学 位 論 文 内 容 の 要 旨
Abstract of Doctoral Thesis

博士の専攻分野の名称　博士（理 学）　　氏　名　　梅 宗維
Degree requested　Doctor of Science　　Applicant name　Zongwei Mei

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Development of metal sulfide/S-doped metal oxide photocatalysts for H_2 evolution from water under visible-light irradiation
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Photocatalytic water splitting is an ideal route to convert solar energy into clean H_2 energy. In the view of efficient utilization of solar energy, the photocatalysts are necessary to be sensitive to visible light, which takes about 43% of the whole solar energy. Furthermore, the photocatalysts should also show efficient separation and migration ability of the photoexcited carriers (electrons and holes), because the photocatalytic reaction utilizes the photoexcited electrons and holes migrating to the surface of the photocatalyst.

In comparison with metal oxides, most metal sulfides and S-doped metal oxides are attractive visible-light-sensitive photocatalysts for H_2 evolution. The S 3*p* orbitals substituting for or hybridizing with O 2*p* orbitals can narrow band gaps by lifting up the top of the valence band. Furthermore, the sulfides and S-doped oxides which contain elements with d^{10} electronic configurations (i.e., Zn and In) show good migration ability of the photoexcited carriers, because their conduction bands are constructed from the hybridized and broadly dispersed *sp* orbitals. However, few efforts have been devoted to the design and synthesis of more efficient photocatalysts based on Zn/In oxide or sulfide. In this thesis, the S-doped oxide and sulfide photocatalysts are studied, which contain In and/or Zn elements, and two strategies are adopted to enhance their energy-conversion-efficiency. The first one is the fabrication of appropriate semiconductor composite, of which the two components show different band potentials for both conduction and valence bands. The second one is the application of nanotechnology for fabricating photocatalyst with intrinsically high photocatalytic activity.

Chapter 1 provides an overview of the photocatalysis, and describes the thermodynamic conditions and main processes for photocatalytic water splitting. This chapter also summarizes the development of semiconductor photocatalysts and strategies of achieving high photocatalytic activities.

Chapter 2 focuses on the fabrication, characterization and discussion of $Zn_5In_2O_8$/surface-S-doped $Zn_5In_2O_8$ composite which was synthesized through *in situ* sulfuration of the vacancy-rich $Zn_5In_2O_8$ in Na_2S/K_2SO_3 aqueous solution under UV-vis light irradiation. For the surface-S-doped layer, the bottom of conduction band was more negative

than that of $Zn_5In_2O_8$, which resulted from the intentionally produced indium vacancy. However, the top of valence band was less positive than that of $Zn_5In_2O_8$ because of the S dopant. Therefore, the photoexcited electrons transferred from the conduction band of the surface-S-doped layer to that of $Zn_5In_2O_8$, and the photoexcited holes transferred from the valence band of $Zn_5In_2O_8$ to that of the surface-S-doped layer. This process enhanced the separation ability of the photoexcited electrons and holes, and accordingly enhanced the photocatalytic activity. The photocatalytic H_2 evolution rate of the sample sulfurized from the vacancy-rich $Zn_5In_2O_8$ was about 17 times higher than that of the sample synthesized by using the as-synthesized $Zn_5In_2O_8$. In this work, it was found that the indium vacancy and surface sulfuration played significant roles in enhancing the photocatalytic activity.

In comparison with the traditional composite, the bulk composite (interpenetrating networks formed by two semiconductors) is more beneficial to the efficient separation of photoexcited electrons and holes. On the other hand, In_2S_3 and $ZnIn_2S_4$ show narrower band gaps than $Zn_5In_2O_8$ and S-doped $Zn_5In_2O_8$, accordingly they can utilize more visible light.

Chapter 3 demonstrates the hierarchical $In_2S_3/ZnIn_2S_4$ bulk composites synthesized by an ion-exchange route under a solvothermal condition. The $In_2S_3/ZnIn_2S_4$ bulk composites showed highly improved photocatalytic activities for H_2 evolution under visible-light irradiation in comparison with the individual In_2S_3 and $ZnIn_2S_4$. The matched band edge potentials of In_2S_3 and $ZnIn_2S_4$, tight and fluent interface of the components facilitated the more effective separation and migration of photoexcited carriers. Therefore, the photocatalytic activities of the $In_2S_3/ZnIn_2S_4$ bulk composites were greatly enhanced.

ZnS with more negative bottom of conduction band is more beneficial for photocatalytic H_2 evolution than $ZnIn_2S_4$ and In_2S_3. However, ZnS is not sensitive to visible light. Cu^{2+} doping is an effective approach to make ZnS sensitive to visible light because Cu 3*d* orbitals can lift up the top of valence band. In chapter 4, $Zn_{1-x}Cu_xS$ ($0 \leq x \leq 0.066$) ultrathin nanocrystallines were synthesized by a complexing-wet-chemical method. The Cu^{2+} additive could be totally doped into the crystal structure of ZnS using this method. The products showed enhanced photocatalytic activities for H_2 evolution without cocatalyst than that synthesized by the traditional coprecipitation method. The enhanced photoactivities resulted from the homogeneous Cu^{2+} dopant and small nanoparticles.

Chapter 5 summarizes the importance and originality of this research, and provides future prospects of this work. The synthesis strategies developed in our work can be used to fabricate other high-performance functional semiconductors. It is also found that the photoexcited electrons on the conduction bands mainly constructed from Zn 4*s*4*p* orbitals show stronger reduction ability than those on the conduction bands mainly constructed from In 5*s*5*p* orbitals. It gives us meaningful information for the design of highly efficient photocatalysts.