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Research Paper

Zinc vacancy-promoted photocatalytic activity and photostability of ZnS for efficient visible-light-driven hydrogen evolution

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ABSTRACT

Zinc sulfide is a superior photocatalyst for H_2 evolution, whereas the wide bandgap restricts its performance to only UV region. In this work, zinc vacancy (V_{Zn}) defects are successfully introduced into ZnS *via* adding sodium sulfide as sulfur source during the hydrothermal reaction. The defective ZnS with different amount of zinc vacancies were employed as catalysts for the examination of vacancy-dependent catalytic activity toward photocatalytic hydrogen evolution under visible light irradiation. Fluorescence emission spectra and XPS results confirm that existence of abundant zinc vacancies on ZnS. These zinc vacancies exhibit remarkable effects on modifying the electronic structure of ZnS as shown in UV–visible absorption spectra and Mott–Schottky plots. Zinc vacancies can raise valence band (VB) position that weaken the oxidative capacity of the holes to protect Zn-deficient ZnS from photocorrsion. And electrochemical and photo-electrochemical experiments also demonstrate that the charge separation and the electrons transfer are more efficient with the introduction of the Zn vacancies in ZnS. The zinc-deficient ZnS-2.5 with optimum amount of Zn vacancies shows superior photocatalytic activity for H_2 evolution that reaches 337.71 ± 3.72 μmol h^{-1} g^{-1} under visible-light irradiation and also exhibits a much higher photostability. The intrinsic modify by self-defects might be a potential strategy for design novel photocatalysts with photocorrosion stability and visible-light activity in photocatalysis proton reduction.

1. Introduction

Photocatalytic hydrogen evolution from water splitting using semiconductor materials for solar conversion has been considered as a desirable approach with clean, environmentally friendly and economical process [1–3]. In the past few decades, numerous efforts have been taken to develop suitable semiconductor photocatalysts to obtained high activities for water splitting [3–7]. However, major limitations to achieve high photocatalytic efficiency using solar energy are restricted by the light absorption and the fast recombination of electron-hole pairs [8]. Common semiconductors, such as TiO_2 and ZnO, mainly absorb UV light, which means they use only about 4% of the solar spectrum [9]. And there is still not finding an ideal photocatalyst for practical use with relatively high productivity under visible light. Therefore, it is important to develop a robust photocatalyst that can efficiently utilize visible light for hydrogen production.

ZnS is a promising n-type semiconductor for photocatalytic hydrogen production due to its rapidly generates photoexcitated electron-hole pairs, and high activity under UV light [10,11]. Unfortunately, the photocatalytic performance of pristine ZnS is restricted by its wide band gap (3.6–3.8 eV), which means that ZnS is only active under UV light and not respond to visible light [9]. Therefore, several attempts have been made to extend the light absorption of ZnS into the visible region for photocatalytic H_2 evolution, such as doping [12–19], coupling with metals sulfide [20,21], structure engineering [22], hybridization [23,24] and so on. For example, it is reported that introducing extrinsic metal elements (Cu , Ni, Cd,…) or nonmetal elements (C, N) to ZnS for enhancing the visible light photocatalysis [13–21]. However, compared with these efforts, the intrinsic modification of ZnS by self-defects for visible-light photocatalystic H_2 evolution are rarely reported.

As is known, the intrinsic nature of materials, such as defect states, crystalline phases, exposed facets, etc., of semiconductor photocatalysts are crucial factors for superior photocatalytic activities, which can regulate the light absorption behavior for robust charge generation, dominate the kinetics of charge transfer for effective charge separation, and organize active sites or facets for charge utilization[22]. Thus, it is of significance to understand the effect of intrinsic properties on ZnS to enhance its visible light photocatalysis. Among these nature of materials, defect engineering is an appealing strategy for enhancing light harvesting in photocatalytic materials [25]. Defects in semiconductor

