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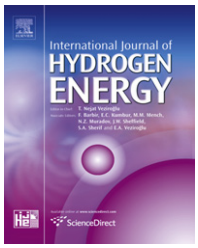

Alkaline earth metal as a novel dopant for chalcogenide solid solution: Improvement of photocatalytic efficiency of $Cd_{1-x}Zn_xS$ by barium surface doping

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ABSTRACT

Novel Ba(x)–$Cd_{0.8}Zn_{0.2}S$ photocatalysts, which has not been reported yet, was synthesized for the first time by thermal sulfuration method. These samples were characterized by X-ray diffraction, X-ray photoelectron spectroscopy, scanning electron microscopy, N_2 absorption–desorption isotherm, ultraviolet visible diffuse reflectance spectroscopy, density functional theory calculation and photoluminescence spectroscopy. Results showed that Ba mainly existed on the surface of $Cd_{1-x}Zn_xS$ particles, because of the largest atom radius compared to Cd and Zn atoms, in the chemical form of Ba–S–Cd/Zn bonding. The successful surface doping finally induces the element gradient from bulk phase to surface, which efficiently promotes the photogenerated charges' transition and separation. On the basis of various characterization results, the mechanism of this promotion effect is proposed. The element gradient efficiently enhances the transition of electrons, while the noticeable doping influence on valence band significantly promotes the holes' migration. Thus, the bulk recombination of photoelectrons and holes was efficiently suppressed, and the hydrogen production was improved efficiently.

1. Introduction

Hydrogen production from water with renewable energy sources is an important subject from the standpoint of both energy and environment [1–4]. Photocatalytic water splitting using semiconductor photocatalysts has attracted lots of attentions as one of the ideal processes for hydrogen production, and has been considered as one of the ultimate solutions to energy and environmental issues [5,6]. During the past several decades, researchers have discovered kinds of semiconductors that have excellent performances in photocatalytic water splitting systems, such as TiO_2 [7,8], $SrTiO_3$ [9], $NaTaO_3$ [10], CdS [11–13], and $CuInS_2$–$AgInS_2$–ZnS [14]. However, almost all of them need noble metal loaded on the surface as co-catalyst in order to efficiently improve the photocatalytic activities, and part of these photocatalysts use noble metal salts as raw materials for preparation. Apparently it is not desirable to use these noble metals of quite high cost in the viewpoint of industrial application. Hence, it is necessary to develop novel photocatalysts with low cost that could efficiently utilize solar spectrum (both ultraviolet region and visible-light region).

As known, $Cd_{1-x}Zn_xS$ solid solution photocatalyst has been studied extensively due to its controllable band structure and excellent performance in photocatalytic hydrogen production under visible-light irradiation, especially in the absence of noble metal co-catalyst. Thus lots of efforts have been made to improve the photocatalytic activity of $Cd_{1-x}Zn_xS$ [15–19]. We

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also presented many methods to modify $Cd_{1-x}Zn_xS$ [20–23], $Cd_{0.8}Zn_{0.2}S$ prepared by thermal sulfuration method and $Cd_{0.1}Cu_{0.01}Zn_{0.89}S$ prepared by coprecipitation method showed quite high activities in the absence of noble metal co-catalyst (Pt). But it is still much lower than Pt loaded CdS [11], Pt loaded PdS/CdS [13] and Ru loaded $CuInS_2$–$AgInS_2$–CuS [24], etc. Thus development of novel approaches for the modification of $Cd_{1-x}Zn_xS$ with improved activity and stability is highly desired.

