ composites powder was obtained followed by overnight drying at 60°C . The $\beta\text{-In}_2\text{S}_3$ and Cu_9S_5 were also prepared by a similar above-mentioned method using respective solution.

2.2. Characterization

The structure and crystallinity of the samples were investigated by X-ray diffraction (XRD) (PANalyticalX'pert) with Cu K α radiation operated at 40 kV/40 mA. Energy dispersive X-ray spectroscopy (EDXS) was recorded using a JEOLJSM-7800F microscopy equipped with EDAX detector. Tecnai G2 F30 electron microscopy was used with an accelerating voltage of 200 kV for observing Transmission electron microscopy (TEM). The X-ray photoelectron spectroscopy (XPS) measurements were performed using a Thermo ESCALAB250Xi X-ray photoelectron spectrometer and all of the binding energies were referenced to the C1s level at 284.6 eV. UV-Vis diffuse reflectance spectra (UV-Vis DRS) were recorded at room temperature on a Shimadzu UV-2600 spectrophotometer equipped with an integrating sphere using BaSO_4 as the reflectance standard. Photocurrent and electrochemical measurement was done with CHI 660D workstation by using Pt as a counter, saturated calomel electrode (SCE) as reference and $\beta\text{-In}_2\text{S}_3$, Cu_9S_5 and $\text{In}_2\text{S}_3/\text{CuS}$ composite modified fluorine doped tin oxide (FTO) glass substrates using doctor blade technique (film thickness: ca. $50 \mu\text{m}$) as working electrodes in the 0.6 M Na_2SO_3 as an electrolyte under visible light irradiation ($\lambda > 420 \text{ nm}$).

2.3. Photocatalytic performance evaluation

A home-made photoreactor (50 mL Pyrex flask) was used for the measurements of photocatalytic activity [23]. 2.5 mg of photocatalyst powder was suspended in an aqueous solution (50 mL) containing Na_2S (0.1 mol L^{-1}) and Na_2SO_3 (0.6 mol L^{-1}) followed by 30 min ultrasonication. After that, the reactor was evacuated with purging Ar for 30 min followed by flowing 3 M H_2S for 3 h at room temperature. After completing the above procedure, the reactor was illuminated by a 300-W Xe lamp with a cutoff filter ($\lambda > 420 \text{ nm}$). The amount of produced hydrogen was monitored at every one hour upto six hours study under photo-catalysis using a Shimadzu GC-2010 Plus gas chromatograph (Ar carrier gas, molecular sieve 5 Å, TCD detector).

The apparent quantum yield (AQY) was calculated according to Eq. (1). The number of evolved H_2 molecules was measured by GC (Shimadzu GC-2010 Plus) and the number of incident photons at 450 nm was determined from the output of a monochromatic LED lamp (89 mW/cm^2).

$$\text{QE}(\%) = \frac{\text{number of reacted electrons}}{\text{number of incident photons}} \times 100$$

$$= \frac{2 \times \text{number of evolved } \text{H}_2 \text{ molecules}}{\text{number of incident photons}} \times 100 \quad (1)$$

3. Results and discussion

3.1. Structure, composition and morphology study

The crystal structure of the as-synthesized samples was analyzed by powder XRD as shown in Fig. 1 and Fig. S1. In the absence of Cu (CH_3COO) $_2\text{H}_2\text{O}$, the obtained sample can be indexed into $\beta\text{-In}_2\text{S}_3$ (JCPDS 32-0456). The diffraction peaks at 27.58, 33.28, 43.79 and 47.93 corresponding to the (311), (400), (511) and (440) planes of $\beta\text{-}$

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