

Short communication

Visible light photocatalytic H₂-production activity of epitaxial Cu₂ZnSnS₄/ZnS heterojunction



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ABSTRACT

Novel visible light driven photocatalyst Cu₂ZnSnS₄/ZnS composites were prepared by two-step hydrothermal method. The two semiconductors in the composites are lattice-matched and form close contact between them. With 0.1% Cu₂ZnSnS₄ grew on ZnS surface, the composite exhibits a high and stable visible light photocatalytic H₂ generation of 432 μmol g⁻¹ h⁻¹. This excellent visible light activity could be attributed to the enhancement of visible light absorption by surficial modification of ZnS with CZTS and the photoinduced interfacial charge transfer from the valence band of ZnS to Cu₂ZnSnS₄ in the close contact interface.

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1. Introduction

As a potential answer to the global energy crisis and environmental pollution, hydrogen production from renewable energy sources has attracted great attention. Photocatalytic water-splitting has been considered as one of the most ideal approaches for clean, economical, environmentally friendly production of hydrogen. Hundreds of active photocatalysts for splitting water have been reported in the past four decades [1–3]. However, most of these photocatalysts can solely absorb the UV light, which accounts for only 4% of the total sunlight, and thus greatly restricts their practical applications [4,5]. The efficiency of solar hydrogen production can be improved by enhancing visible light absorption and photogenerated charge transfer [6–8].

Metal sulfides have been intensively studied in photocatalysis because of their suitable bandgap and catalytic functions [9–12]. The well-known II–VI group transition metal sulfides ZnS has the highly negative reduction potentials of excited electrons under irradiation. However, it only responds to UV light due to its wide band gap (3.6–3.8 eV). Many methods have been applied to improve the visible light driven H₂ evolution activity, such as doping transition-metal ions (i.e., Cu²⁺, Ni²⁺, and Pb²⁺) [13–15], decorating plasmonic nanoparticles on surface [16,17], composting suitable narrow bandgap semiconductors [18,19]. Developing low-toxic and cost-effective ZnS-based photocatalysts with high visible light driven H₂ production activities is still a challenge.

Recently, kesterite Cu₂ZnSnS₄ (CZTS) has been studied widely as a most valuable absorber candidate for low cost solar cell, which has a direct band gap energy of (1.0–1.5 eV) and high absorption coefficient [20, 21]. As an environmental friendly and earth-abundant material, CZTS has great potential applications in photodegradation of pollutions and photocatalytic production of hydrogen and other value-added chemical [22,23].

In this work, we reported the fabrication of CZTS-ZnS composites by two step hydrothermal method for the first time. Their highly visible light-driven photocatalytic H₂-production activity were evaluated in aqueous solutions containing Na₂S and Na₂SO₃ without Pt cocatalyst. The origin for their visible light induced response and enhanced visible light H₂-production activity were explained by the photoinduced interfacial charge transfer (IFCT) from the valence band of ZnS to Cu₂ZnSnS₄. In the photoinduced IFCT process, the closed contact between the two lattice-matched materials CZTS and ZnS surface is considered to play the critical role.

2. Experimental

2.1. Prepare of photocatalysts

2.1.1. Preparation of ZnS

All reagents are of analytical purity and used without further purification. ZnS is prepared by hydrothermal method. 10 mmol Zn(AC)₂ and 50 mmol thiourea were dissolved in 70 mL of H₂O under vigorous stirring. After 30 min, the mixture was transferred into 100 mL Teflon-lined stainless steel autoclave and maintained at 170 °C for 5 h. After cooling,

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the products were sequentially washed with distilled water and absolute ethanol several times and then dried under vacuum.

2.1.2. Preparation of $\text{Cu}_2\text{ZnSnS}_4/\text{ZnS}$

3 mmol of the as-prepared ZnS was dispersed into 60 mL of ethylene glycol, then CuCl_2 , ZnCl_2 , SnCl_2 , and TAA were added according to the stoichiometric ratio and loading amount of CZTS. The mixture was poured into autoclaves (100 mL) and kept at 180 °C for 15 h. After cooling, the product was filtered and washed with absolute ethanol and deionized water for several times, and dried under 60 °C. Five samples with different CZTS loading (0%, 0.05%, 0.1%, 1% and 10%) were prepared and recorded as n% CZTS-ZnS, where n = precursor molar ratios. CZTS was synthesized by the same method without ZnS.

2.2. Characterization

The XRD was measured on a Bruker D8 Advance X-ray diffractometer. SEM images were obtained on a Nova NanoSEM 230 microscopy (FEI Corp). TEM images were using TEM-JEOL JEM 2010F microscope. UV-vis diffuse reflection spectra were tested on a Varian Cary 500 Scan UV-vis-NIR spectrophotometer. STEM-mapping was conducted on FEI Tecnai F20. XPS measurements were carried on an ESCALAB 250 photoelectron spectroscopy system. The Brunauer–Emmett–Teller (BET) specific surface area were measured by ASAP2020M. Photocurrents were measured on an electrochemical analyzer (Zahner, Germany). The working electrode was made by dip-coating catalyst slurry (10 mg mL^{-1} in EtOH) on FTO glass, and followed by air-drying. 0.2 M Na_2SO_4 was used as electrolyte.

