

## Template synthesis of $\text{ZnIn}_2\text{S}_4$ for enhanced photocatalytic $\text{H}_2$ evolution using triethanolamine as electron donor



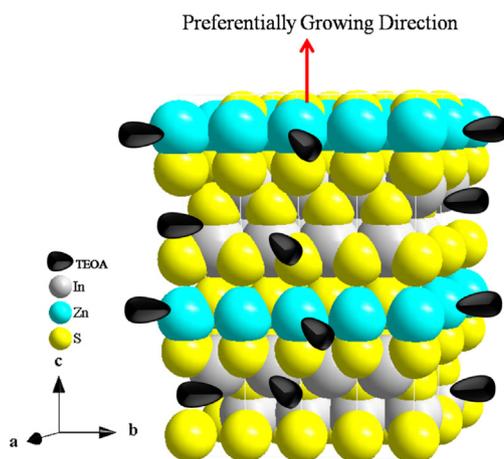
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### HIGHLIGHTS

- $\text{ZnIn}_2\text{S}_4$  photocatalyst was synthesized using triethanolamine (TEOA) as a template.
- TEOA improves growth of  $\text{ZnIn}_2\text{S}_4$  along c-axis and adsorption of TEOA on catalyst.
- Template-synthesized  $\text{ZnIn}_2\text{S}_4$  exhibits higher activity than that without TEOA.
- Reaction conditions on  $\text{H}_2$  evolution from TEOA solution are optimized.

### GRAPHICAL ABSTRACT



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### ABSTRACT

A series of ZIS-x [ZIS and x represent the  $\text{ZnIn}_2\text{S}_4$  and the addition amount of TEOA (mmol) in the synthesis process, respectively] were synthesized via a hydrothermal method using triethanolamine (TEOA) as a template. The as-synthesized photocatalysts were characterized by X-ray diffraction (XRD), energy dispersive X-ray spectroscopy (EDX), scanning electron microscopy (SEM), Ultraviolet-visible (UV-vis) diffuse reflection spectroscopy and Brunauer–Emmett–Teller (BET) surface area measurement. The effects of TEOA on the crystal structures, morphologies and optical properties of ZIS-x products were investigated. The photocatalytic activity was tested in the reaction of  $\text{H}_2$  evolution from aqueous TEOA solution under visible light irradiation ( $\lambda \geq 420$  nm). It was found that the activity of ZIS-x synthesized in TEOA solution was higher than that of ZIS-0 synthesized in pure water. This can be attributed to the facts that ZIS-x is composed of single  $\text{ZnIn}_2\text{S}_4$  and more TEOA can be adsorbed on ZIS-x surface, which improves the separation of an electron-hole pair. When TEOA was used as an electron donor, it can enhance notably photocatalytic  $\text{H}_2$  evolution with its simultaneous degradation. The effect of TEOA concentration on the  $\text{H}_2$  evolution rate is consistent with a Langmuir–Hinshelwood kinetic model. The optimal amount of Pt

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loaded on the photocatalyst is 0.50 wt%, and the optimal pH for photocatalytic H<sub>2</sub> evolution is 13. On the optimal condition, the rate of hydrogen evolution over ZIS-2.0 is 2 times as high as that of ZIS-0 during 20 h irradiation.

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## 1. Introduction

With the rapid development of modern industry and cities, the shortage of common fossil energy resource and water-pollution become more and more serious. Great efforts have been made to develop new energy resources and environmental cleaning technologies. Photocatalytic water splitting by solar light has been considered as one of the most promising routes for renewable hydrogen evolution [1–6].

The efficiency of photocatalytic hydrogen evolution from pure water is in general very low because of the recombination of photoinduced electrons and holes. In order to achieve higher efficiency for hydrogen evolution, most researches have involved electron donors as sacrificial agents, which can react irreversibly with the photoinduced holes. For practical application, the electron donor should be cheap and easy to obtain. One good way is to use organic pollutants in water as electron donors [7–11]. TEOA is an industrial product extensively used in cosmetics, polymers, paints and many other applications [12]. When present in ecosystem, it can cause considerable damage to animals and humans due to its carcinogenic nature and suspected endocrine disruptor qualities. Although TEOA could be removed by adsorbents [13–16], it is of more interest to combine photocatalytic hydrogen evolution with destruction of TEOA.

