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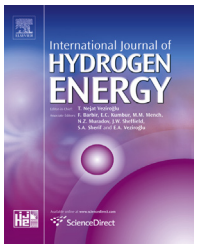

The effect of annealing on the photocatalytic activity of $Zn_xCd_{1-x}S$ arrays and characterization for the optimization of the photocatalysts

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ABSTRACT

$Zn_xCd_{1-x}S$ photocatalyst arrays are prepared using a piezoelectric dispensing system with zinc nitrate, cadmium acetate and thiourea as precursors, a water-glycerol mixture as the reaction solvent and fluorine-doped tin oxide glass as a support. The arrays are annealed in Ar ambient at annealing temperatures that range from 100 to 500 °C. The photocatalytic performance of these arrays is evaluated using scanning electrochemical microscopy (SECM) with a scanning optical fiber that is connected to a Xenon lamp, under visible light and UV–visible light irradiation. The spot for the nominal CdS that is annealed at 200 °C exhibits the highest photocurrent. The screening results are confirmed by bulk film studies. XPS measurements show that a significant amount of CdO exists in the nominal CdS films that are annealed at a temperature less than 200 °C. An increase in the annealing temperature significantly improves the crystalline nature and decreases the amount of CdO. The increase photocatalytic activity of the nominal CdS photoelectrode that is annealed at a temperature of 200 °C may be due to the effective separation of photo-generated electron–hole pairs and highly active reaction sites because of the formation of the hetero-structured $(CdS)_{0.74}$–$(CdO)_{0.26}$ composites and the small grain size of photocatalysts.

Introduction

Photocatalytic water splitting is a successful method for the conversion of solar energy into hydrogen energy [1–3]. Since Fujishima and Honda first reported the photoelectrochemical decomposition of water into hydrogen on a TiO_2 electrode that was irradiated by UV light in 1972 [4], intensive efforts have been made to find active photocatalysts for splitting water. However, most photocatalysts are active only in the UV range of light, which is only ~4% of the solar spectrum. To increase the efficiency of light conversion, it is important to develop visible-light-driven photocatalysts. CdS, with a band gap of 2.4 eV, is a promising semiconductor photocatalyst for the production of hydrogen using sunlight because it has a sufficiently negative flat band potential and exhibits good absorption in the visible zone of the solar spectrum [5,6]. However, noble metals such as Pt must be deposited on CdS to provide active sites for hydrogen production. CdS is also prone to photo-corrosion after prolonged irradiation [7]. Many studies have tried to improve the activity and stability of CdS. Combining CdS and ZnS to form a $Zn_xCd_{1-x}S$ solid solution is one effective way to control photoactivity. The hybrid structures combine the advantages of the constituent materials

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and provide better performance than their individual counterparts. $Zn_xCd_{1-x}S$ exhibits improved physical and chemical properties [8]. The band gap from 2.2 eV to 3.12 eV is infinitely tunable by changing the composition.

$Zn_xCd_{1-x}S$ solid solutions have been studied extensively because they rapidly generate electron–hole pairs when irradiated with visible light and because of the negative potential of photoexcited electrons, the tunable band gap, their resistance to photocorrosion and their high surface activity [9–13]. Lei et al. reported an obvious increase in the photocurrent density for graphene-$Zn_{0.8}Cd_{0.2}S$ composites, compared to graphene-$Zn_xCd_{1-x}S$ composites with other Zn/Cd ratios [9]. The highest rate of H_2 evolution of 6.03 mmol h^{-1} g^{-1} was achieved for $Zn_{0.83}Cd_{0.17}S$/CNTs [10]. Gong et al. demonstrated that a $Zn_{0.5}Cd_{0.5}S$ solid solution exhibits the highest H_2 production rate of 7.42 mmolh^{-1} g^{-1}, which is much higher than that for the optimal Pt-loaded CdS [11]. Zheng et al. concluded that $Zn_{0.4}Cd_{0.6}S$/reduced graphene oxide allows the most efficient photo-gradation of methylene blue (98%) [12]. Xing et al. found that $Zn_{0.2}Cd_{0.8}S$ with a band gap of 2.35 eV gives the greatest hydrogen yield [13]. There are conflicting reports of the optimal composition of $Zn_xCd_{1-x}S$ photocatalysts.