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photocatalysts not only can introduce new energy levels to narrow the band gap that produce visible-light activity, but also can serve as adsorption sites where the charge transfer and prevent the recombination of photogenerated charge carriers. It is worth noting that controlling the amount of defects is great important to photocatalytic reaction, because excessive amount defects can act as recombination centers for charge carriers and hence decreasing the photocatalytic activity. Vacancy defects can play an important role in modifying the electronic structure and the properties of photoexcited charge carriers by introducing additional energy levels and consequently enhanced the photocatalytic activity of photocatalyst. For example, oxygen vacancies are one of kind of intrinsic defects in crystals, which have been found to play a crucial role in TiO_2 [26,27], ZnO [28,29], Fe_2O_3 [30], BiOCl [31] photocatalysts for improving visible-light photocatalytic response. Furthermore, the nitrogen vacancies also can significantly redshift the absorption edge of g-C_3N_4 with superior visible-light photocatalytic performance compared to pristine g-C_3N_4 [32–35]. Recently, it is reported that S vacancies in ZnS can induce an excellent photocatalytic activity for H_2 production under visible light [22,36]. And the photocatalytic activity of ZnS increases steadily with increasing the concentration of S vacancies, which can serve as photosensitization units that induce visible light response and as active sites that trap electrons for proton reduction [22]. Moreover, the Zn vacancies (V_{Zn}) are also beneficial to modify the light absorption behavior and narrow the bandgap of ZnS film for photocatalysis under visible-light irradiation. It is reported that the Zn-deficient ZnS film with a band gap of ~2.4 eV was fabricated by pulsed laser deposition (PLD) by control the N_2 background pressure. It exhibits a high photocurrent density of 1.5 mA cm^{-2} under visible light irradiation ($\lambda \geq 435$ nm) [37]. Most recently, ZnS nanoparticles were prepared using ultrasonic methods with Zn vacancy and interstitial sulfur states, exhibited more outstanding photocorrosion stability and photocatalytic activity for degrading reactive black 5 (RB5) under visible light irradiation [38]. These results clearly indicate Zn vacancies engineering is a potential approach for regulate the light absorption behavior and photostability in photocatalysis. However, each of these approaches to prepare zinc deficient ZnS has inherent limitations (low crystallinity, cannot large-scale preparation, etc.) and affords limited control over the type and abundance of zinc defect that they can introduce. And also, there has no systematically research on Zn vacancies in ZnS with an aim for photocatalytic hydrogen evolution under visible light irradiation. Therefore, it is desirable to develop a facile approach for introducing zinc vacancy into ZnS with an enhanced visible-light photocatalytic response and photocatalytic corrosion resistant for hydrogen evolution.

In this work, we report a facile hydrothermal strategy to introduce zinc vacancies in the ZnS structure *via* adding sodium sulfide (Na_2S) as sulfur source. The zinc-deficient ZnS-2.5 with optimum amount of Zn vacancies can be as an efficient photocatalyst for H_2 production operating under visible-light irradiation. The effects of zinc vacancy-related properties on the visible-light photocatalytic activity of ZnS are investigated. The prepared zinc-deficient ZnS samples exhibit enhanced visible-light absorption with increasing the amount of zinc vacancies, which can be easily controlled by varying amount of Na_2S used during the hydrothermal reaction. Furthermore, the introduction of zinc vacancies serve as defects energy levels above the valence band (VB) in ZnS, which act as an acceptor levels for the photoinduced holes that improve charge carrier separation rate and weaken the oxidative capacity of the holes to protect Zn-deficient ZnS from photocorrsion. This work highlights the critical role of defects in the wide-bandgap metal sulfide photocatalysts for optimizing the optical response, and photocatalytic performance.

2. Experimental

All the chemicals in the experiments were of analytical reagent grade and used without further purification.

