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Photocatalytic hydrogen production under visible-light irradiation on $(\text{CuAg})_{0.15}\text{In}_{0.3}\text{Zn}_{1.4}\text{S}_2$ synthesized by precipitation and calcination

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ABSTRACT

This study investigates the photocatalytic hydrogen production over nanosized $(\text{CuAg})_{0.15}\text{In}_{0.3}\text{Zn}_{1.4}\text{S}_2$ photocatalysts prepared via precipitation and calcination. The photocatalysts were characterized by X-ray diffraction, transmission electron microscopy, scanning electron microscopy, N_2 adsorption-desorption, and UV-Vis absorption spectroscopy. The results show that calcination temperature and time significantly influence the crystallinity, specific surface area, and visible-light absorption capacity of the photocatalysts. The photocatalyst activity was studied under visible-light irradiation with KI as the electron donor. The results indicate that the $(\text{CuAg})_{0.15}\text{In}_{0.3}\text{Zn}_{1.4}\text{S}_2$ photocatalyst prepared at a calcination temperature of 600 °C for 5 h yields the highest photocatalytic activity (H_2 production rate of $1750 \mu\text{mol g}^{-1} \text{h}^{-1}$ and quantum yield of 12.8% at $420 \pm 5 \text{ nm}$), approximately 6 times larger than that of catalysts prepared without thermal treatment.

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1. Introduction

As the energy crisis and environmental pollution have become increasingly prominent, development of clean and sustainable new energy is indispensable. Great progress has been achieved in photocatalytic H_2 production technologies since the photochemical splitting of water over a TiO_2 electrode was first reported by Fujishima et al. [1]. So far, most reported photocatalysts have large band gap energy ($E_g > 3.0 \text{ eV}$) and so they are only active under ultraviolet light, which occupies only 5%

of the solar spectrum [2–6]. Designing visible-light-driven photocatalysts with high photocatalytic activity and visible-light absorption to make full use of the solar spectrum has therefore been an important research focus.

The band gap energies of metal sulfides are low enough to allow them to effectively absorb visible light to produce H_2 [7,8]. However, binary sulfide photocatalysts, such as CdS and Bi_2S_3 , can oxidize themselves using the photogenerated valence band holes (also known as photooxidation and photodecomposition) and become unstable during photocatalytic reactions

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[9,10]. Multicomponent metal sulfides, such as $\text{Zn}_{0.8}\text{Cd}_{0.2}\text{S}$ [11], ZnIn_2S_4 [12,13], $(\text{CuIn})_x\text{Zn}_{2(1-x)}\text{S}_2$ [14,15], and $(\text{CuAg})_x\text{In}_{2-x}\text{Zn}_{2(1-2x)}\text{S}_2$ [16,17], can have significantly improved stability and photocatalytic activity. $(\text{CuAg})_{0.15}\text{In}_{0.3}\text{Zn}_{1.4}\text{S}_2$ photocatalysts have been considered a new class of visible-light-driven photocatalysts because they can use visible light of up to about 650 nm in wavelength [18] and their constituent elements have high natural abundance and low toxicity. Recently, we have successfully prepared $(\text{CuAg})_{0.15}\text{In}_{0.3}\text{Zn}_{1.4}\text{S}_2$ photocatalysts through calcination at 600 °C and evaluated their photocatalytic activity, kinetics, and stability [16,19].

In this study, we prepared $(\text{CuAg})_{0.15}\text{In}_{0.3}\text{Zn}_{1.4}\text{S}_2$ photocatalysts via a precipitation and calcination method and evaluated the effects of calcination temperature and time on their structure, morphology, and optical properties. The effects of calcination conditions on photocatalytic H_2 production using KI as the electron donor under visible-light irradiation were investigated.

2. Experimental

2.1. Catalyst preparation

Briefly, $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (6.37 g), AgNO_3 (0.42 g), and $\text{In}(\text{NO}_3)_3 \cdot 3.6\text{H}_2\text{O}$ (1.85 g) were dissolved in 200 mL deionized water using a magnetic stirrer. The solution was purged with N_2 for 10 min to remove dissolved oxygen before adding 0.24 g CuCl_2 . The solution was then purged with pure H_2S gas for 15 h under magnetic stirring. During this process, some flocculent yellow precipitate formation could be observed. The precipitate was ultrasonicated (Q125, QSonica LLC) at 125 W for 30 min and then recovered using vacuum filtration with a 0.1- μm membrane. The resulting solid was thoroughly washed with deionized water and vacuum dried at 95 °C for 1 h. Finally, the yellow product was placed into a tube furnace and calcined under pure H_2S gas at different temperatures ($T = 400\text{--}700$ °C) and times ($t = 1\text{--}7$ h). The prepared photocatalysts were labeled as T - t .

To study the effect of Ru cocatalyst loading on the photocatalytic activity, before the photocatalytic reaction, 0–1.2 wt% (Ru weight basis) RuCl_3 was added to the photocatalytic reactor system and was irradiated with a 300-W Xe lamp for 20 min (photocatalytic reduction process).

2.2. Catalyst characterization

The crystallinity of the photocatalysts was determined by X-ray diffraction (XRD) on a Philips X'pert diffractometer using $\text{Cu } K_\alpha$ radiation ($\lambda = 0.154178$ nm). Diffractograms were collected for $2\theta = 10^\circ\text{--}70^\circ$. The crystallite size was estimated from the Scherrer equation [16]. The morphology of the photocatalysts was observed by transmission electron microscopy (TEM; FEI-Tecna F20 FEG) with an accelerating voltage of up to 200 kV. Scanning electron microscopy (SEM) was carried out on a Zeiss Ultra60 microscope equipped with energy-dispersive X-ray spectroscopy (EDS) to analyze the elemental composition. UV-Vis absorption spectra were measured using a Beck-

man spectrophotometer (DU7400) in the spectral region of 200–800 nm. BET surface area was measured using the N_2 adsorption-desorption method on a Micromeritics ASAP 2020 physisorption analyzer.

