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Cu-modified $Zn_6In_2S_9$ photocatalyst for hydrogen production under visible-light irradiation

Shota Fukuishi1, Hideyuki Katsumata1, Ikki Tateishi2, Mai Furukawa1, and Satoshi Kaneco1

Department of Applied Chemistry, Graduate School of Engineering, Mie University, Tsu, Mie, Japan 1

Global Environment Center for Education & Research, Mie University, Tsu, Mie, Japan 2

INTRODUCTION & AIM

・Growing environment and energy problems caused by fossil fuels

We focused on hydrogen.

・Hydrogen = Clean Energy for the Next Generation

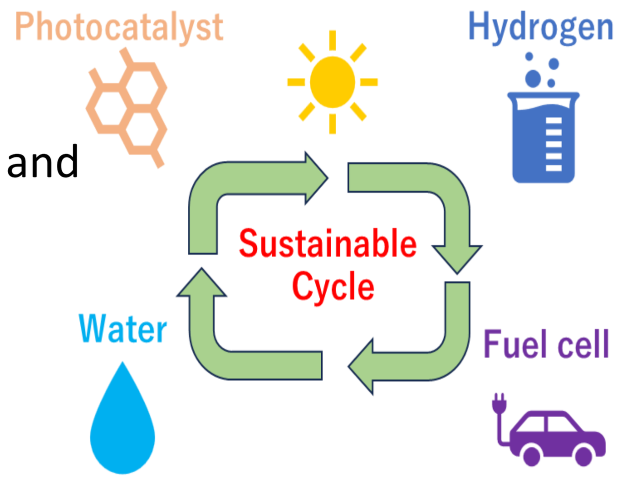
・Hydrogen production method

→ Water splitting using semiconductor photocatalysts

Photocatalytic method of hydrino generation

・The energy from light is used to separate electrons and holes to reduce water.

・Green hydrogen production method that does not emit carbon dioxide.