2.1. Synthesis of zinc-deficient ZnS photocatalysts

ZnS photocatalysts with different molar ratio of Zn/S were prepared by a one-pot hydrothermal method. Typically, 10 mmol $Zn(Ac)_2{\cdot}2H_2O$ with diffident molar ratio of $Na_2S{\cdot}9H_2O$ was dissolved in 30 mL deionized water to form a white slurry solution under magnetic stirring condition at room temperature. After stirring for 60 min, the white slurry precursor solution was then transferred into a 50 mL Teflon-lined autoclave and maintained at 200 °C for 20 h. Finally, the grey white precipitate was obtained by centrifugation and washed several times with deionized water and ethanol and vacuum dried at 60 °C overnight. The molar ratio of $Zn(Ac)_2{\cdot}2H_2O$ to $Na_2S{\cdot}9H_2O$ was fixed as 1:1, 1:1.5, 1:2, 1:2.5, 1:3 (namely, molar ratio Zn/S = 1:1, 1:1.5, 1:2, 1:2.5, 1:3) and obtained products were named as ZnS-*X*, that is, ZnS-1, ZnS-1.5, ZnS-2,ZnS-2.5, ZnS-3, respectively.

2.2. Characterizations

Powder X-ray diffraction (PXRD) data were collected using a Rigaku Ultima III X-ray diffractometer using Cu Kαradiation ($\lambda = 1.54056$ Å). Scanning electron microscope (SEM) images were recorded with a Hitachi S4800 FE-SEM system. Transmission electron microscope (TEM) and high-resolution transmission electron microscope (HRTEM) images were obtained by using a JEM-2100 electron microscope. Visible Raman spectra were recorded on a Horiba confocal LabRAM Aramis spectrometer using a 532 nm single-frequency excitation laser. Chemical states of the obtained samples were characterized by a PHI 5000 Versa Probe X-ray photoelectron spectrometer (a monochromatic Al Ka X-ray radiation). All of the binding energies of all elements were calibrated by the C 1s peak at 284.6 eV. UV–vis spectra were collected using a Shimadzu UV-3600 spectrometer, $BaSO_4$ was used as reference. The photoluminescence (PL) spectra were taken on a Varian Cary eclipse Fluorescence spectrometer with an excitation wavelength of 320 nm. The Zn content for ZnS samples were analyzed by chemical titration and the detailed experiment can be seen in supporting information.

2.3. Photocatalytic hydrogen evolution

The photocatalytic hydrogen evolution reactions were conducted in a side-irradiation Pyrex reactor, which connected to a glass-closed gas circulation system at ambient temperature. In a typical photocatalytic experiment, 50 mg of catalyst power was suspended in 400 mL aqueous solution containing Na_2S and Na_2SO_3 as the sacrificial agent of the hole. Before visible light irradiation, the reactant system was degassed by evacuation to remove air and ensure that the reaction system was under anaerobic conditions, and then was irradiated by a 300-W Xe lamp with a cutoff filter of 420 nm for H_2 evolution under magnetic stirring condition. The amount of hydrogen evolution was analyzed by an online gas chromatograph (GC-14C, Shimadzu, TCD, Ar as carrier).

2.4. Electrochemical measurements

The photoelectrochemical measurement was performed on an electrochemical analyzer (Chenhua CHI 660D) in a standard three-electrode cell. The working electrodes were prepared by drop-coating homogeneous catalyst suspensions directly onto the precleaned indium tin oxide glass (ITO glass) surfaces (1 × 2 cm). Platinum wire was used as the counter electrode, and a saturated calomel electrode (SCE) was used as the reference electrode. $E^0 = 0.241$ V vs. NHE at 25 °C for saturated calomel electrode. Na_2SO_4 (0.5 M, pH = 0.68) aqueous solution was used as supporting electrolyte. The Mott–Schottky curves were taken under dark with a voltage of 5 mV at three frequencies of 1.0, 1.5 and 2.0 kHz, respectively. The potential ranged from −1.7 to 1.0 V (vs. SCE). Electrochemical impedance spectroscopy (EIS) plots were collected at open circuit potential (0.5 V vs. SCE), with the frequency