Water splitting and CO_2 reduction using Z-scheme system with various metal sulfides as a reducing photocatalyst responding visible light up to 600 nm

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Abstract: Photocatalytic water splitting and CO_2 reduction have been extensively studied as a method for artificial photosynthesis. In the present study, we developed new Z-scheme systems using $Cu_{1-y}Ag_yGa_{1-x}In_xS_2$ as a reducing photocatalyst with RGO-(CoOx/$BiVO_4$) as an O_2-evolving photocatalyst. Z-schematic water splitting and CO_2 reduction were achieved under visible light irradiation when $Cu_{0.8}Ag_{0.2}Ga_{0.8}In_{0.2}S_2$ with visible light response up to 600 nm was used.
Keywords: Z-schematic water splitting, Z-schematic CO_2 reduction, Metal sulfide photocatalyst.

1. Introduction

Photocatalytic water splitting and CO_2 reduction are attractive reactions to convert photon energy to chemical energy. Metal sulfides are an attractive material group for efficient solar H_2 evolution as well as CO_2 reduction from an aqueous solution containing sulfur compounds of sacrificial reagents, whereas they are unfavorable for water oxidation to form O_2 because of photocorrosion.[1-3] Recently, we successfully applied such photocorrosive metal sulfides as a reducing photocatalyst in a Z-scheme system.[3-6] For example, Z-schematic water splitting and CO_2 reduction were achieved under visible light irradiation using Pt-loaded $CuGaS_2$ as a reducing photocatalyst and RGO-(CoOx/$BiVO_4$) as an O_2-evolving photocatalyst.[6] However, the $CuGaS_2$ responds to visible light up to 540 nm. To utilize sunlight efficiently, metal sulfides that can absorb wide range of visible light should be used as the reducing photocatalyst. We have also reported that $Cu_{1-y}Ag_yGa_{1-x}In_xS_2$ shows the activity for sacrificial H_2 evolution utilizing visible light up to 800 nm.[7,8] In this study, we demonstrated Z-schematic water splitting under visible light irradiation using $Cu_{1-y}Ag_yGa_{1-x}In_xS_2$ and an RGO-(CoOx/$BiVO_4$). The developed Z-scheme system was also applied to CO_2 reduction using water as the sole electron donor under visible light irradiation as a simple suspension system.

2. Experimental

Various sulfides were synthesized by a solid-state reaction. A Pt cocatalyst as an active site for H_2 evolution was loaded by an adsorption method. $BiVO_4$ was synthesized by a liquid-solid state reaction. A CoOx cocatalyst as an active site for O_2 evolution was loaded by an impregnation method. An RGO-(CoOx/$BiVO_4$) composite was prepared by photocatalytic reduction of graphene oxide. Z-schematic water splitting and CO_2 reduction were carried out in 1 atm of Ar and CO_2, respectively. A 300 W Xe arc lamp with a cut-off filter was used as a light source.

3. Results and discussion

Figure 1 shows diffuse reflectance spectra of $Cu_{0.8}Ag_{0.2}Ga_{1-x}In_xS_2$ solid solutions. The absorption edge of $Cu_{0.8}Ag_{0.2}Ga_{1-x}In_xS_2$ solid-solutions shifted to longer wavelength from 540 nm to 800 nm with an increase in the value of x, because the conduction band level formed by In 5s5p is lower than that of Ga 4s4p.[8] The Pt-loaded $Cu_{0.8}Ag_{0.2}Ga_{1-x}In_xS_2$ solid-solutions were used as an H_2-evolving photocatalyst to construct a Z-scheme system by combining together with RGO-(CoOx/$BiVO_4$) as an O_2-evolving photocatalyst. The Z-scheme systems with Pt-loaded $Cu_{0.8}Ag_{0.2}Ga_{1-x}In_xS_2$ ($x \leq 0.6$) showed activities for water splitting under visible light irradiation. CO_2 reduction was also carried out using the Z-scheme systems under a CO_2 atmosphere. When $Cu_{0.8}Ag_{0.2}Ga_{1-x}In_xS_2$ ($x \leq 0.2$) was used, steady CO evolution was observed as the reduction product of CO_2 in addition to H_2 and O_2 evolution due to water splitting under visible light irradiation. A ratio of reacted electrons to holes estimated from the evolved CO, H_2, and O_2 was unity, indicating that water was used as the sole electron donor in the present Z-schematic CO_2 reduction. Thus, $Cu_{0.8}Ag_{0.2}Ga_{0.8}In_{0.2}S_2$ (x = 0.2) with visible light response up to 600 nm was successfully used in the Z-scheme system for both water splitting and CO_2 reduction.

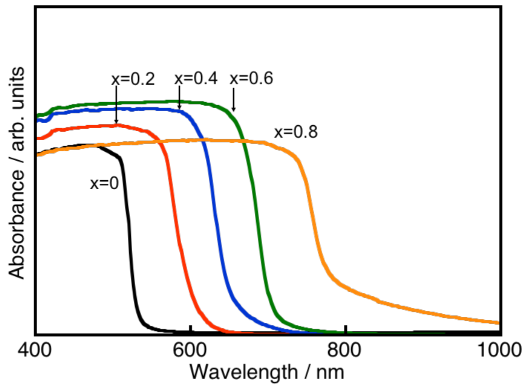

Figure 1. Diffuse reflectance spectra of $Cu_{0.8}Ag_{0.2}Ga_{1-x}In_xS_2$

4. Conclusions

$Cu_{0.8}Ag_{0.2}Ga_{1-x}In_xS_2$ ($0.2 \leq x \leq 0.8$) solid-solutions possessed red-shifted absorption edges than $Cu_{0.8}Ag_{0.2}GaS_2$ (x = 0). The absorption edge shifted to longer wavelength with an increase in the value of x. Pt-loaded $Cu_{0.8}Ag_{0.2}Ga_{1-x}In_xS_2$ ($x \leq 0.6$) functioned as an H_2-evolving photocatalyst in a Z-scheme system upon combining with RGO-(CoOx/$BiVO_4$) as an O_2-evolving photocatalyst. Among them, the Z-scheme system using the $Cu_{0.8}Ag_{0.2}Ga_{0.8}In_{0.2}S_2$ with visible light response up to 600 nm showed the activity for CO_2 reduction to CO accompanied by suitable O_2 evolution. Thus, we successfully developed new Z-scheme systems for water splitting and CO_2 reduction under visible light irradiation.

References

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