The energy of visible light in solar spectrum accounts for 45%. It is urgent to develop efficient visible-light-driven photocatalysts. ZnIn<sub>2</sub>S<sub>4</sub>, an important semiconducting material of ternary chalcogenides, has been extensively studied as a potential eco-friendly photocatalyst, because of its suitable band gap for visible light absorption and considerable chemical stability [17–20]. Lei et al. synthesized ZnIn<sub>2</sub>S<sub>4</sub> by a simple hydrothermal method and first treated ZnIn<sub>2</sub>S<sub>4</sub> as an efficient visible-light-driven photocatalyst for H<sub>2</sub> evolution [21]. Since then, many efforts have been made to develop a variety of ZnIn<sub>2</sub>S<sub>4</sub> photocatalysts with specific morphologies (i.e. nanotubes, nanoribbons, nanowires, and flower-like microspheres) as well as new preparative methods [22–25]. Shen et al. prepared ZnIn<sub>2</sub>S<sub>4</sub> with different morphology and crystallinity via a solvothermal/hydrothermal method and found that aqueous-mediated ZnIn<sub>2</sub>S<sub>4</sub> possessed the best crystallinity and exhibited the highest photocatalytic activity for H<sub>2</sub> evolution under visible light irradiation [26]. Moreover, they found the photocatalytic activity of ZnIn<sub>2</sub>S<sub>4</sub> could be further enhanced when it was prepared via a hydrothermal method in the presence of surfactant Cetyltrimethylammonium bromide (CTAB) [27]. Our group prepared ZnS–ZnIn<sub>2</sub>S<sub>4</sub> photocatalysts by a facile solvothermal process [22] and single ZnIn<sub>2</sub>S<sub>4</sub> by a NaCl-assisted method [28,29], and found that they exhibited good performance for the efficient H<sub>2</sub> evolution under visible light irradiation. Peng and co-workers synthesized a series of ZnIn<sub>2</sub>S<sub>4</sub> flower-like microspheres consisting of flakes via a facile template-free hydrothermal method. The as-prepared products showed a steady photoactivity for H<sub>2</sub> evolution [30].

For efficient photocatalytic hydrogen evolution with destruction of TEOA, the enhanced adsorption of the electron donor on ZnIn<sub>2</sub>S<sub>4</sub> is a key factor. In the present study, we synthesized a series of ZIS-x photocatalysts via a hydrothermal method using TEOA as a template. The effects of TEOA on the crystal structures,

morphologies and optical properties of ZIS-x products were investigated. The photocatalytic hydrogen evolution from aqueous TEOA solution over as-prepared samples under visible light irradiation ( $\lambda \geq 400$  nm) was studied in detail. We found that pollutant TEOA as both the synthesis template and electron donor in photocatalytic hydrogen evolution, can not only affect the performance of ZIS-x but also improve the adsorption of the electron donor on ZIS-x, which promotes the degradation of the pollutant and hydrogen evolution. To our knowledge, similar work has not been reported.

## 2. Experimental

### 2.1. Synthesis of ZnIn<sub>2</sub>S<sub>4</sub>

All chemicals are analytical grade and used as received without further purification. ZnIn<sub>2</sub>S<sub>4</sub> products were prepared via a hydrothermal method using TEOA as a template. In a typical process, different amounts of TEOA (1.5, 2.0 and 3.0 mmol), ZnSO<sub>4</sub>·7H<sub>2</sub>O (2.0 mmol), In<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>·6H<sub>2</sub>O (2.0 mmol) and excessive thioacetamide (TAA, 10.0 mmol) were dissolved in 40 mL distilled water in a 250 mL flask. The mixture was stirred at 80 °C for 3 h and then refluxed at 120 °C for 3 h. A yellow product was filtered and washed with distilled water, absolute ethanol for several times, and then dried in vacuum at 80 °C. The obtained ZnIn<sub>2</sub>S<sub>4</sub> was labeled as ZIS-x (x: amount of TEOA). ZnIn<sub>2</sub>S<sub>4</sub> was also prepared by the same procedure without TEOA, which was denoted as ZIS-0.

### 2.2. Characterization

X-ray diffraction studies were carried out using an XD-2/3 polycrystalline X-ray diffractometer with nickel-filtered Cu K<sub>α</sub> radiation as the X-ray source. UV–vis absorption spectra of the samples was determined on a Hitachi U-4100 spectrophotometer fitted with an integrating sphere diffuse reflectance accessory, using BaSO<sub>4</sub> as the reference (BaSO<sub>4</sub> has no absorption to the near ultraviolet and infrared spectra). Each sample was loaded into a powder holder to be sure that the sample thickness was about 1 mm. The scanning electron microscopy images were taken on a Quanta 200F field emission scanning electron microscope equipped with an energy dispersive spectrometer. The specific surface area of the samples were measured by N<sub>2</sub> adsorption at 77 K on DA-BET surface analyzer (JW-DA, China) and calculated by the Brunauer–Emmett–Teller (BET) method. All of the samples were degassed in vacuum at 150 °C over 3 h prior to BET measurements, and helium was used as carrier gas.

### 2.3. Photocatalytic reaction

The photocatalytic reaction was performed in a closed system (Pyrex cell, side irradiation). The top of the cell was sealed with a silicone rubber septum. Sampling was made intermittently through the septum. The light source was a 400 W high pressure mercury lamp equipped with a filter to cut off light of wavelength below 420 nm. 0.050 g of photocatalyst was dispersed in 100 mL aqueous solution, which contained 0.50 mol/L TEOA,  $1.27 \times 10^{-5}$  mol/L H<sub>2</sub>PtCl<sub>6</sub> (calculated Pt deposition amount: 0.50 wt%). The pH value of mixed solution was adjusted by using 0.1 mol/L sodium hydrox-

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