2.3. Photocatalytic H_2 reaction

Photocatalytic H_2 production was performed in a 780-mL gas-tight stainless steel reactor. The cross-sectional area and height of the reactor were 71 cm^2 and 11 cm, respectively. A quartz glass cover on the top of the reactor allowed light to pass through. The reaction vessel was submerged in a water bath to maintain the operating temperature (25 °C). A photocatalyst suspension was prepared by dispersing 0.3 g of the catalyst in 300 mL KI aqueous solution (0.2 mol/L). The pH of this system was then adjusted to 2.0 using HCl, and the system was held in suspension under continuous mixing using a magnetic stirrer. The system was purged with N_2 for 30 min prior to irradiation to remove dissolved oxygen. The light source was a 300-W Xe lamp (Perkin Elmer, PE300BF) equipped with a high performance hot mirror (400–690 nm, Edmund Optics). H_2 production was monitored by gas chromatography (Agilent GC-6890, HP-MS5 column, TCD detector, N_2 carrier). The photocatalytic H_2 production rate ($\mu\text{mol g}^{-1} \text{h}^{-1}$) was calculated as number of H_2 molecules produced per unit time/photocatalyst amount.

Under the same photocatalytic conditions, the quantum yield (QY) was measured using a band-pass interference filter ($\lambda = 420 \pm 5$ nm) and a spectroradiometer (Spectral Evolution, SR-1100) and was defined as $\text{QY} = (\text{number of } \text{H}_2 \text{ molecules produced} \times 2) / (\text{number of incident photons} \times 100\%)$.

3. Results and discussion

3.1. Characterization and analysis of photocatalysts

Figure 1 shows the XRD patterns of the as-precipitated sample and $(\text{CuAg})_{0.15}\text{In}_{0.3}\text{Zn}_{1.4}\text{S}_2$ photocatalysts calcined for 5 h at different temperatures. The as-precipitated sample had wide

Fig. 1. XRD patterns of the as-prepared $(\text{CuAg})_{0.15}\text{In}_{0.3}\text{Zn}_{1.4}\text{S}_2$ photocatalyst and those calcined at different temperatures for 5 h.

Table 1Specific surface area, crystallite size, and band gap of the $(\text{CuAg})_{0.15}\text{In}_{0.3}\text{Zn}_{1.4}\text{S}_2$ photocatalysts.

Photocatalyst	Specific surface area (m^2/g)	Crystallite size (nm)	Band gap (eV)
As-prepared	3.2	21.4	2.72
400°C-5h	8.2	27.4	2.15
500°C-5h	7.3	29.7	1.95
600°C-5h	7.6	27.0	1.93
700°C-5h	5.6	33.4	2.23
600°C-1h	8.4	25.1	2.39
600°C-3h	7.9	26.4	2.12
600°C-7h	7.4	27.2	1.92

diffraction peaks with low intensity indicating its low crystallinity. After calcination, two pronounced peaks were observed at $2\theta = 28.5^\circ$ and 47° , which correspond to the ZnS (111) and (220) crystal planes. As the calcination temperature increased, the intensity of the diffraction peaks became stronger, suggesting an increase in crystallinity. At 600 °C, the diffraction peaks were sharp and high. Table 1 lists the crystallite sizes and the BET surface areas of the catalysts. The BET surface areas agreed well with previously reported results [18]. The photocatalyst calcined at 600 °C had the smallest particle size and higher BET surface area, whereas the photocatalyst calcined at 700 °C had the largest particle size and the smallest BET surface area. Clearly, calcination temperature significantly influences the crystallinity and specific surface area. Low calcination temperature reduces the crystallinity and increases the BET surface area of the photocatalyst, while high calcination temperature increases the crystallite sizes and decreases the BET surface area. The photocatalyst activity largely depends on optimization of its crystallinity and surface area [20,21].

Figure 2 shows SEM and TEM micrographs of the $(\text{CuAg})_{0.15}\text{In}_{0.3}\text{Zn}_{1.4}\text{S}_2$ photocatalyst (600°C-5h). The photocatalyst was clearly composed of crystallized particles with high dispersion and apparent crystal structure. The diameters of single particles were approximately 30–50 nm, which is consistent with the XRD results.

Because the photocatalyst calcined at 600 °C had high surface area and crystallinity, the XRD patterns of samples calcined at 600 °C for different times were studied and are shown in Fig. 3. The positions of the observed diffraction peaks did not change significantly with increasing calcination time. At a calcination time of 1 h, the diffraction peaks were relatively wide and low. As the calcination time increased, the diffraction peaks

Fig. 2. TEM (a) and SEM (b) images of $(\text{CuAg})_{0.15}\text{In}_{0.3}\text{Zn}_{1.4}\text{S}_2$ (600°C-5h) photocatalyst. **Fig. 3.** XRD patterns of $(\text{CuAg})_{0.15}\text{In}_{0.3}\text{Zn}_{1.4}\text{S}_2$ calcined at 600 °C for different times.

gradually became slightly sharper and stronger in intensity, indicating gradually increasing crystallinity. As shown in Table 1, increasing the calcination time caused increased particle size and decreased surface area of the photocatalysts.

Figure 4(a) shows the UV-Vis absorption spectra of $(\text{CuAg})_{0.15}\text{In}_{0.3}\text{Zn}_{1.4}\text{S}_2$ calcined at 600 °C for different times. The as-prepared and calcined photocatalysts had obvious absorption in the visible light region. The band gap (E_g) of a photocatalyst can be calculated according to $\alpha h\nu = A(h\nu - E_g)^{n/2}$ [22,23], where α , h , ν , and A are the absorption coefficient, Planck's constant, light frequency, and a constant, respectively.