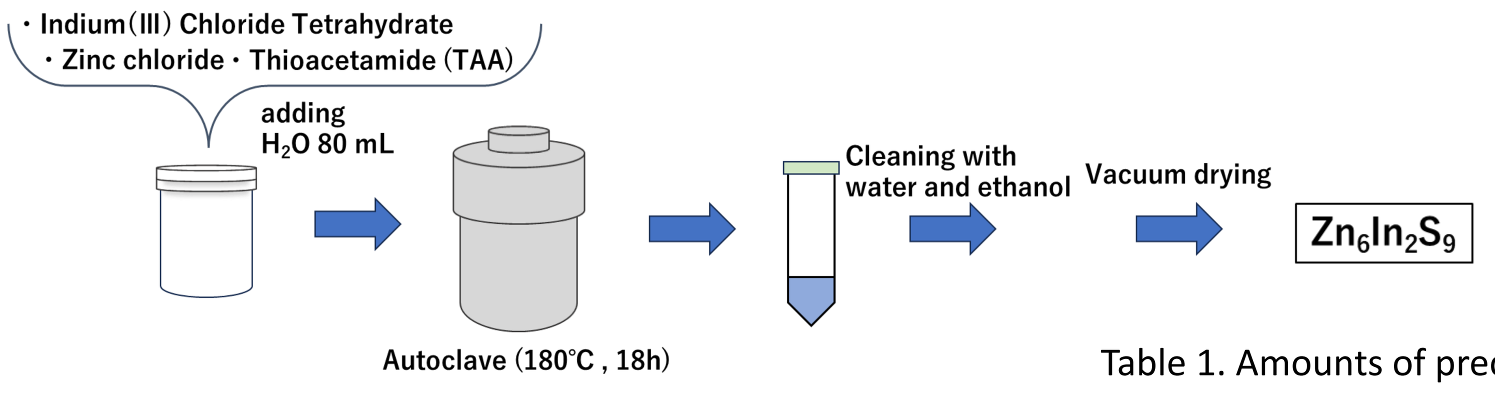
・Advantages of $Zn_6In_2S_9$

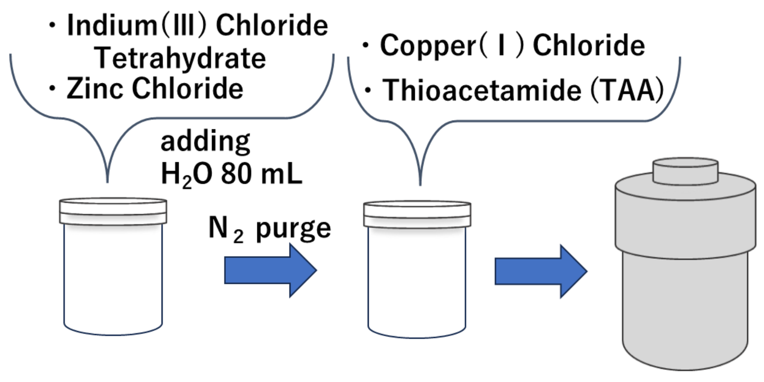
- Narrow band gap ・Visible light responsiveness
- Chemical stability ・Unique two-dimensional layered structure
- Cost can be reduced compared to $ZnIn_2S_4$

・This study

The aim of this study was to improve the photocatalytic activity of indium zinc sulfide while reducing the use of expensive indium.

METHOD





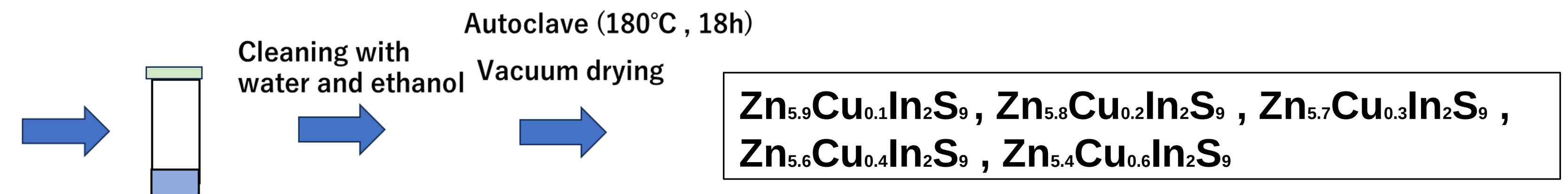


Fig. 1. Preparation of zinc indium sulfide.

Table 1. Amounts of precursors.

	$ZnCl_2$ (mmol)	$InCl_3 \cdot 4H_2O$ (mmol)	TAA (mmol)	CuCl (mmol)
$Zn_6In_2S_9$	2.700	0.900	4.050	0.000
$Zn_{5.9}Cu_{0.1}In_2S_9$	2.655	0.900	4.050	0.045
$Zn_{5.8}Cu_{0.2}In_2S_9$	2.610	0.900	4.050	0.090
$Zn_{5.7}Cu_{0.3}In_2S_9$	2.565	0.900	4.050	0.135
$Zn_{5.6}Cu_{0.4}In_2S_9$	2.520	0.900	4.050	0.180
$Zn_{5.4}Cu_{0.6}In_2S_9$	2.430	0.900	4.050	0.270

Table 2. Experimental conditions.

Photocatalyst	Photocatalysts (40 mg) / Pt (1.2 mg : 3.0 wt%)
Medium	Water (18.8 mL), 0.50 M Na_2SO_3 / 0.70 M Na_2S (20.0 mL), H_2PtCl_6 (1.2 mL : 30 ppm)
Reactor	Pyrex glass vessel (Volume:123 mL)
Temperature	Room temperature (25 ℃)
Light source	Xenon lamp (λ ≧ 420 nm, 10 mW/cm²)
Analysis	Gas chromatography (TCD)

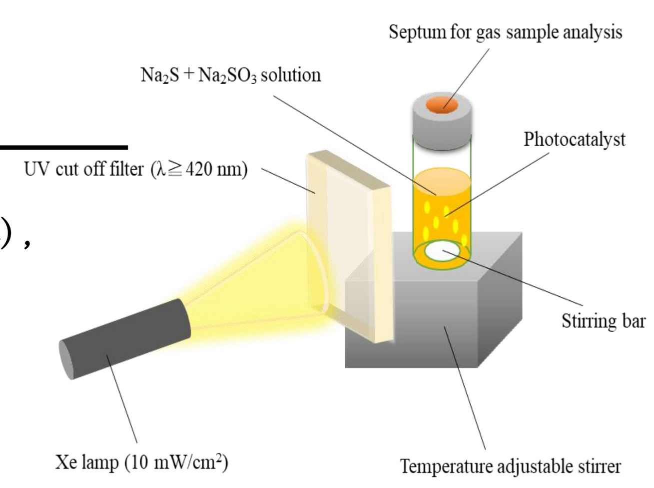


Fig. 2. Photoreactor for photocatalytic hydrogen production.

