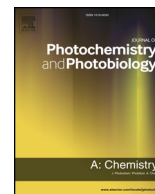




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# Facile synthesis of ternary CdIn<sub>2</sub>S<sub>4</sub>/In(OH)<sub>3</sub>/Zn<sub>2</sub>GeO<sub>4</sub> nanocomposite with enhanced visible-light photocatalytic H<sub>2</sub> evolution

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## ABSTRACT

A novel in situ hydrolysis reaction method has been developed for the controllable synthesis of ternary CdIn<sub>2</sub>S<sub>4</sub>/In(OH)<sub>3</sub>/Zn<sub>2</sub>GeO<sub>4</sub> nanocomposite. The CdIn<sub>2</sub>S<sub>4</sub> and In(OH)<sub>3</sub> content in the ternary system can be conveniently tuned by varying the pH value of the reaction system. The ternary CdIn<sub>2</sub>S<sub>4</sub>/In(OH)<sub>3</sub>/Zn<sub>2</sub>GeO<sub>4</sub> (pH = 6.5) nanocomposite sample exhibited the highest photocatalytic H<sub>2</sub> production rate of 1426.90 μmol h<sup>-1</sup> g<sup>-1</sup>, without the assistance of a noble metal. A possible mechanism of H<sub>2</sub>-production activity was proposed. The photo-generated electrons in the CB of CdIn<sub>2</sub>S<sub>4</sub> can transfer to the CB of In(OH)<sub>3</sub> and Zn<sub>2</sub>GeO<sub>4</sub>, resulting in a rapid separation of photo-generated electrons and holes. This work can not only provide an excellent candidate for visible-light H<sub>2</sub> evolution, but also provide an efficient strategy for designing of new system with high activity for solar hydrogen generation.

## 1. Introduction

Photocatalytic water splitting is a promising technology for the utilization of solar energy in the production of renewable hydrogen [1–6]. To date, numerous active photocatalysts have been extensively applied in photocatalytic processes [7–12]. However, most of these photocatalysts are active toward UV-light and the hydrogen generation efficiency of these developed photocatalysts is still low for practical applications [13–16]. Therefore, it is imperative to develop highly active, low cost and stable photocatalysts driven by sunlight.

Cadmium indium sulfide (CdIn<sub>2</sub>S<sub>4</sub>), which has a suitable narrow band gap (2.0–2.4 eV), has received great interest for photocatalytic H<sub>2</sub> production [17–19]. However, CdIn<sub>2</sub>S<sub>4</sub> suffers from severe photo-corrosion and fast recombination of photo-generated charge carriers under visible light. Therefore, it is still a challenge to develop a new modification method that can enhance the photocatalytic activity of CdIn<sub>2</sub>S<sub>4</sub>. Recently, composite photocatalysts with three or more components for improving the separation efficiency of photo-generated charge carriers have attracted extensive scientific interest [20–25]. The construction of ternary or multi-component nanocomposites may induce multistep charge transfer and further promote the charge separation more efficiently, thus lead to better photocatalytic performance than the binary ones [26–30]. Therefore, designing CdIn<sub>2</sub>S<sub>4</sub>-

based ternary or multi-component nanocomposites by choosing appropriate constituents is a powerful strategy to further optimize the photocatalytic activity of CdIn<sub>2</sub>S<sub>4</sub>.

However, the construction of ternary or multi-component nanocomposites is usually accompanied by increasing cost and a more complicated multi-step synthesis route [31–35]. Consequently, it is urgently necessary to develop a facile and effective method to synthesize CdIn<sub>2</sub>S<sub>4</sub>-based ternary or multi-component nanocomposites with enhanced photocatalytic performance.

In this study, we demonstrate a novel in situ hydrolysis reaction method to prepare ternary CdIn<sub>2</sub>S<sub>4</sub>/In(OH)<sub>3</sub>/Zn<sub>2</sub>GeO<sub>4</sub> nanocomposite. During the process of preparing CdIn<sub>2</sub>S<sub>4</sub>/Zn<sub>2</sub>GeO<sub>4</sub> nanocomposite, indium ions can hydrolyze into In(OH)<sub>3</sub> when the pH value of the reaction system was high enough. So it is convenient to obtain CdIn<sub>2</sub>S<sub>4</sub>/In(OH)<sub>3</sub>/Zn<sub>2</sub>GeO<sub>4</sub> nanocomposite by a simple hydrothermal strategy by adjusting the pH value of the reaction solution. The CdIn<sub>2</sub>S<sub>4</sub> and In(OH)<sub>3</sub> content in the ternary system can be conveniently tuned by varying the pH value. The ternary nanocomposite of CdIn<sub>2</sub>S<sub>4</sub>/In(OH)<sub>3</sub>/Zn<sub>2</sub>GeO<sub>4</sub> exhibited enhanced photocatalytic H<sub>2</sub> evolution activity as compared to all the related pure samples and binary composite photocatalysts. Further research results indicate that the high efficiency of photocatalytic H<sub>2</sub> production of the nanocomposite should be ascribed to the positive synergistic effect of CdIn<sub>2</sub>S<sub>4</sub>, In(OH)<sub>3</sub> and Zn<sub>2</sub>GeO<sub>4</sub> for