Fig. 4. UV-Vis absorption spectra (a) and band gap values from the plots of $(\alpha h\nu)^2$ versus $h\nu$ (b) for $(\text{CuAg})_{0.15}\text{In}_{0.3}\text{Zn}_{1.4}\text{S}_2$ photocatalysts with different calcination time. (1) As-prepared; (2) 600°C-1h; (3) 600°C-3h; (4) 600°C-5h; (5) 600°C-7h.

Based on the type of optical transition observed (Fig. 4(a)), the band gap transition of $(\text{CuAg})_{0.15}\text{In}_{0.3}\text{Zn}_{1.4}\text{S}_2$ is direct ($n = 1$), and its band gap can therefore be determined from the plot $(ah\nu)^2$ versus $h\nu$ (Fig. 4(b)). Band gaps were obtained by plotting a tangent line over the slope of the curve in Fig. 4(b) and extrapolating it to the horizontal axis, and are listed in Table 1. The photocatalyst activity depends to some extent on the width of its band gap. A narrow band gap can enhance the use of visible light, resulting in high photocatalytic activity [8,24]. The band gaps of the calcined photocatalysts were narrower than that of the non-calcined photocatalyst, probably because the calcined photocatalysts had high crystallinity and increased light refractive index, resulting in a shift of the absorption edges to longer wavelength and a narrower band gap [25,26]. The particle size of the photocatalysts was similar when the calcination temperature was in the range of 400–600 °C. However, their crystallinity increased with calcination temperature (Fig. 1), leading to a red shift of the absorption edges and lowering of the band gap of the photocatalysts [25,26]. Further increase in calcination temperature from 600 to 700 °C decreased the crystallinity and caused a blue shift of the absorption edges, leading to a broader band gap [27].

As shown in Table 1, with increasing calcination time, the band gap of the photocatalysts decreased gradually, and the absorption edges exhibited a red shift. The band gap of the photocatalyst calcined for 7 h was reduced to 1.92 eV and had a strong absorption in the visible light region (i.e., the absorption edge reached approximately 645 nm). Because the crystallinity of the photocatalysts increased with calcination time (Fig. 3), the light refractive index of the photocatalysts was enhanced, resulting in a red shift of the absorption edges and thus a narrow band gap [25,26]. In addition, the band gaps of the photocatalysts calcined for 5 and 7 h were similar, indicating that further increase in calcination time would have less significant influence on their visible-light absorption.

Figure 5(a) shows the EDS results for the $(\text{CuAg})_{0.15}\text{In}_{0.3}\text{Zn}_{1.4}\text{S}_2$ photocatalyst (600°C-5h), which confirm the presence of Cu, Ag, In, Zn, and S elements in the calcined sample. After $(\text{CuAg})_{0.15}\text{In}_{0.3}\text{Zn}_{1.4}\text{S}_2$ was loaded with Ru, a characteristic peak of Ru was observed in Fig. 5(b). This result indicates that Ru was successfully loaded on the photocatalyst surface using the photocatalytic reduction process.

3.2. Photocatalytic activity

3.2.1. Effect of Ru loading on photocatalytic H_2 production over $(\text{CuAg})_{0.15}\text{In}_{0.3}\text{Zn}_{1.4}\text{S}_2$

Figure 6 shows the influence of Ru loading on the photocatalytic production of H_2 over $(\text{CuAg})_{0.15}\text{In}_{0.3}\text{Zn}_{1.4}\text{S}_2$ (600°C-5h). The photocatalytic H_2 production increased significantly with Ru loading, as the increasing numbers of Ru particles deposited on the photocatalyst became catalytically active sites and promoted charge separation and transfer across the interface. Additional Ru loading beyond 0.7 wt% did not enhance the H_2 production rate. Excessive Ru surface loading may lead to the Ru particles acting as electron traps and thus could enhance the probability of electron and hole recombination.

Fig. 5. EDS of the $(\text{CuAg})_{0.15}\text{In}_{0.3}\text{Zn}_{1.4}\text{S}_2$ photocatalyst (600°C-5h) without Ru loading (a) and with Ru loading (b).

The photocatalytic activity reached a maximum level (H_2 production rate of $1750 \mu\text{mol g}^{-1} \text{h}^{-1}$ and the quantum yield of 12.8% at $420 \pm 5 \text{ nm}$) at a Ru loading of 0.7 wt%, which was significantly higher than the reported data (7.4% quantum yield) [17].

3.2.2. Effect of calcination conditions on photocatalytic H_2 production

Figure 7(a) shows the influence of calcination temperature on the photocatalytic production of H_2 over $(\text{CuAg})_{0.15}\text{In}_{0.3}\text{Zn}_{1.4}\text{S}_2$ (Ru loading 0.7 wt%). The photocatalytic activity of the photocatalysts increased gradually with calcination temperature from the initial 400 °C and reached a maximum level ($1750 \mu\text{mol g}^{-1} \text{h}^{-1}$) at 600 °C. According to the characterization re-

Fig. 6. Effect of Ru loading on photocatalytic H_2 production over $(\text{CuAg})_{0.15}\text{In}_{0.3}\text{Zn}_{1.4}\text{S}_2$ (600°C-5h) and time course of H_2 production over 0.7 wt% Ru-loaded $(\text{CuAg})_{0.15}\text{In}_{0.3}\text{Zn}_{1.4}\text{S}_2$ (inset). Reaction conditions: KI aqueous solution (0.2 mol/L) 300 mL, photocatalyst 0.3 g, pH 2.0, 300 W Xe lamp with a high performance hot mirror (400–690 nm).

