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Preparation and Characterizations of $In_{0.1}Sn_xZn_{0.85-2x}S$ Powder Photocatalysts for Hydrogen Production under Visible Light Irradiation

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Abstract. A series of $In_{0.1}Sn_xZn_{0.85-2x}S$ solid solutions was synthesized by hydrothermal method and employed as photocatalyst for photocatalytic hydrogen evolution under visible light irradiation. The structures, optical properties and morphologies of the solid solutions were studied by X-ray diffraction, diffuse reflectance UV–visible spectroscopy and field emission scanning electron microscopy. From the characterizations, it was confirmed that $In_{0.1}Sn_xZn_{0.85-2x}S$ solid solution can be obtained and they have nano-sized particles. The highest photocatalytic activity was observed on $In_{0.1}Sn_{0.03}Zn_{0.79}S$ photocatalyst, with average rate of hydrogen production 3.05 mmol/h, which was 1.2 times higher than the $In_{0.1}Zn_{0.85}S$ photocatalyst.

Introduction

In the past decades, considerable attention has been focused on the utilization of solar energy into chemical energy by photocatalytic production of hydrogen from water [1,2]. Most of metal sulfides semiconductors are known to possess absorption in the visible light region. Therefore, this group of semiconductor is a promising material to develop new visible light active photocatalysts for hydrogen evolution from water. However, metal sulfides such as CdS are known for its self-photocorrosion and Cd^{2+} is harmful for the environment. Therefore, new approaches to synthesize more stable solid solution using environmentally safe metal sulfides have been increasing nowadays. One of such materials is indium-based sulfide material. The In_2S_3 has band gap of 2.0-2.2 eV [3] and it can form solid solution with ZnS [4,5]. Moreover, it was reported that $ZnIn_2S_4$ [6,7], $(AgIn)_xZn_{2(1-x)}S_2$ [8] and $ZnS\text{-}CuInS_2\text{-}AgInS_2$ [9] were active under visible light for photocatalytic hydrogen production from water. Recently, we reported that the addition of Sn into the $Cd_{0.1}Zn_{0.9}S$ solid solution successfully increased the photocatalytic activity of the $Cd_{0.1}Zn_{0.9}S$ [10]. It was found that the $Cd_{0.1}Sn_xZn_{0.9-2x}S$ nanoparticles with high crystallinity were obtained when they were synthesized by using hydrothermal method. In the present study, a new type of photocatalyst, *i.e.*, $In_{0.1}Sn_xZn_{0.85-2x}S$, was prepared by hydrothermal method. It was found that $In_{0.1}Sn_xZn_{0.85-2x}S$ showed higher photocatalytic activity than the $In_{0.1}Zn_{0.85}S$ solid solution for hydrogen production under visible light irradiation.

Experimental

Synthesis of Solid Solution. A series of $In_{0.1}Sn_xZn_{0.85-2x}S$ (x = 0.01, 0.03, or 0.05 mol) solid solution sample was synthesized in a similar way to the previous literatures [10, 11]. In a typical synthesis for $In_{0.1}Sn_{0.01}Zn_{0.83}S$, $In(NO_3)_2.xH_2O$ (Aldrich, 98%), $SnCl_4.5H_2O$ (GCE chemicals, 98%), $Zn(CH_3COO)_2.2H_2O$ (GCE chemicals, 98%), and thioacetamide (Merck, 99%) of appropriate mol ratio were dissolved in 50 mL of distilled water and then added into an autoclave and sealed. The solution was heated in an oven at 433 K for 8 h and then cooled to room temperature naturally. The precipitates were washed with distilled water for several times and dried in vacuum at room temperature.