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the improvement in harvesting capacity of visible light, charge carrier separation and transfer properties. This work can not only provide a green and simple way to enhance the solar photocatalytic H<sub>2</sub>-production activity of CdIn<sub>2</sub>S<sub>4</sub> under the notable synergetic effect of Zn<sub>2</sub>GeO<sub>4</sub> and In(OH)<sub>3</sub>, but also provide an efficient strategy for designing of new system with high activity for solar hydrogen generation.

## 2. Experimental

### 2.1. Preparation of Zn<sub>2</sub>GeO<sub>4</sub> and In(OH)<sub>3</sub>

All chemicals were analytical grade and used without further purification. The preparation of Zn<sub>2</sub>GeO<sub>4</sub> is as follows. 0.10 g sodium dodecyl sulfate (SDS) was dissolved into deionized water under stirring. Then, 1.1 g Zn(CH<sub>3</sub>COO)<sub>2</sub>·2H<sub>2</sub>O and 0.27 g GeO<sub>2</sub> were added into the above solution in turn. The pH value of the solution was adjusted to 6.5. The mixture was stirred at room temperature for 1 h, followed by transferring the mixture into a 100 ml Teflon-lined autoclave, sealed and maintained at 453 K for 12 h. After cooling to room temperature, the resulted solid was collected by centrifugation and washed several times with deionized water and ethanol. The solid was dried in an oven at 353 K for 5 h.

The preparation of In(OH)<sub>3</sub> is as follows: 0.782 g In(NO<sub>3</sub>)<sub>3</sub>·4.5H<sub>2</sub>O was dissolved in deionized water. The pH value of the solution was adjusted to 6.5. The mixed solution was then transferred into a 100 ml Teflon-lined autoclave and heated at 433 K for 12 h. The remaining steps are the same as Zn<sub>2</sub>GeO<sub>4</sub>.

### 2.2. Preparation of CdIn<sub>2</sub>S<sub>4</sub> and CdIn<sub>2</sub>S<sub>4</sub>/Zn<sub>2</sub>GeO<sub>4</sub>

In a typical procedure, Cd(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (2 mmol), In(NO<sub>3</sub>)<sub>3</sub>·4H<sub>2</sub>O (4 mmol) were added by stoichiometric ratio, double excess of thioacetamide (TAA) were dissolved in deionized water. The pH value of the solution was adjusted to 4.5. After further stirring for 30 min, the mixed solution was transferred into a 100 ml Teflon-lined autoclave. The autoclave was sealed and maintained at 433 K for 12 h and cooled to room temperature naturally. The product was collected by centrifugation, then filtered and washed with deionized water and ethanol for several times. The final product was obtained after drying in an oven at 353 K for 5 h.

The preparation of CdIn<sub>2</sub>S<sub>4</sub>/Zn<sub>2</sub>GeO<sub>4</sub> is as follows: Cd(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (2 mmol), In(NO<sub>3</sub>)<sub>3</sub>·4H<sub>2</sub>O (4 mmol) were added by stoichiometric ratio, double excess of thioacetamide (TAA) were dissolved in deionized water. Afterwards, the pH value of the suspension was adjusted to 4.5. Then the as-prepared Zn<sub>2</sub>GeO<sub>4</sub> (0.3 g) was added into the above solution. After stirring for 30 min, the mixed suspension was transferred into a 100 ml Teflon-lined autoclave. The autoclave was sealed and maintained at 433 K for 12 h and then cooled to room temperature naturally. The product was collected by centrifugation, then filtered and washed with deionized water and ethanol for several times. The final product was obtained after drying in an oven at 353 K for 5 h.