Fig. 7. Effects of calcination temperature (a) and calcination time (b) on photocatalytic H₂ production over 0.7 wt% Ru-loaded (CuAg)_{0.15}In_{0.3}Zn_{1.4}S₂. Reaction conditions: KI aqueous solution (0.2 mol/L) 300 mL, photocatalyst 0.3 g, pH 2.0, reaction time 24 h, 300 W Xe lamp with a high performance hot mirror (400–690 nm).

sults, the photocatalyst calcined at 600 °C had the highest crystallinity and the smallest particle size (or the higher specific surface area), which explained its high photocatalytic activity. However, the further increase in calcination temperature from 600 to 700 °C decreased the photocatalytic activity, probably because of the increased crystallite size of the photocatalyst particles. Moreover, the H₂ production rate of the non-calcined photocatalyst was only 15% that of the photocatalyst calcined at 600 °C, indicating that calcination is critical for improving the photocatalyst activity.

Figure 7(b) shows the influence of calcination time on the photocatalytic production of H₂ over (CuAg)_{0.15}In_{0.3}Zn_{1.4}S₂ with 0.7 wt% Ru loading. The crystallinity of the photocatalyst increased gradually (Fig. 3) with calcination time from 1 to 5 h, resulting in improved photocatalytic activity due to suppressed recombination of photogenerated electrons and holes [7,28]. Moreover, the surface area of the photocatalysts decreased from 8.4 to 7.4 m²/g with increasing calcination time, thus resulting in a decrease of surface active sites of the photocatalyst. Therefore, the crystallinity and surface area of the present photocatalysts determine their activity [20,21]. The photocatalyst activity increased with calcination time from 1 to 5 h and then did not improve with further increment of time.

The visible-light absorption capability of the photocatalysts increased with calcination time (Fig. 4), indicating that the

Table 2

Electron affinity, ionization energy, and element electronegativity values.

Atom	<i>A</i> (eV)	<i>I</i> (eV)	<i>x</i> (eV)
Cu	1.235	7.7264	4.48
Ag	1.302	7.5762	4.44
In	0.30	5.7864	3.04
Zn	−0.87	9.3942	4.26
S	2.077	10.3600	6.22

photocatalysts could absorb more photons and promote the excitation of photogenerated electrons under visible-light irradiation (400–690 nm), resulting in increased photocatalytic H₂ production. Meanwhile, no significant differences in the light absorption properties of the photocatalysts calcined for 5 or 7 h were observed, as indicated by their very similar H₂ production rates.

3.3. Photocatalytic mechanism of (CuAg)_{0.15}In_{0.3}Zn_{1.4}S₂

To evaluate the photocatalytic mechanism of the (CuAg)_{0.15}In_{0.3}Zn_{1.4}S₂ photocatalyst, we analyzed the band structure of the obtained photocatalysts. The conduction band edge potential (*E*_{CB}) and valence band edge potential (*E*_{VB}) of the photocatalysts at the point of zero charge can be calculated using the following equations [29,30]:

$$E_{CB} = X - E^c - 1/2E_g \quad (1)$$

$$X = \left\{ x_{Cu}^{0.15} \times x_{Ag}^{0.15} \times x_{In}^{0.3} \times x_{Zn}^{1.4} \times x_S^2 \right\}^{1/4} \quad (2)$$

$$x = 1/2(A + I) \quad (3)$$

$$E_{VB} = E_{CB} + E_g \quad (4)$$

where *E*_g is the band gap of the photocatalyst (Table 1); *E*^c is the energy of free electrons on the hydrogen scale (~4.5 eV); *X* is the absolute electronegativity of the semiconductor, which is the geometric mean of the electronegativity of the constituent atoms (*x*); *A* is the atom electron affinity; *I* is the first ionization energy. The data of *A* and *I* obtained from Ref. [31] and the calculated *x* values are listed in Table 2. The positions of *E*_{CB} and *E*_{VB} of the photocatalysts prepared under different calcination conditions are illustrated in Fig. 8.

Fig. 8. Photocatalytic mechanism of (CuAg)_{0.15}In_{0.3}Zn_{1.4}S₂ photocatalysts prepared under different calcination conditions. (1) As-prepared; (2) 400°C-5h; (3) 500°C-5h; (4) 600°C-5h; (5) 700°C-5h; (6) 600°C-1h; (7) 600°C-3h; (8) 600°C-7h.

As shown in Fig. 8, when the energy of incident light ($h\nu$) is larger than that of the band gap, the electrons in the valence band leap to the conduction band to generate photogenerated electrons (e^-) and holes (h^+). Ru particles on the photocatalyst surface can act as electron traps and thereby promote the separation of the photogenerated charges. The H^+ ions in the reaction solution are reduced by the electrons to form H_2 . Therefore, loading of the photocatalyst with Ru increases its photocatalytic activity. Meanwhile, the photogenerated holes are captured by the electron donor I^- , which is oxidized to I_3^- at an initial pH of 2.0 [19,32,33].

Besides morphology, crystallinity, specific surface area, particle size, etc, an appropriate band gap and E_{CB} are prerequisite for photocatalytic H_2 production under visible-light irradiation. As shown in Fig. 8, $(CuAg)_{0.15}In_{0.3}Zn_{1.4}S_2$ photocatalysts prepared at different calcination conditions exhibited band gaps of 1.9–2.7 eV, and therefore all the photocatalysts were able to absorb visible-light photons (< 3.0 eV) [7]. In addition, the E_{CB} values of the photocatalysts were lower than the redox potential of H^+/H_2 , allowing the reduction of H^+ to H_2 [8]. The $(CuAg)_{0.15}In_{0.3}Zn_{1.4}S_2$ photocatalyst prepared at 600 °C for 5 h had a narrow band gap and suitable E_{CB} , and showed the highest photocatalytic activity.

