Co-catalyst-free ZnS-SnS2 porous nanosheets for clean and recyclable photocatalytic H2 generation

Lijing Wang a, Gan Jin b, Yanhong Shi a, Hao Zhang b, Haiming Xie a, Bai Yang b, **, Haizhu Sun a, *

a College of Chemistry, National Local United Engineering Laboratory for Power Batteries, Northeast Normal University, Changchun 130024, People's Republic of China
b State Key Laboratory of Supramolecular Structure and Materials, College of Chemistry, Jilin University, Changchun 130012, People's Republic of China

Abstract

Two-dimensional (2D) ZnS-SnS2 porous nanosheets are designed as clean and low cost photocatalysts for water splitting. The composites successfully combine high photoelectron reduction potential of ZnS with the sufficient sunlight harvesting ability of SnS2. Moreover, SnS2 acts as an effective electron transfer medium from ZnS to SnS2 due to the construction of quasi-type II structure. This greatly promotes the transfer of electron-hole pairs and effectively inhibits their recombination. Especially, the unique porous nanosheets structure maintains them high specific surface area and countless reactive sites, which increases the reactants' contact area and facilitates the migration of carriers upon photocatalysis. This further suppresses the charge recombination and improves the photocatalysts' stability. As a result, an optimized specific surface area of 246.7 m2 g−1 and photocatalytic H2 generation rate of 536 μmol h−1 g−1 are achieved in the absence of a surfactant and co-catalyst, which is 10 times higher than ZnS and 17 times higher than SnS2. In addition, the porous nanosheets have fairly good photocatalytic stability and can be reused at least five cycles without obvious changes in activity and structure. This work successfully presents the potential of ZnS and SnS2-based photocatalyst for clean and low cost hydrogen production from water splitting.

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1. Introduction

As a useful strategy to address the ever-increasing global energy crisis, photocatalytic water splitting shows great potential for clean, low cost, and environmental-friendly hydrogen generation [1–9]. Meanwhile, tin disulfide (SnS2) has attracted much attention in photocatalysis because of its suitable band gap of 2.18–2.44 eV, which bring it an outstanding visible light sensibility. Moreover, its advantages of low toxicity, natural abundance, and favorable stability make it a promising photocatalyst [10–14]. However, current studies on SnS2 are mainly focused on the photodegradation of organic dyes or reduction of toxic ions, owing to its low conduction band potential. Only few literatures exist regarding water splitting by employing SnS2 as a catalyst, which always involve in the usage of either a surfactant or co-catalyst [15–18]. For example, Yan et al. designed Te/SnS2/Ag artificial nanoleaves as a photocatalyst for water spitting by using polyvinylpyrrolidone (PVP) as the surfactant [15]. In addition, Pt co-catalyst was used when evaluating the photocatalytic performance of SnS2 in order to increase the reaction active sites and suppress the charge recombination as well as reverse reactions [16]. The presence of surfactant and co-catalyst partially compensates for the low photocatalytic activity caused by its inherent band defect [19,20]. However, the high cost of noble metals co-catalysts and the complicated multiple wash process required for surfactant are not desirable for practical applications. Whereas other reports about SnS2-based catalyst without the assist of co-catalyst or surfactant always suffer from low crystallinity and efficiency [18]. Hence, it is still a challenge to prepare well-crystallized, cost-effective and highly active SnS2-based photocatalysts for H2 generation without co-catalyst or surfactant.

Semiconductor coupling is another effective way to overcome the inherent weak negative reduction potential of SnS2 [21,22]. As one of the first discovered semiconductors, zinc sulfide (ZnS) has numerous benefits, such as nontoxicity, low cost, high photoexcited...
electrons reduction potential, and rapid generation of carriers under light irradiation [23–25]. However, the photocatalytic activity of ZnS is limited by the large band gap and fast recombination of electron-hole pairs. Therefore, ZnS can be combined with SnS2 to form semiconductor heterojunction. This will compensate for their respective deficiencies in band gap structures, and hence improve the photocatalytic activity and stability by promoting the effective separation and transfer of charge carriers. In addition, the construction of porous structure is an effective approach to improve the photocatalytic activity by offering high porosity and specific surface area [26], which is comparable to the use of co-catalyst and surfactant in improving the number of active sites and charge transfer ability [27]. However, as far as we know, there is no report about the synthesis of ZnS-SnS2 porous nanosheets, let alone the application in water splitting for hydrogen production.

Herein, for the first time, well-crystallized, cost-effective ZnS-SnS2 porous nanosheets are successfully prepared following a simple two-step method. By changing the Sn/Zn molar ratio x, a series of samples are designed and labeled as ZTSx (x = 0, 0.05, 0.2 and 0.5), respectively. A significant improvement of photocatalytic H2 activity is achieved by the ZTS-0.2 porous nanosheets than ZnS and SnS2. In addition, the possible mechanism for the improved photocatalytic activity is also put forward.

2. Experimental details

2.1. Materials

Zinc chloride (ZnCl2), anhydrous sodium sulfate (Na2SO4), anhydrous sodium sulfate (Na2SO4), methanol, glycerol, lactic acid, triethanolamine and thiauene were from Beijing Chemical Factory. Ethylenediamine (en) and tin chloride pentahydrate (SnCl4·5H2O) were from Aladdin. Sodium sulfide nonahydrate (Na2S·9H2O>98%) was from Xilong Chemical Co., Ltd.