RESULTS & DISCUSIONS

H_2 production

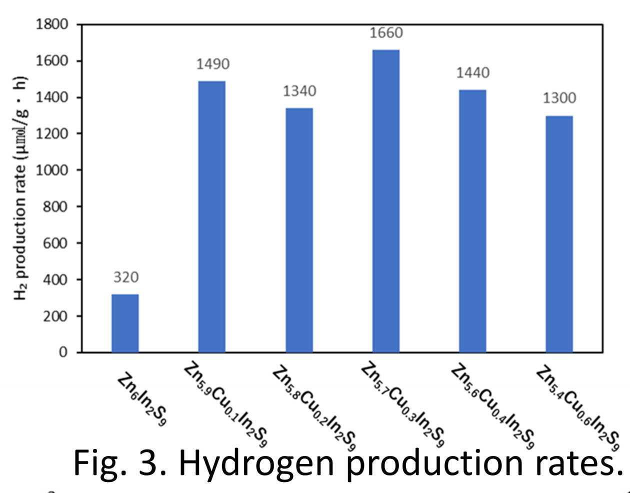


Fig. 3. Hydrogen production rates.

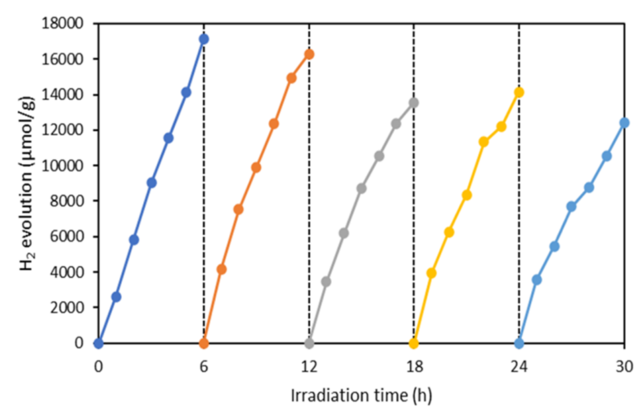


Fig. 4. Cycling tests of $Zn_{5.7}Cu_{0.3}In_2S_9$.

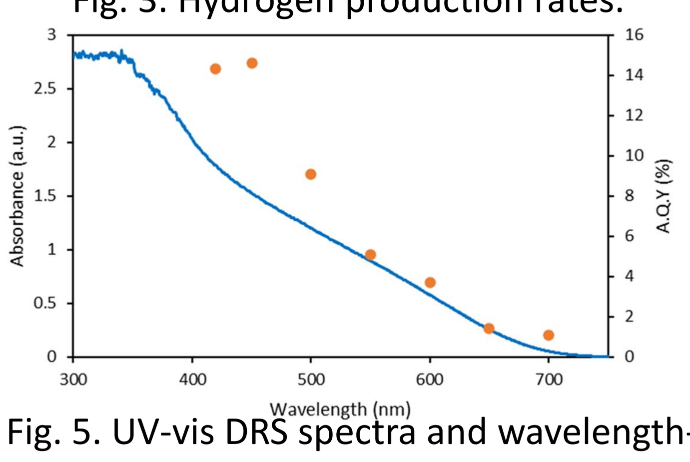


Fig. 5. UV-vis DRS spectra and wavelength-dependent AQY of $Zn_{5.7}Cu_{0.3}In_2S_9$.

・The hydrogen production rate of $Zn_{5.7}Cu_{0.3}In_2S_9$ is approximately five times higher than that of $Zn_6In_2S_9$.

・Fig. 4 showed good hydrogen production activity even after 30 hours.

・Fig. 5 showed that the trend was consistent with DRS spectrum results, confirming that hydrogen production occurs from the photocatalyst.

Photocatalytic activity

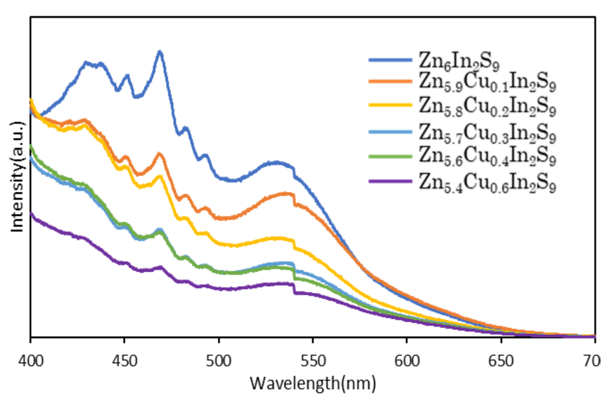


Fig. 6. PL spectra of photocatalysts.