4. Conclusions

The present $(CuAg)_{0.15}In_{0.3}Zn_{1.4}S_2$ photocatalysts had small diameters (30–50 nm) and obvious absorption in the visible light region by adjusting calcination temperature and calcination time. Low calcination temperature (e.g., 400 °C) decreased the crystallinity and thus decreased the photocatalytic activity of the $(CuAg)_{0.15}In_{0.3}Zn_{1.4}S_2$ photocatalysts; excessively high

temperature caused increased particle size and decreased surface area of the photocatalyst, leading to a decrease in photocatalytic H_2 production. Extension of calcination time was able to increase the crystallinity, visible-light absorption, and photocatalytic activity of the $(CuAg)_{0.15}In_{0.3}Zn_{1.4}S_2$ photocatalysts. The $(CuAg)_{0.15}In_{0.3}Zn_{1.4}S_2$ (0.7 wt% Ru loading) photocatalyst calcined at 600 °C for 5 h exhibited the highest H_2 production rate ($1750 \mu\text{mol g}^{-1} \text{h}^{-1}$) and quantum yield at 420 ± 5 nm (12.8%), approximately 6 times higher than those of the non-calcined photocatalyst.

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Graphical Abstract

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Photocatalytic hydrogen production under visible-light irradiation on $(CuAg)_{0.15}In_{0.3}Zn_{1.4}S_2$ synthesized by precipitation and calcination

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The visible light absorbance, crystallinity, and band structure of $(CuAg)_{0.15}In_{0.3}Zn_{1.4}S_2$ photocatalysts showed apparent dependence on calcination temperature and time. Consequently, photocatalytic activity and H_2 production rate were significantly influenced by calcination processes.

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沉淀煅烧法合成 $(\text{CuAg})_{0.15}\text{In}_{0.3}\text{Zn}_{1.4}\text{S}_2$ 光催化剂及可见光下的制氢性能

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摘要: 研究了沉淀煅烧法制备的纳米级 $(\text{CuAg})_{0.15}\text{In}_{0.3}\text{Zn}_{1.4}\text{S}_2$ 光催化剂以及产氢效率, 并采用X射线衍射、透射电镜、扫描电镜、 N_2 吸附-脱附、紫外-可见吸收光谱等手段对催化剂进行了表征。结果表明, $(\text{CuAg})_{0.15}\text{In}_{0.3}\text{Zn}_{1.4}\text{S}_2$ 的结晶度、比表面积和吸收可见光能力与煅烧温度和煅烧时间有关。在可见光下, 以KI为电子给体, 考察了不同条件对光催化产氢能力的影响。发现在600 °C煅烧5 h时所制的 $(\text{CuAg})_{0.15}\text{In}_{0.3}\text{Zn}_{1.4}\text{S}_2$ 光催化剂产氢活性最高, 产氢速率为 $1750 \mu\text{mol g}^{-1} \text{h}^{-1}$, 量子效率在 $420 \pm 5 \text{ nm}$ 达到12.8%, 比未煅烧催化剂的光催化活性提高了约6倍。

关键词: 光催化剂; 多金属复合硫化物; 制氢; 煅烧; 光催化活性; 可见光

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1. 前言

随着能源短缺和环境污染问题日益突出, 开发清洁可持续的新能源已迫在眉睫。自Fujishima等^[1]在 TiO_2 光电极上分解水得到氢气后, 光能催化制氢技术获得了空前的关注与迅猛的发展。目前已开发的大多数光催化剂禁带宽度比较大($E_g > 3.0 \text{ eV}$), 因此只能利用太阳光谱中约5%的紫外光^[2-6]。为了充分利用太阳能, 研发高活性的能吸收可见光的催化剂成为最近的研究热点。

金属硫化物的禁带宽度较小, 可有效吸收可见光进行光催化产氢^[7,8]。但是二元硫化物光催化剂, 例如 CdS 和 Bi_2S_3 , 在光催化过程中, 由于光生空穴氧化光催化剂自身而导致其本身不稳定(光氧化以及光分解)^[9,10]。研

究发现, 多金属复合硫化物能显著地提高稳定性和光催化活性, 其中包括 $\text{Zn}_{0.8}\text{Cd}_{0.2}\text{S}$ ^[11], ZnIn_2S_4 ^[12,13], $(\text{CuIn})_x\text{Zn}_{2(1-x)}\text{S}_2$ ^[14,15]和 $(\text{CuAg})_x\text{In}_{2-x}\text{Zn}_{2(1-2x)}\text{S}_2$ ^[16,17]。作为一种新型的可见光响应光催化剂, $(\text{CuAg})_{0.15}\text{In}_{0.3}\text{Zn}_{1.4}\text{S}_2$ 能吸收可见光波长到650 nm^[18], 并且由于组分元素的高自然丰度和低毒性而备受关注。本课题组系统地研究了600 °C煅烧形成的 $(\text{CuAg})_{0.15}\text{In}_{0.3}\text{Zn}_{1.4}\text{S}_2$ 光催化剂的催化产氢性能、动力学以及胶体稳定性^[16,19]。

本文采用沉淀煅烧法合成了 $(\text{CuAg})_{0.15}\text{In}_{0.3}\text{Zn}_{1.4}\text{S}_2$ 光催化剂, 分析了煅烧温度和煅烧时间对催化剂的结构、表面形貌和光学性质的影响, 并以KI为电子给体, 考察了煅烧条件对 $(\text{CuAg})_{0.15}\text{In}_{0.3}\text{Zn}_{1.4}\text{S}_2$ 在可见光下光催化产氢活性的影响。