2.2. Synthesis of ZnS(en)0.5

ZnS(en)0.5 nanosheets were synthesized according to the method described in previous literature [28]. First, 272.6 mg ZnCl2 and 304 mg thiourea were gradually added into 60 mL ethylenediamine, followed by constant stirring for 30 min. The mixture was then transferred to a Teflon-lined autoclave, sealed well, and reacted at 180 °C for 18 h. After gradually cooling to room temperature, the white precipitate was washed with deionized water and absolute ethyl alcohol several times and dried at 60 °C for 12 h.

2.3. Synthesis of ZnS-SnS2

ZnS-SnS2 porous nanosheets were obtained using ZnS(en)0.5, SnCl4·5H2O and Na2S·9H2O as precursors according to the preparation of CuS/ZnS nanosheets. First, 1 mmol of ZnS(en)0.5 nanosheets were dispersed in water with ultrasound for at least 10 min, followed by the quick addition of different amount of SnCl4·5H2O. The obtained ZnS-SnS2 porous nanosheets were set as ZTSx (x = 0, 0.05, 0.2, 0.5) according to the Sn/Zn feed ratio. During the hydrothermal process, porous ZnS nanosheets were formed by the decomposition of en ligands on ZnS(en)0.5. Due to the excess amount of free Sn4+, ZnS was partly transformed into SnS2, and then certain amount of Na2S·9H2O (0.1, 0.2, 0.8, 2 mmol) was added to assist the sufficient growth of SnS2 and the introduction of Zn vacancy (VZn) on the surface of ZnS. Meanwhile, with the addition of SnCl4·5H2O, the white mixture gradually changed to yellow, and became a deeper yellow with the increase in SnCl4·5H2O content. After constant stirring for at least 30 min, the above products were moved into autoclaves and stayed at 150 °C for 24 h. Finally, the precipitate was cooled and washed with deionized water and absolute ethyl alcohol for three times, respectively, then dried at 60 °C for 12 h. SnS2 was prepared with the same procedure in the absence of ZnS(en)0.5 nanosheets.

2.4. Characterization

XRD was operated by a Shimadzu XRD-6000 diffraction system with high-intensity Cu Ka radiation. SEM and EDS images were characterized on a Hitachi S–4800 at the voltage of 5.0 kV. TEM and EDS images were equipped with a JEOL 2010 at an accelerating voltage of 200 kV. XPS was drawn by a VG ESCALAB MKII spectrometer to study the valence states of the existence elements. UPS experiment was performed using a VG Scienta R3000 analyzer in ultrahigh vacuum with a base pressure of 1 × 10–10 mbar. A monochromatized He Ia irradiation from a discharged lamp supplies photons with 21.22 eV. UV–vis absorption spectra were studied using a Shimadzu UV–3600 spectrophotometer. PL spectra and fluorescence decay curves of the catalyst powder were done with RF–5301PC and FL3890 instruments, respectively. BET was examined using an autosorb-IQ instrument (TriStar III3020) of America. Electron spin resonance (ESR) signals were obtained from JEOL JES-FA200 X-band spectrometer.

3. Results and discussion

3.1. The structure and morphology of ZTSx

From Scheme 1, ZnS(en)0.5 nanosheets are firstly prepared through a solvothermal method by using ZnCl2 and thiourea as low toxic reactants. Then, porous ZnS nanosheets are formed by the decomposition of en ligands of ZnS(en)0.5. The pores are beneficial to enhance the reactive sites during the photocatalysis. The ZTSx porous nanosheets are eventually obtained by in situ growth of SnS2 on the surface of porous ZnS nanosheets. The content of Sn can be easily tuned by changing the amount of SnCl4·5H2O. Therefore, the properties of the resulted ZTSx porous nanosheets photocatalyst such as the specific surface area, photoabsorption, as well as the carrier separation and transfer ability can be easily controlled. The composition of ZTSx porous nanosheets with increasing Sn feed ratio examined by electronic differential system (EDS) are listed in Table S1, from which increased Sn content (from 0 to 16.8%) and decreased Zn content (from 48.5 to 22.6%) can be observed, indicating that part of ZnS may be exchanged to SnS2.

The morphologies of ZnS(en)0.5 and ZTS-0.2 are characterized by using scanning electron microscope (SEM) and transmission electron microscope (TEM) images in Fig. 1. They have 2D nanosheets structures with the size of about 600 nm. Meanwhile, ZTS-0.2 appears with rougher surface compared to ZnS(en)0.5 nanosheets due to the growth of SnS2. TEM images further confirm the rough surface of ZTS-0.2 with numerous small pores, which is attributed to the decomposition of ZnS(en)0.5, while the lattice spacing of 0.31 nm is corresponding to the (002) plane of the hexagonal ZnS, while the lattice spacing of 0.27 nm is assigned to the (200) plane of wurtzite ZnS, which is in keep with the XRD result in Fig. S1 (a detail discussion is offered in supporting information). Furthermore, several small clusters with poor crystallization are homogenously dispersed on the surface of ZnS nanosheets (marked by red circle in Fig. 1d), one of the lattice spacing of 0.25 nm corresponds to (103) plane of SnS2, which is consistent with the results from the EDS and XPS spectra in Fig. S2 (a detail description is given in supporting information). Mapping pictures (Fig. 1e) of ZTS-0.2 porous nanosheets further reveal that Zn, Sn and S elements are homogenously distributed in the whole

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