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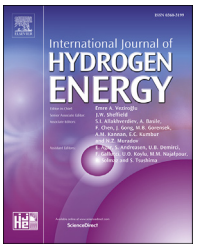

Facile preparation of ZnS/CdS core/shell nanotubes and their enhanced photocatalytic performance

*Zhenli Wang, Haiyue Zhang, Hongwei Cao, Lichao Wang, Ziyao Wan, Yufeng Hao, Xitao Wang**

Collaborative Innovation Center of Chemical Science and Engineering (Tianjin), Tianjin Key Laboratory of Applied Catalysis Science and Technology, College of Chemical Engineering and Technology, Tianjin University, Tianjin 300072, China

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ABSTRACT

In this paper, ZnS/CdS core/shell nanotubes were successfully synthesized by combining hydrothermal treatment and ion exchange conversion, and the significant influence of CdS content in the shell on photo absorption and photocatalytic activity was also investigated. The core/shell nanotubes structure of CdS deposition on both sides of ZnS nanotube was confirmed by scanning electron microscopy (SEM) and high resolution transmission electron microscopy (HRTEM). The room temperature PL spectra of ZnS/CdS core/shell nanotubes indicated that CdS on the shell can reduce the recombination of photon-generated electron and hole. The photocatalytic activity tests prove that ZnS/CdS nanotubes have much higher photocatalytic hydrogen production activity than ZnS nanotube and CdS nanotube. Under the irradiation of visible light, the highest photocatalytic hydrogen production rate of 110 μmol h^{-1} g^{-1} is observed over the ZnS/CdS core/shell nanotubes with CdS/ZnS molar ratio of 1:4, which is about 11.02 and 5.56 times more active than ZnS nanotube and CdS nanotube, respectively. The improved performance of ZnS/CdS samples can be due to the strong photo response in the visible light region and the efficient separation of electron–hole pairs.

Introduction

The development of clean and renewable energy has been one of the hottest subjects in recent decades as a result of the global energy crisis and environmental pollution [1–3]. The production of hydrogen has received a lot of attention because of its potential application as a clean source of energy. However, the industrial hydrogen production consumes a large amount of unrenewable fossil fuels, and also results in huge emission of CO_2 [4]. One way to address this issue is the use of solar energy over semiconductor photocatalysts or molecular catalysts for hydrogen (H_2) production. Extensive efforts have been focused on finding suitable semiconductors for this purpose, including metal oxides, metal hydroxides, oxynitrides, sulfides, and metal-free semiconductors [5–10]. However, the most widely studied semiconductors, such as TiO_2 and ZnO have an obvious drawback: it only absorbs photons below 400 nm (UV), consequently, visible photons, largely available at the earth surface, cannot be used to activate these catalysts [11]. Up to date, many strategies have been employed to improve the photocatalytic efficiencies of photocatalysts in the visible range by different modified methods,

* *Corresponding author.*
E-mail address: wangxt@tju.edu.cn (X. Wang).

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such as doped with nonmetal/metal element [12–16]. Unfortunately, the methods used are not completely controlled. Thus, in order to have a feasible technology the use of catalysts responsive in the visible range is urgent and indispensable.

Zinc sulfide (ZnS) is an important semiconductor and nanostructured ZnS offers unique photonic, electronic, and catalytic properties. Also it is not toxic, water insoluble and comparatively inexpensive [17,18]. In addition, ZnS was proven to be an effective photocatalyst owing to the rapid generation of electron–hole pairs by photoexcitation and highly negative reduction potentials of excited electrons. However, the bandgap of ZnS is 3.66 eV [19], which is too large to visible light response. In this regard, chemical modification was often used as an innovative strategy in the design of visible-light-responsive ZnS-based photocatalysts, many approaches including doping with metal ions to form solid solution and combining with various narrow bandgap semiconductors have been applied to make ZnS a visible light responsive photocatalyst.