2. 实验部分

2.1. 催化剂制备

将 6.37 g $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 0.42 g AgNO_3 和 1.85 g $\text{In}(\text{NO}_3)_3 \cdot 3.6\text{H}_2\text{O}$ 溶解在 200 mL 去离子水中, 在剧烈磁力搅拌的条件下用 N_2 吹脱 10 min, 以去除水中的 O_2 . 然后加入 0.24 g CuCl , 同时, 在剧烈搅拌的条件下通 H_2S 气体 15 h; 待得到絮凝状黄色沉淀物后, 用超声波破碎仪 (QSonica LLC, Q125) 在功率 125 W 处理 30 min. 超声后的沉淀物再用 0.1 μm 膜进行真空抽滤, 用去离子水反复冲洗, 所得产物在 95 $^\circ\text{C}$ 下真空干燥 1 h. 最后, 黄色产物装入管式炉中, 在 H_2S 气氛下经不同温度 ($T = 400\text{--}700\text{ }^\circ\text{C}$) 煅烧不同时间 ($t = 1\text{--}7\text{ h}$), 冷却后所得样品标记为 $T\text{-}t$.

光催化反应前, 加入 0–1.2 wt% (Ru 计重标准) 的 RuCl_3 溶液, 用 300 W 氙灯辐照 20 min (光催化还原法) 使 Ru 负载在 $T\text{-}t$ 样品上.

2.2. 催化剂表征

样品的晶体结构采用 Philips 公司 X'pert 型 X 射线衍射 (XRD) 仪测定, $\text{Cu } K_\alpha$ 靶线 ($\lambda = 0.154178\text{ nm}$), 扫描范围 $2\theta = 10^\circ\text{--}70^\circ$. 根据 Scherrer 公式^[16] 计算合成样品的晶粒大小. 透射电镜 (TEM) 观察在 FEI-Tecna F20 FEG 型高分辨透射电镜上进行, 加速电压为 200 kV. 扫描电镜 (SEM) 观察在 Zeiss 公司 Ultra 60 型电镜上进行, 并配以 X 射线衍射能谱 (EDS) 仪分析样品的元素组成. 样品的紫外-可见吸收光谱 (UV-Vis) 在 Bechman 公司的 DU7400 型紫外-可见吸收光谱仪上获得, 波长范围 200–800 nm. 样品的比表面积采用 N_2 吸附-脱附法在 Micromeritics 公司 ASAP 2020 型全自动氮吸附仪上测定.

2.3. 光催化反应

光催化反应是在 780 mL 密闭不锈钢反应器中进行, 该反应器的截面积和高度分别是 71 cm^2 和 11 cm. 在反应器的上面有石英盖允许光通过, 外部使用循环水控温系统 (25 $^\circ\text{C}$). 将 0.3 g 的光催化剂分散到 300 mL KI 水溶液 (0.2 mol/L) 中, 用 HCl 调节 pH 为 2.0, 进行磁力搅拌, 保持催化剂的悬浮状态. 反应前用 N_2 吹脱反应液 30 min 以排除反应体系中的溶解氧, 用 300 W 氙灯 (Perkin Elmer, PE300BF) 辐照, 在光源和反应器之间加上高性能热镜片 (400–690 nm, Edmund Optics). 生成的 H_2 通过 Agilent 公司的气相色谱仪 (GC-6890, HP-MS5 柱, TCD 检测器, N_2 载气) 进行分析. 光催化产氢速率 ($\mu\text{mol g}^{-1}\text{ h}^{-1}$) 为单位质量催化剂单位时间产生 H_2 的微摩尔数.

在相同反应条件下, 利用 300 W 氙灯加上滤波片得

到波长在 $420 \pm 5\text{ nm}$ 的可见光 (入射光子数可由光辐射计 (Spectral Evolution, SR-1100) 测量), 其表观量子效率 (QY) = (产生 H_2 的分子数 $\times 2$) / 入射光子数 $\times 100\%$.

3. 结果与讨论

3.1. 催化剂的表征与分析

图 1 为沉淀所得的催化剂前驱体以及在不同温度下煅烧 5 h 所得样品的 XRD 谱. 由图可见, 沉淀所得前驱体的衍射峰比较宽且强度很低, 表明其结晶度很差. 经高温煅烧后, 样品在 $2\theta = 28.5^\circ$ 和 47° 处出现明显的衍射峰, 对应于 ZnS 的 (111) 和 (220) 晶面; 随着煅烧温度的增加, 所得样品衍射峰逐渐增强, 表明其结晶度逐渐提高; 至 600 $^\circ\text{C}$ 时, 样品衍射峰尖锐, 强度最大, 说明此时样品的结晶度最好. 表 1 给出了各样品的粒径和比表面积. 本文所测比表面积大小与文献一致^[18]. 由表可见, 在 600 $^\circ\text{C}$ 所得样品的粒径最小, 比表面积较大, 而 700 $^\circ\text{C}$ 时粒径最大, 比表面积最小. 可见, 煅烧温度对 $(\text{CuAg})_{0.15}\text{In}_{0.3}\text{Zn}_{1.4}\text{S}_2$ 结晶度和比表面积的影响较大: 温度过低, 样品颗粒结晶度不高, 比表面积大; 温度过高会引起催化剂颗粒变大, 比表面积降低. 研究表明^[20,21], 光催化剂的产氢活性取决于样品结晶度和比表面积的权衡.

图 2 为 $(\text{CuAg})_{0.15}\text{In}_{0.3}\text{Zn}_{1.4}\text{S}_2$ (600 $^\circ\text{C}$ -5h) 样品的 SEM 和 TEM 照片. 由图可知, 催化剂呈明显颗粒形状, 具有良好的分散性和明显的晶面结构; 其粒径为 30–50 nm, 与 XRD 结果一致.