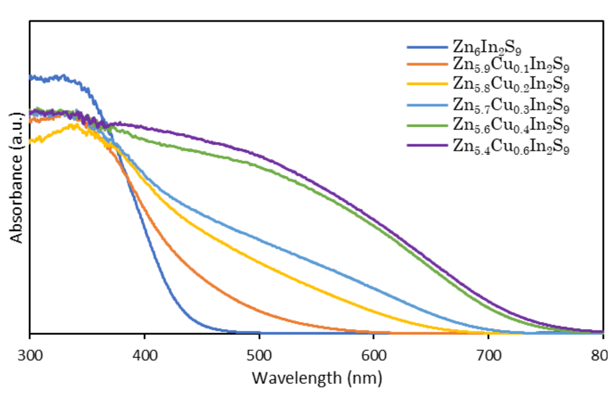


Fig. 7. DRS spectra of photocatalysts.

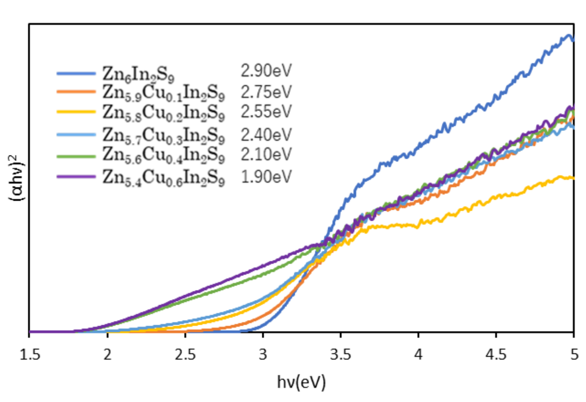


Fig. 8. Tauc plots of photocatalysts.

・The recombination of electron-hole pairs is suppressed.

・The absorption in the visible light region was expanded by adding copper.

・The band gap was narrowed by adding copper.

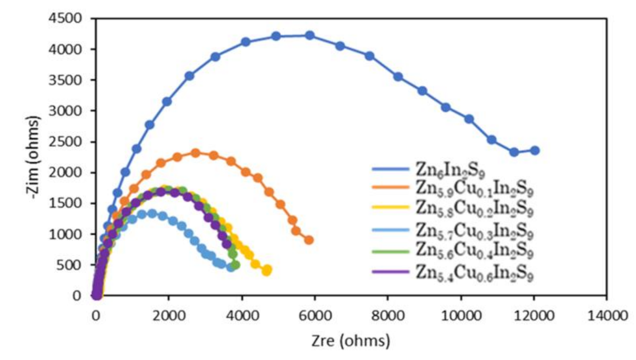


Fig. 9. EIS Nyquist plots of photocatalysts.

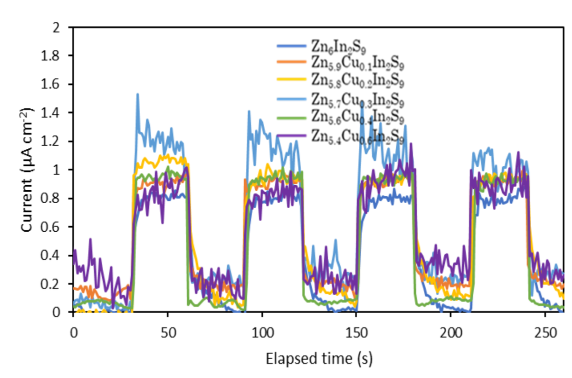


Fig. 10. Transient photocurrent response of photocatalysts.

・It can be seen that the addition of copper results in a lower interfacial resistance than the original indium zinc sulfide.

・The current value of $Zn_{5.7}Cu_{0.3}In_2S_9$ was the highest, indicating high charge transfer efficiency.