### 2.3. Preparation of CdIn<sub>2</sub>S<sub>4</sub>/In(OH)<sub>3</sub> and CdIn<sub>2</sub>S<sub>4</sub>/In(OH)<sub>3</sub>/Zn<sub>2</sub>GeO<sub>4</sub> (CIZ)

The synthesis of CdIn<sub>2</sub>S<sub>4</sub>/In(OH)<sub>3</sub> is similar to that of CdIn<sub>2</sub>S<sub>4</sub>. All of the experimental conditions are same except the pH value of the solution was adjusted to 6.5. The synthesis of CdIn<sub>2</sub>S<sub>4</sub>/In(OH)<sub>3</sub>/Zn<sub>2</sub>GeO<sub>4</sub> is similar to that of CdIn<sub>2</sub>S<sub>4</sub>/Zn<sub>2</sub>GeO<sub>4</sub>. All of the experimental conditions are same except the pH value of the suspension was adjusted to 6.0, 6.5, 7.0, respectively. The composite samples prepared at pH value equal to 6.0, 6.5, 7.0 are denoted as CIZ-6.0, CIZ-6.5 and CIZ-7.0, respectively.

### 2.4. Characterization

The crystal phases of the as-prepared samples were measured by X-

ray diffraction (XRD, Bruker D8 Advance X-ray diffractometer) with Cu K $\alpha$  radiation at 40 kV and 40 mA. Emission scanning electron microscopy (FESEM, Hitachi S-4800) and transmission electronic micrograph (TEM, Hitachi, H-7650) were used to detect the morphology of the samples. The HRTEM was conducted on a JEM-2100 electron microscope, operated at an acceleration voltage of 200 kV. The Brunauer–Emmett–Teller (BET) specific surface areas ( $S_{\text{BET}}$ ) of the samples were measured by a by nitrogen adsorption using a Quantachrome NOVA 4000e nitrogen adsorption apparatus. X-ray photoelectron spectroscopy (XPS) measurements were performed in a VG-ESCALAB250 electronic spectrometer using an Al K $\alpha$  excitation source ( $h\nu = 1486.6$  eV). The position of the C1 s peak was taken as a standard (with a banding energy of 284.6 eV). The UV–vis diffuse reflectance spectra of samples were detected on a UV–vis spectrophotometer (U-3010, Hitachi, Japan). The fluorescence spectra of the samples were measured using the Hitachi F-4600 fluorescence spectrophotometer.

### 2.5. Photocatalytic hydrogen production

The photocatalytic H<sub>2</sub> production experiments were performed in a 100 ml Pyrex flask at ambient temperature and atmosphere pressure. A 300 W Xe lamp (PLS-SXE300C, Beijing Perfectlight Co. Ltd., China) containing a UV-cut off filter ( $\lambda \geq 420$  nm) was used as a light source. In a typical photocatalytic experiment, 0.05 g of photocatalyst powder was suspended in aqueous solution containing 0.25 M Na<sub>2</sub>SO<sub>3</sub> and 0.35 M Na<sub>2</sub>S as sacrificial reagents. Before visible light irradiation, suspensions of the photocatalyst were dispersed by an ultrasonic bath and were bubbled using nitrogen for 30 min to remove the oxygen and to obtain the anaerobic conditions in the reaction system. The produced H<sub>2</sub> was detected using an online gas chromatography (GC7900, N<sub>2</sub> carrier, 5 Å molecular sieve column, TCD detector). The reaction was continued for 3 h.

The apparent quantum efficiency (QE) was measured by the analogical photocatalytic reaction condition, but the light source was changed into high power LED (420 nm, PLS-LED100B, Beijing Perfectlight Co. Ltd., China). The QE was evaluated by the following equation: The QE for H<sub>2</sub> evolution was calculated according to the following equation:

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

$$= \frac{2 \times \text{number of evolved } H_2 \text{ molecules}}{\text{number of incident photons}} \times 100\%$$

### 2.6. Photoelectrochemical measurements

For the photoelectrochemical measurements, the working electrode with an active area of 1 × 1 cm<sup>2</sup> was prepared by doctor blading of a slurry containing sample and Iso Propyl alcohol onto the surface of FTO conductive glass and then dried in an oven at 333 K for 12 h. A 300 W Xe lamp was used as light source. Photocurrent measurements were performed on an electrochemical workstation (CHI660E, ShangHai) in a three-electrode quartz cell with a 0.5 M Na<sub>2</sub>SO<sub>4</sub> electrolyte solution, using the fabricated sample electrode as the working electrode, Pt wire and Ag/AgCl (saturated 0.3 M KCl) were used as counter electrode and reference electrode, respectively. The electrochemical impedance spectra (EIS) of the above-mentioned working electrodes in the three-electrode system were also recorded via a computer controlled over a frequency range of 0.01–10<sup>5</sup> Hz with an AC amplitude of 5 mV under visible light illumination. 0.5 M Na<sub>2</sub>SO<sub>4</sub> aqueous solutions were used as the electrolyte.

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