由于 600 $^\circ\text{C}$ 所制催化剂具有较大的比表面积和理想的结晶度, 因此, 本文进一步研究了在该温度煅烧不同时间所得样品的 XRD 谱, 结果见图 3. 可以看出, 随着煅烧时间的延长, 样品衍射峰位置变化不大, 表明煅烧时间对样品晶体结构的影响较小. 当煅烧时间为 1 h 时, 样品的衍射峰较宽且低; 随着煅烧时间的增加, 样品的衍射峰逐渐变强, 表明其结晶度逐渐提高. 另外, 如表 1 所示, 随着煅烧时间的增加, 所得样品晶粒粒径逐渐增大, 因而比表面积逐渐减小.

图 4(a) 为 600 $^\circ\text{C}$ 煅烧不同时间所制 $(\text{CuAg})_{0.15}\text{In}_{0.3}\text{Zn}_{1.4}\text{S}_2$ 的 UV-Vis 谱. 可以看出, 沉淀前驱体及其煅烧后的催化剂在可见光区都有明显的吸收. 通过公式 $ah\nu = A(h\nu - E_g)^{n/2}$ ^[22,23] 计算各个样品的禁带宽度 (E_g), 其中 a 为吸收系数, h 为普朗克常数, ν 为光频率, A 为常数. 根据材料光学跃迁类型 (见图 4(a)), $(\text{CuAg})_{0.15}\text{In}_{0.3}\text{Zn}_{1.4}\text{S}_2$ 是直接跃迁, 即 $n = 1$. 因此可以利用 $(ah\nu)^2$ 对 $h\nu$ 作图, 结果见图 4(b), 并由各曲线线性段的

切线与横坐标的截距得样品的 E_g , 结果列于表1. 光催化剂活性很大程度上取决于其禁带宽度的大小: 禁带宽度越小, 可见光的利用率就越高, 其光催化活性就越大^[8,24]. 如表1所示, 经煅烧后, 催化剂的禁带宽度减小, 这是由于其结晶度明显提高(见图1), 使得催化剂的光折射率增加, 因而其吸收光向长波移动^[25,26], 即禁带宽度变窄. 当煅烧温度为400–600 °C时, 催化剂颗粒粒径相差很小, 但其结晶度随着温度升高而逐渐提高(见图1), 使得催化剂的吸收波长红移^[25,26], 最终减小了催化剂的禁带宽度; 当温度继续升至700 °C, 催化剂的结晶度变差, 从而致使其吸收光发生蓝移, 最终禁带宽度变大^[27].

由表1可见, 随着煅烧时间的增加, 所制催化剂的禁带宽度逐渐减小, 其吸收边界逐渐红移; 至7 h时禁带宽度减小到1.92 eV, 且在可见光区具有较强的吸收性能, 其吸收边界达到645 nm. 这是因为催化剂的结晶度随着煅烧时间的增加而提高(见图3), 从而增加了催化剂的光折射率, 使其吸收波长红移^[25,26], 即禁带宽度逐渐减小. 另外, 煅烧5 h和7 h所制催化剂的禁带宽度很接近, 表明继续增加煅烧时间对样品的可见光吸收能力影响很小.

图5(a)为 $(\text{CuAg})_{0.15}\text{In}_{0.3}\text{Zn}_{1.4}\text{S}_2$ (600 °C-5h) 催化剂的EDS谱. 可以看出, 经煅烧后催化剂含有大量的Cu, Ag, In, Zn和S元素. 图5(b)为 $(\text{CuAg})_{0.15}\text{In}_{0.3}\text{Zn}_{1.4}\text{S}_2$ 催化剂负载Ru的EDS谱. 可以看出, 样品中除了含有上述元素之外, 还含有少量的Ru元素, 说明采用光催化还原法成功地使Ru负载到催化剂表面上.

3.2. 光催化制氢性能

3.2.1. Ru载量对 $(\text{CuAg})_{0.15}\text{In}_{0.3}\text{Zn}_{1.4}\text{S}_2$ 光催化制氢性能的影响

图6为Ru载量对 $(\text{CuAg})_{0.15}\text{In}_{0.3}\text{Zn}_{1.4}\text{S}_2$ (600 °C-5h) 光催化制氢性能的影响. 由图可见, 随着Ru载量的增加, H_2 产量逐渐增加, 这是因为Ru颗粒在催化剂表面成为活性中心, 加快了光生电子的转移和有效阻止光生电子空穴对的再结合. 当Ru载量超过0.7 wt%后, H_2 产量没有明显增加. 这是因为Ru可能成为光生电子的捕获阱, 增加了电子和空穴的复合几率, 致使光催化产氢能力很难再提高. 在Ru载量为0.7 wt%时 $(\text{CuAg})_{0.15}\text{In}_{0.3}\text{Zn}_{1.4}\text{S}_2$ 制氢速率最大, 为 $1750 \mu\text{mol g}^{-1} \text{h}^{-1}$, 420 ± 5 nm处的量子效率为12.8%, 明显高于文献值(7.4%)^[17].

3.2.2. 煅烧条件对 $(\text{CuAg})_{0.15}\text{In}_{0.3}\text{Zn}_{1.4}\text{S}_2$ 光催化制氢性能的影响

图7(a)考察了煅烧温度对 $(\text{CuAg})_{0.15}\text{In}_{0.3}\text{Zn}_{1.4}\text{S}_2$ (Ru载量0.7 wt%)光催化活性的影响. 由图可见, 当煅烧温

度从400升到600 °C时, 所制催化剂分解水制氢活性逐渐增加至最高, 为 $1750 \mu\text{mol g}^{-1} \text{h}^{-1}$. 由前文可知, 600 °C所得样品的结晶度最高, 粒径最小, 比表面积较大, 因而光催化活性最高. 继续增加煅烧温度至700 °C时, 所得光催化剂活性降低, 这是由于催化剂颗粒变大所致. 还可以看出, 未经煅烧的催化剂产氢速率仅是600 °C合成样品的15%, 说明经煅烧后光催化剂活性明显提高.

