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Photocatalytic hydrogen production under visible light over $Cd_{0.1}Sn_xZn_{0.9-2x}S$ solid solution photocatalysts

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ABSTRACT

A series of $Cd_{0.1}Sn_xZn_{0.9-2x}S$ solid solution was successfully 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 Sn can form solid solution with $Cd_{0.1}Zn_{0.9}S$ and the high crystallinity can be maintained as well. Among all samples, the highest photocatalytic activity was observed on $Cd_{0.1}Sn_{0.01}Zn_{0.88}S$ photocatalyst, with average rate of hydrogen production 3.52 mmol/h, which was *ca.* 1.5 times higher than the $Cd_{0.1}Zn_{0.9}S$ photocatalyst. In addition to the high activity, the $Cd_{0.1}Sn_{0.01}Zn_{0.88}S$ also showed high stability at long irradiation time. The role of Sn in preventing electron-hole recombination and photocorrosion was proposed.

1. Introduction

Hydrogen appears to be one of the most promising energy as it is considered to be clean and environmental-friendly energy [1–3]. However, currently, hydrogen is industrially produced by steam methane reforming with large amount of CO_2 co-product [4]. In contrast, photocatalytic production of hydrogen *via* water splitting has the greatest potential to provide CO_2-free hydrogen in large scale [5]. In order to utilize solar energy, development of visible light-driven photocatalysts is highly required.

One of potential visible light-driven photocatalysts is CdS since it has wide absorption of visible light and high flat band potential for reducing water [6,7]. However, CdS is subjected to photocorrosion since the photogenerated holes oxidize the photocatalyst itself. Many attempts to improve CdS activity have been reported, such as combining CdS with other semiconductors [8–12], addition of cocatalysts [13–18], using support materials [8,13,14,19,20], as well as designing the nanostructures, such as CdS nanowires [9,15] and nanorods [21]. On the other hand, ZnS has been reported as a good photocatalyst for hydrogen production [22–24]. However, the band gap is too large for visible light response, therefore, metal ions such as Ni^{2+} [22] and Cu^{2+} [23] were doped into ZnS. Other approach for band gap engineering is combining ZnS with CdS to form solid solution [25]. It was found that the band gap energy of the solid solutions is tuneable by changing the composition [26–29], and the optimized composition gave high photocatalytic activity and quantum efficiency under visible light for hydrogen production [26–28].

For the CdS–ZnS solid solution, larger amount of ZnS is beneficial as the conduction band and valence band would shift to more negative and positive positions, respectively. However, this makes the band gap of the solid solution wider than the CdS itself. For hydrogen production, a visible light-

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