As an important chalcogenide compound, cadmium sulfide (CdS) has been widely used for photocatalytic hydrogen production due to its favorable negative conduction band (−0.87 vs NHE) [20] and narrow bandgap energy (2.1 eV), which makes CdS a more suitable semiconductor for absorbing visible light and performing the reduction of protons (H^+) during the water splitting when compared to others [18–22]. It has been reported that highly crystalline CdS with a high specific surface possesses very high photocatalytic activity for H_2 evolution in the presence of sacrificial reagents. Nonetheless, CdS suffers from severe photocorrosion and fast recombination of photogenerated charge carriers under visible light [32]. For conquering these drawbacks, many attempts have been made to enhance the photoelectric and photocatalytic properties of CdS, including the loading of noble metals, morphologies and crystal facet control, semiconductors composites, transition metal ion doping etc [23–41]. Li et al. [32] have fabricated a stable and efficient hydrogen generation system of Pt–PdS/CdS catalyst film, and quantum efficiency of up to 93% was obtained. Xin [42] and coworkers have synthesized a series of nanostructured Pt/CdS composite photocatalysts and investigated the effects of annealing temperature and different sacrificial reagents on H_2 evolution rates. Wang et al. [43] have also found that ZnS helps to suppress the recombination of electron–hole pairs generated by CdS and improve stability of CdS–ZnS samples. Liu et al. [44] have prepared three-dimensional CdS–ZnS composites by depositing CdS nanoparticles on the surfaces of ZnS, which exhibited enhancing photocatalytic activities due to the efficient separation of the photogenerated electrons and holes. Jindal et al. [45] synthesized CdS/ZnS nanoslabs with thickness of 85 nm using ethylenediamine as the solvent and the chelating ligand. Recently, the dual semiconductor CdS/ZnS has become a focus due to its higher photocatalytic activity as compared to their constituent sulphides [46]. However, to our knowledge, there are few reports on the preparation of ZnS/CdS core/shell nanotubes and their application in photocatalytic hydrogen production.

In this study, the ZnS/CdS core/shell nanotubes with different CdS content in the shell of ZnS were synthesized by combining hydrothermal treatment and ion exchange conversion. The photocatalytic performance of nanocomposites was evaluated by H_2 production from an alcohol/triethanolamine mixed aqueous solution to illustrate the importance of the structure of ZnS/CdS core/shell nanotubes and Zn/Cd molar ratio in the shell for the transportation and separation of photo-generated charges.

Experimental

The preparation of ZnS/CdS core/shell nanotubes

Materials

All chemical reagents were of analytical grade and used without further purification.

The preparation of ZnO nanorods

0.5 g PVP was dispersed in 50 mL deionized water under ultrasonication for 0.5 h, 150 mL solution of $Zn(NO_3)_2$ (0.41 mol L^{-1}) was added slowly in this solution, then the mixture was kept in an ice bath with magnetic stirring for 0.5 h. NaOH solution(5 mol L^{-1}) was added dropwise to the above solution until a transparent solution was formed. Then, the mixture was heated to 60 °C and kept for 6 h under magnetic stirring. Finally, the white precipitate was collected after centrifugal separation, and washed with deionized water and absolute ethanol for three times, respectively and dried at 60 °C overnight.

The preparation of ZnS nanotube

The as-prepared ZnO nanorods were dispersed in an aqueous solution of ammonium thioacetate (1 mol L^{-1}) under ultrasonication for 1 h, and the mixture was allowed to heat to 90 °C and kept for 7 h under magnetic stirring [48]. Finally, the white precipitate was collected after centrifugal separation, and washed with deionized water and absolute ethanol for three times, respectively and dried at 60 °C overnight.

The preparation of ZnS/CdS nanotubes

The as-prepared ZnS nanotube was dispersed in 20 mL deionized water under ultrasonication for 0.5 h, then 40 mL ethanol solution of $Cd(NO_3)_2$ was added in this solution. The suspension was transferred into a Teflon-lined stainless steel autoclave. Subsequently, the autoclave was kept at 200 °C for 4 h and cooled down to room temperature. The product was collected after centrifugal separation, and washed with deionized water and absolute ethanol for three times, respectively and dried at 60 °C overnight.

By varying the addition amount of $Cd(NO_3)_2$ ($Cd(NO_3)_2$/ZnS molar ratios: 1:5, 1:2.5, 1.5:2.5 and 1.5:1), three ZnS/CdS nanotubes with theoretical molar ratios of ZnS/CdS of 4:1, 1.5:1, 1:1.5 (marked as ZnS/CdS-1, ZnS/CdS-2 and ZnS/CdS-3) and CdS nanotubes was prepared. Theoretically, the ZnS nanotube would be transformed completely into CdS nanotubes when $Cd(NO_3)_2$/ZnS molar ratio is 1.5 during the preparation. So, we defined this sample as CdS nanotubes.

Characterization

The morphologies of samples were characterized by a Hitachi S-4800 scanning electron microscope (SEM, 5 kV).

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