图7(b)为煅烧时间对 $\text{Ru}/(\text{CuAg})_{0.15}\text{In}_{0.3}\text{Zn}_{1.4}\text{S}_2$ (Ru载量0.7 wt%)产氢性能的影响. 由于当样品煅烧时间从1 h升到5 h时, 所得催化剂的结晶度逐渐提高(见图3), 从而减少了光生电子和空穴的复合中心, 抑制它们的再结合, 使得光催化剂活性逐渐增加^[7,28]; 另外, 催化剂的比表面积从8.4降至7.4 m^2/g , 使其表面活性中心减少. 催化剂的结晶度和比表面积共同影响样品的光催化活性^[20,21]. 因此, 催化剂的光催化活性先随煅烧时间的延长而增加, 到5 h后其产氢速率不再增加.

另外, 催化剂的光吸收能力随着煅烧时间的增加而逐渐提高(见图4), 说明在可见光(400–690 nm)辐照下, 催化剂可以吸收的光子数在逐渐增加, 使其光生电子/空穴对增多, 因而光催化活性得到提高; 同时, 在5–7 h时样品的光吸收能力相似, 催化剂的产氢率没有明显变化.

3.3. $(\text{CuAg})_{0.15}\text{In}_{0.3}\text{Zn}_{1.4}\text{S}_2$ 的光催化机理

为了深入研究 $(\text{CuAg})_{0.15}\text{In}_{0.3}\text{Zn}_{1.4}\text{S}_2$ 催化剂的光催化机理, 我们对催化剂的能带结构进行了分析. 在零电荷点的导带/价带的电位可通过以下公式^[29,30]计算:

$$E_{\text{CB}} = X - E^{\text{C}} - 1/2E_{\text{g}} \quad (1)$$

$$X = \left\{ x_{\text{Cu}}^{0.15} \times x_{\text{Ag}}^{0.15} \times x_{\text{In}}^{0.3} \times x_{\text{Zn}}^{1.4} \times x_{\text{S}}^2 \right\}^{1/4} \quad (2)$$

$$x = 1/2(A + I) \quad (3)$$

$$E_{\text{VB}} = E_{\text{CB}} + E_{\text{g}} \quad (4)$$

其中 E_{CB} 和 E_{VB} 分别是催化剂的导电电位和价带电位; E_{g} 为催化剂的禁带宽度(见表1); E^{C} 是氢的电子自由能(~4.5 eV); X 是半导体的绝对电负性, 可以通过计算组成原子的电负性(x)的几何均值; A 是原子的电子亲和能; I 是原子的电离能. 在物化手册^[31]中可以查到 A 和 I 的数据, 计算得到的 x 值列于表2, 在不同煅烧条件下合成的 $(\text{CuAg})_{0.15}\text{In}_{0.3}\text{Zn}_{1.4}\text{S}_2$ 催化剂的导带与价带的电位位置示于图8.

如图8所示, 当光照射半导体光催化剂时, 如果光子的能量($h\nu$)高于催化剂的禁带宽度(E_{g}), 则催化剂的电子从价带跃迁到导带, 产生光生电子(e^-)和空穴(h^+). Ru在催化剂表面担当了电子的捕获阱, 促进了催化剂光生电

子空穴对的分离; 分离出的光生电子能还原反应溶液里的 H^+ 而产生 H_2 ; 因此, 表面负载的Ru提高了催化剂的光催化活性. 同时, 光生空穴被电子给体捕获, 在光催化反应pH初始值为2.0时, I^- 被氧化为 I_3^- [19,32,33].

在光解水制氢反应中, 除了考虑光催化剂的形态、结晶度、比表面积和粒径等, 合适的禁带宽度和导带电位也是发生反应的先决条件. 由图8可见, 不同煅烧条件下合成的 $(\text{CuAg})_{0.15}\text{In}_{0.3}\text{Zn}_{1.4}\text{S}_2$ 催化剂的禁带宽度在1.9–2.7 eV, 因此能够有效吸收可见光光子(< 3.0 eV) [7]. 另外, 这些催化剂的导带电位都比 H^+/H_2 的氧化还原电位低, 因此都能还原 H^+ 生成 H_2 [8]. 在600 °C煅烧5 h时合成的 $(\text{CuAg})_{0.15}\text{In}_{0.3}\text{Zn}_{1.4}\text{S}_2$ 具有较小的禁带宽度和合适的导带电位, 该催化剂表现出最高的光催化活性.

4. 结论

通过调节煅烧温度和煅烧时间使得所制 $(\text{CuAg})_{0.15}\text{In}_{0.3}\text{Zn}_{1.4}\text{S}_2$ 光催化剂的粒径大部分在30–50 nm, 且在可见光区都有明显的吸收. 结果表明, 煅烧温度过低催化剂的结晶度不高, 光催化能力低; 温度过高会使催化剂粒径变大, 比表面积降低, 因而光催化活性降低. 另外, 煅烧时间的延长提高了催化剂的结晶度、可见光吸收能力和光催化活性. 在600 °C煅烧5 h时合成的 $(\text{CuAg})_{0.15}\text{In}_{0.3}\text{Zn}_{1.4}\text{S}_2$ (Ru载量0.7 wt%)表现出最高的光催化活性, 产氢速率为 $1750 \mu\text{mol g}^{-1} \text{h}^{-1}$, 420 ± 5 nm处的量子效率为12.8%, 比未煅烧的光催化剂活性提高了约6倍.