The photocatalytic performance for hydrogen generation over La-modified $ZnIn_2S_4$ under visible light

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Introduction

Research on new energy systems based on clean and renewable energy sources has attracted considerable attention owing to the energy crisis and environmental pollution caused by fossil fuel consumption. Hydrogen is a high-fuel-value, high-efficiency, long-term storage and clean energy. Among the available photochemical systems, hydrogen production from the splitting of water using a visible-light photocatalyst is one of the most important targets.

$ZnIn_2S_4$ has recently been studied for its unique optoelectronic and catalytic property [1]. In our previous research [2], a series of rare earth (RE) ions (La^{3+}, Ce^{3+}, Gd^{3+}, Er^{3+} or Y^{3+}) modified $ZnIn_2S_4$ photocatalysts (RE-$ZnIn_2S_4$) have been reported and La greatly improve the photocatalytic activity. To understand the effects of La modification better, La^{3+} modified porous $ZnIn_2S_4$ were systematically prepared, and their properties were characterized and their photocatalytic activity were evaluated by photocatalytic hydrogen production from the splitting of water under visible-light irradiation.

Materials and Methods

The catalysts was prepared by a hydrothermal method [2]. In the photocatalytic experiments, a 350 W Xe lamp was used as the light source and the UV part of the light was removed by a cut-off filter (λ>420nm). In all experiments, 200 mL of deionized water containing 0.2 g of catalyst and 0.25 M Na_2SO_3/0.35 M Na_2S was added into the reaction cell. Argon gas was bubbled through the reaction mixture for 30 min before reaction started. Pt as a cocatalyst was photodeposited in situ on the photocatalyst from the precursor of $H_2PtCl_6 \cdot 6H_2O$. The temperature was kept at 25 ± 1 □.

Results and Discussion

Table 1. Absorption edge, band gap, BET and total pore volume of various $ZnIn_2S_4$ samples.

La content (wt.%)	0	0.02	0.1	0.5	1.0	2.0	5.0	10.0
Absorption edge (nm)	540	542	541	548	540	543	535	539
Band gap (ev)	2.29	2.28	2.29	2.28	2.29	2.28	2.30	2.30
BET(m^2/g)	95.1	102.9	114.7	118.5	122.8	120.3	107.9	101.2
Total pore volume (cm^3/g)	0.0814	0.1029	0.1134	0.1198	0.1211	0.1201	0.1182	0.1018

The absorption edge, band gap, BET and total pore volume of various $ZnIn_2S_4$ samples listed in **Table 1**. As shown in **Table 1**, the absorption edge and band gaps of $ZnIn_2S_4$ modified by La ions are quite close to that of unmodified $ZnIn_2S_4$. These results indicate the band structure of $ZnIn_2S_4$ would not be changed. Therefore, the modification of La ions does not cause an essential difference on the light absorption property of $ZnIn_2S_4$. Compared with unmodified $ZnIn_2S_4$, the BET surface area and total pore volume of modified $ZnIn_2S_4$ samples firstly increases with the adding of La and then decreases. The highest BET and total pore volume is achieved when about 1.00 wt% La is added. This finding indicates that the addition of La providing a greater BET surface area and total pore volume to the catalyst.

Fig. 1 shows the time course of photocatalytic hydrogen evolution over $ZnIn_2S_4$ samples under visible light irradiation. As can be seen, the hydrogen production rate firstly increases with the adding of La, and then sharply decreases. The highest catalytic activity is achieved when about 1.00 wt% La is added. The result shows that the modification of La has an obvious effect on the photocatalysis of $ZnIn_2S_4$.

Fig. 1. Photocatalytic activities of $ZnIn_2S_4$ samples

Significance

The addition of La has modified the properties of $ZnIn_2S_4$ catalyst. The efficiency of hydrogen production from water under visible-light irradiation increased by 54%, 102%, 113%, 129%, 97%, 67% and 35% when 0.02 wt%, 0.1 wt%, 0.5 wt%, 1.0 wt%, 2.0 wt%, 5.0 wt% and 10.0 wt% of La were added to the $ZnIn_2S_4$ catalyst respectively. The activity order is closely related to the BET surface area and total pore volume.

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