During the past several decades, foreign elements (transition metals and nonmetal elements) doping have been extensively attempted to develop visible-light driven photocatalysts, which will introduce impurity levels in the forbidden band and result in the enhanced absorption in visible region [25,26]. However, although these photocatalysts become colored with doping of foreign elements ions, the photocatalytic activities drastically decrease as the formation of recombination centers for photogenerated electrons and holes. Obviously, it is hard to achieve satisfactory improved photocatalytic efficiency by this modification, which aims at visible-light driven photocatalysts design. Considering the continuous controlled band gap of $Cd_{1-x}Zn_xS$ solid solution photocatalyst, these transition metals and nonmetal elements doping seems to be not suitable. On the contrary, Kudo et al. have reported that alkaline earth metals doping can significantly improve the activity of $NaTaO_3$ with no influence on its band structure [27]. Li et al. also reported alkaline earth metals doped TiO_2 has a good performance in photocatalytic H_2 evolution reaction [28]. So the question is whether such doping can be successfully applied to chalcogenide photocatalysts. These facts have motivated us to be interested in the investigation of alkaline earth metal doping effect on the CdS–ZnS solid solutions. Thus, in our previous report, we tried to dope Sr into CdS–ZnS solid solutions by coprecipitation method, and finally found that doped Sr efficiently improved the charge separation and resulted in much higher photocatalytic activities [29]. Obviously, alkaline earth metals also can promote the photocatalytic behavior of chalcogenide photocatalysts. But the crystallinity of these Sr doped CdS–ZnS prepared by coprecipitation method were quite poor. Meanwhile, the mechanism how the doping alkaline earth metals affect on the charge transition is not clear yet, which is also not demonstrated by previous reports. So coupled alkaline earth metal doping with other advanced synthesis method could be expected to further enhance the photocatalytic activity, and systemic investigation on the mechanism of alkaline metal doping will be beneficial for the future semiconductor modification.

In this work, we further improved the photocatalytic efficiency of $Cd_{1-x}Zn_xS$ by coupling novel two-step thermal sulfuration method with alkaline earth metal doping [11,21], and systemically investigated the effect of doping on the photocatalytic process so as to direct the modification of sulfide semiconductors in the future. Alkaline earth metal Ba was doped into $Cd_{1-x}Zn_xS$ for the first time by thermal sulfuration of corresponding mixed oxide precursors and resulted in a series of novel Ba(x)–$Cd_{0.8}Zn_{0.2}S$ photocatalysts with Ba enrichment surface layer and none doped CdS–ZnS core. These photocatalysts exhibited much higher photocatalytic activities for hydrogen production than $Cd_{0.8}Zn_{0.2}S$. Through the characterization of the resulting photocatalysts, we systemically demonstrated the mechanism how surface Ba doping influenced the charge transition process.

2. Experimental sections

2.1. *Synthesis of Ba doped CdS–ZnS photocatalysts*

Ba doped CdS–ZnS photocatalysts were prepared by thermal sulfuration method as reported previously by us [11,21]. In a typical process: (a) An appropriate amount of $Ba(CH_3COO)_2\cdot 2H_2O$, $Cd(CH_3COO)_2\cdot 2H_2O$ and $Zn(CH_3COO)_2\cdot 2H_2O$ (atomic ration, Ba: Cd: Zn = x: 0.8–x: 0.2) were dissolved in deionized water. (b) Solid mixture obtained by vaporizing the aqueous solution was heated in a quartz tube at 400 °C for 2 h in flowing air to obtain a homogeneous mixture of BaO, CdO

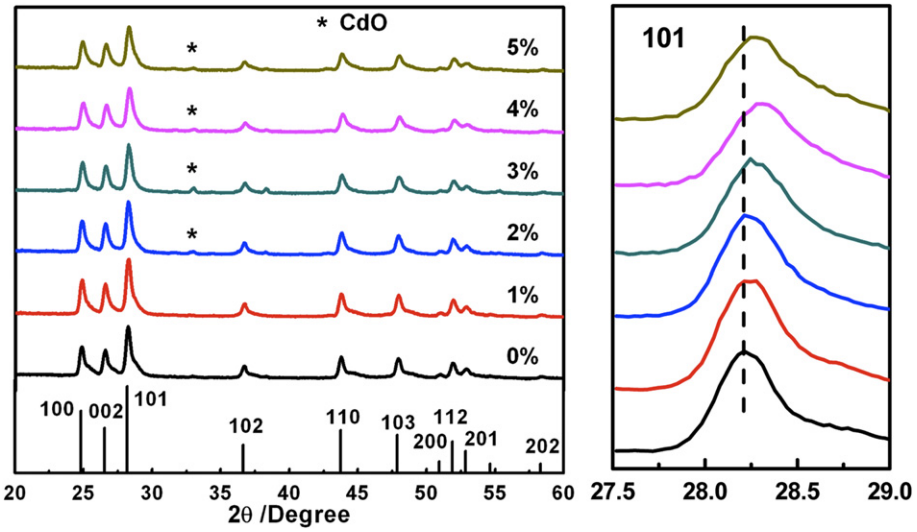

Fig. 1 – X-ray diffraction patterns of Ba(x)–$Cd_{0.8}Zn_{0.2}S$ photocatalysts: The values of x are 1%, 2%, 3%, 4%, and 5%.