Structure

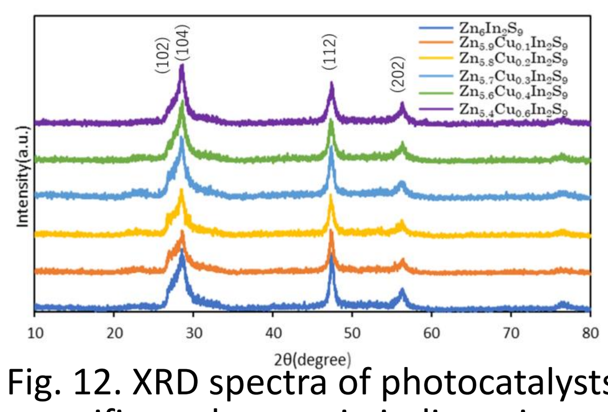


Fig. 12. XRD spectra of photocatalysts.

・The specific peaks seen in indium zinc sulfide were present in all catalysts.

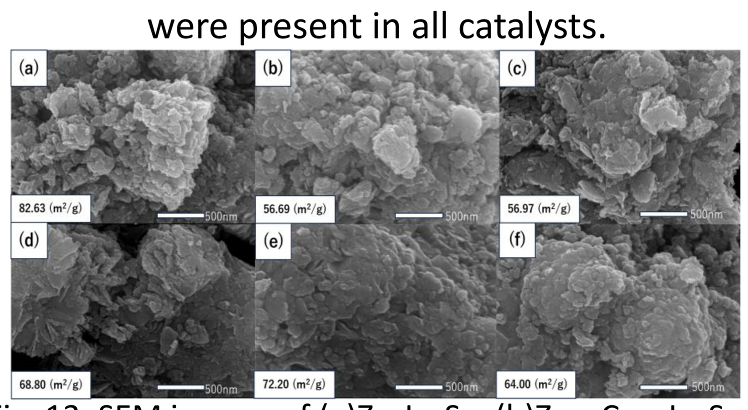


Fig. 13. SEM images of (a)$Zn_6In_2S_9$, (b)$Zn_{5.9}Cu_{0.1}In_2S_9$, (c) $Zn_{5.8}Cu_{0.2}In_2S_9$, (d)$Zn_{5.7}Cu_{0.3}In_2S_9$, (e)$Zn_{5.6}Cu_{0.4}In_2S_9$ and (f) $Zn_{5.4}Cu_{0.6}In_2S_9$

・The addition of copper did not change the appearance of the catalyst much.

・The specific surface area also dropped slightly with the addition of copper.

Mechanism

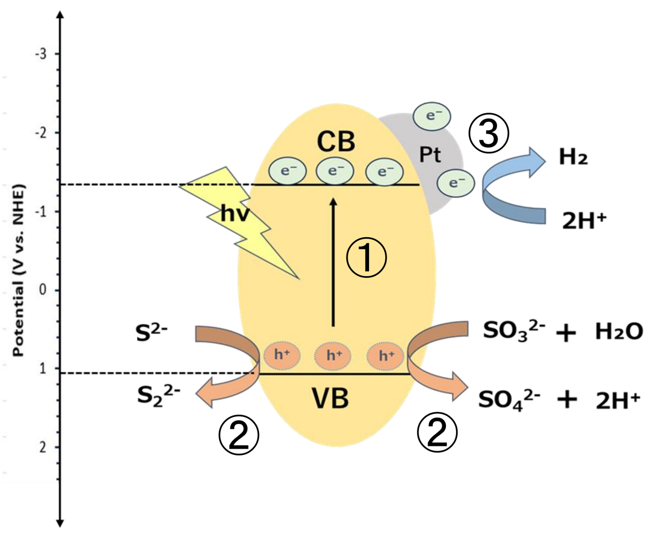


Fig. 14. Mechanism of photocatalytic H_2 production with $Zn_{5.7}Cu_{0.3}In_2S_9$.

①Electrons and holes are separated by light irradiation.

②The holes oxidize the sacrificial agent, producing protons.

③Photoexcited electrons in the conduction band reduce H^+ on Pt, producing hydrogen.

CONCLUSION

・The hydrogen production rate of $Zn_{5.7}Cu_{0.3}In_2S_9$ is approximately five times higher than that of $Zn_6In_2S_9$.

・$Zn_{5.7}Cu_{0.3}In_2S_9$ showed high stability.

・The addition of copper caused an expansion of the light absorption range and suppression of recombination of electron-hole pairs.

・The addition of copper did not change the structure.

FUTURE WORK / REFERENCES

・J. Ye, Z. Fan, Z. Wang, Y. Wang, J. Li, Y. Xie, Y. Ling and Y. Chen, Fuel, 373(2024)132401.