2.3. Photocatalytic reactions

Photocatalytic H_2 production performances were evaluated with a gas-closed circulated system accompanied with a top-irradiation Pyrex cell. 300-W Xe lamp (CHF-XM300) with cut-off filter ($\lambda \geq 420 \text{ nm}$) was used as visible light source. 0.05 g photocatalyst was added to 100 mL aqueous solution containing 0.1 M Na_2S and 0.1 M Na_2SO_3 as sacrificial reagents. The amount of H_2 was detected every 2 h by an on-line gas chromatograph (GC-8A). The incident light intensity of visible light was tested using Spectroradiometer ILT950. The total number of incident photons was tested by calibrated silicon

photodiode. The apparent quantum yield (AQY) was calculated according to the following equations:

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

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

3. Result and discussion

3.1. XRD

Fig. 1 shows the XRD patterns of the as-prepared catalysts. The ZnS sample shows three characteristic peaks located at 29.0°, 48.3° and 57.4°, which are indexed to the (111), (220) and (311) diffraction planes of ZnS, respectively (JCPDS 79-0043), consistent with the previous report [24]. The CZTS shows three peaks located at 28.5°, 47.3° and 56.1° which are indexed to the (112), (220) and (312) diffraction planes of CZTS, respectively (JCPDS 26-0575). Interestingly, the XRD peaks of ZnS are very close to that of CZTS, indicating their crystal structures are almost the same, just as shown in Fig. 1b (lattice parameters: for ZnS, $a = b = c = 5.41 \text{ \AA}$; for CZTS, $a = b = 5.43 \text{ \AA}$, $c = 10.85 \text{ \AA}$). It suggests that nearly defect-free interfaces can be formed using the two lattice-matched semiconductors, which could greatly enhance charge separation in photocatalytic reaction. As expected, all the CZTS-ZnS composites exhibit almost the same XRD peaks as ZnS and CZTS.

3.2. Morphology and microstructure

The morphologies of the as-synthesized samples were characterized by SEM. As shown in Fig. S1a, spheres with size of about several micrometers are observed for the ZnS sample. For the 0.1% CZTS/ZnS composite, the monodisperse ZnS spheres exhibit no obvious change, except that many tiny CZTS nanosheets uniformly inlaid into the spherical surface (Fig. 2a), suggesting the strong adhesion between the CZTS and the ZnS [25]. When the CZTS loading content is up to 1%, the ZnS spheres are overgrown with the tiny CZTS nanosheets, and thus many small aggregates of CZTS appear without attaching to the ZnS spheres (Fig. S1c). Further increasing the CZTS to 10%, there are more aggregates of CZTS presented to encapsulate the ZnS spheres (Fig. S1d) [26].

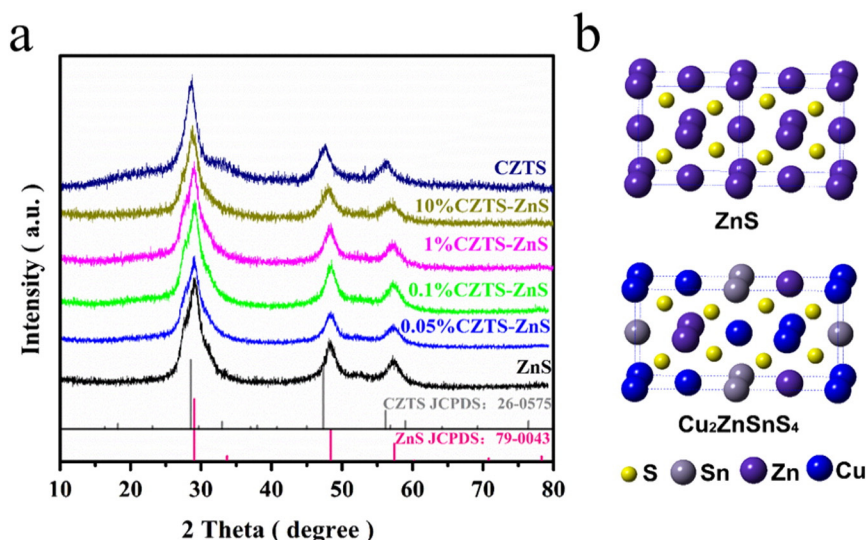


Fig. 1. (a) XRD patterns of ZnS, CZTS and CZTS-ZnS samples with different molar ratios; (b) the crystal structures of ZnS and CZTS.

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