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# Preparation and characterization of In and Cu co-doped ZnS photocatalysts for hydrogen production under visible light irradiation

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## ABSTRACT

In this work, a new photocatalysts In(0.1),Cu(x)-ZnS ( $x=0.01, 0.03, 0.05$ ) is successfully synthesized using simple hydrothermal method. The physical and chemical properties of the In and Cu co-doped ZnS photocatalyst were characterized by X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM), diffuse reflectance UV-visible spectroscopy (DR UV-visible) and photoluminescence spectroscopy (PL). The photocatalytic activity of the as-prepared In and Cu co-doped ZnS for hydrogen production from water with  $\text{Na}_2\text{SO}_3$  and  $\text{Na}_2\text{S}$  as sacrificial agent under visible light irradiation ( $\lambda \geq 425 \text{ nm}$ ) was investigated. The presence of co-dopants facilitated the separation of electron-hole as well as increases the visible light absorption. The absorption edge of the co-doped ZnS photocatalyst shifted to longer wavelength as the amount of Cu increases. This indicates that the absorption properties depended on the amount of Cu doped. The photocatalytic activity of single doped In(0.1)-ZnS was significantly enhanced by co-doping with Cu under visible light irradiation. The highest photocatalytic activity was observed on In(0.1),Cu(0.03)-ZnS with the hydrogen production rate of  $131.32 \mu\text{mol/h}$  under visible light irradiation. This is almost 8 times higher than single doped In(0.1)-ZnS.

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## 1. Introduction

Hydrogen production under light irradiation with the assistance of semiconductor photocatalyst has been regarded as an attractive solution to resolve the global energy and environmental problems [1–4]. As large portion of solar light consist of visible light, the development of visible light active photocatalyst that are able to utilize most of the solar light are important.

CdS is one of the most extensively studied metal sulfide photocatalyst for visible light hydrogen production [5–13]. The band gap positions of CdS are ideal for hydrogen production. However, CdS is prone to photocorrosion since the holes in the valence band tend to oxidize CdS [14]. Moreover, Cd metal ions are toxic. Thus, the search for a new metal sulfide photocatalyst that are less toxic is greatly explored.

Recently, some multi component metal sulfides have been reported to be more stable and show higher photocatalytic activity under visible light [15–18]. The host for multi-component metal

sulfides are generally ZnS. This is because ZnS possess high conduction band that are essential for photocatalytic hydrogen production [19–21]. Since ZnS are not visible light active, the modifications of ZnS by doping with foreign elements [22–25] or forming solid solution with narrow band gap semiconductor [15–18] are often done. Studies on photocatalytic hydrogen production utilizing  $\text{In}_2\text{S}_3$  photocatalyst with band gap of 2.0–2.2 eV [26] under visible light showed good efficiency [27]. The binary metal sulfides of  $\text{Zn}_m\text{In}_2\text{S}_{m+3}$  was also studied and proven to have high photocatalytic activity for hydrogen production [15]. On the other hand, Cu metal dopant is often used in photocatalytic hydrogen production to improve the visible light absorption [22,23,28–30]. Thus, the addition of Cu to this binary metal sulfide is proposed to further improve the photocatalytic activity by enhancing the visible light absorption to longer wavelength.

In this work, it is proposed that In(0.1),Cu(x)-ZnS photocatalyst, will show an enhanced photocatalytic activity for hydrogen production as compared to single doped ZnS photocatalyst. Herein, the In(0.1),Cu(x)-ZnS was successfully prepared by hydrothermal method and the photocatalytic hydrogen production activity was investigated. The benefits of co-dopants in improving the photocatalytic performance for hydrogen production were also investigated.

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