Photocatalysis on semiconductor particles involves three main stages: photo absorption, charge separation and migration, and surface chemical reactions [1–3]. The first two stages are governed by the structural and electronic properties of the photocatalysts [14]. The annealing temperature significantly affects the structure, the surface morphology, the optical properties and the photocatalytic activity of photocatalysts. Therefore, the annealing temperature is extremely critical to the performance of a film. During high temperature air treatment at more than 400 °C and acidic water washing, a $Cd(OH)_2$–CdO–CdS composite layer is formed on the CdS surface [15]. An increase in the annealing temperature results in an increase in the crystallinity and the mean grain size of the films and a decrease in the band gap for CdS [16–18]. Most studies focus on the structural, optical and electrical properties of CdS films but few correlate the structural, optical and electrical properties of the CdS films with photocatalytic activity. Few studies have determined the effect of annealing on the photocatalytic activity of the CdS photocatalyst. This study reports, for the first time, the effect of both the annealing temperature and the composition on the photocatalytic activity of $Zn_xCd_{1-x}S$ arrays.

This study determines the effect of annealing temperature on photocatalytic activity for $Zn_xCd_{1-x}S$ arrays. The photocatalyst arrays are rapidly screened using SECM, with an optical fiber in Na_2SO_4/Na_2SO_3 solution. The photochemical properties of the bulk film photoelectrode are compared with the SECM results. The optimal photoelectrode is further characterized using X-ray diffraction (XRD), scanning electron microscopy (SEM), X-ray photoelectron spectrometry (XPS) and UV–vis spectroscopy. The flat potentials and the incident photon to current conversion efficiencies (IPCEs) for the photoelectrode are respectively measured using the Mott–-Schottky method and the lock-in technique. The effect of annealing on the structural and optical properties and the photocatalytic activity of potential photocatalysts is determined.

Experimental

Chemicals and materials

The $Zn(NO)_3$, $Cd(CH_3COO)_2$ and CH_4N_2S used were all of reagent grade and were used as received. Deionized water and glycerol were used at a volumetric ratio of 3:1 as a solvent to dissolve the chemicals. The Zn, Cd and S precursor solutions were prepared at respective concentrations of 0.1, 0.1 and 0.2 M. F-doped tin oxide (FTO) coated glasses ($1.5 \times 3 \times 0.2$ cm^3) were used as the conducting substrates. The substrates were cleaned using sonication and soaked in isopropanol before use.

Preparation of the photocatalyst arrays

Photocatalyst arrays were fabricated using a dispensing system (CHI model 1550, CHI Instrument) that consists of a piezoelectric dispenser and XYZ stepping motors connected to a computer. The FTO substrate was placed under the platform of the dispensing system and its position was controlled using the XYZ stepping motors with a preprogrammed pattern. A voltage pulse of 100 V was applied to the dispenser, to eject the desired number of drops of precursor solution onto the substrate. The distance between adjacent spots was about 1000 μm. Each spot contained a total of 20 drops and the number of moles of metal ions on each spot was constant. The Zn, Cd and S precursor solutions were loaded and dispensed onto the FTO substrate in sequence. After each dispensing step, the dispenser was washed and refilled with new metal salts. Finally, the array of photocatalyst mixtures was agitated for 20 min, using an agitator to ensure thorough mixing. The arrays were annealed at various temperatures from 100 °C to 500 °C for 12 h in an argon atmosphere, using a tube furnace (21100, Barnstead).

Screening of the photocatalyst arrays

Screening measurements were performed using a PC-controlled CHI model 900C SECM (CHI Instruments, Austin, TX) with an optical fiber, as described in the literature [19]. In brief, a 200 μm optical fiber (FIA-P200-SR, Ocean Optics) was connected to a 150 W xenon lamp (SXE-150, Collimage International Co.) and this combination was attached to the tip holder of an SECM. The photocatalyst arrays on the FTO substrate were placed in an SECM cell, the surface of which was exposed at the bottom through an O-ring. A Pt wire and a saturated Ag/AgCl electrode were respectively used as counter and reference electrodes. A 0.1 M Na_2SO_3/Na_2SO_4 solution acted as a sacrificial donor and was used as the electrolyte. The optical fiber was positioned perpendicular to the surface of the array at a distance of 500 μm and the apparatus scanned across the surface at 500 μms^{-1}. The substrate potential was maintained at 0 V versus Ag/AgCl. A filter of wavelength 420 nm was used to block the UV portion of the light for the visible light illumination experiments. The photocurrent that was produced during the scan was recorded and displayed as a two-dimensional image.