

Effect of Copper Doping on the Hydrogen Production of NiZnS Photocatalyst

권지원 · 김수경 · 김주현 · 박종현

University of Seoul, Chemical Engineering, 삼종접합



Abstract

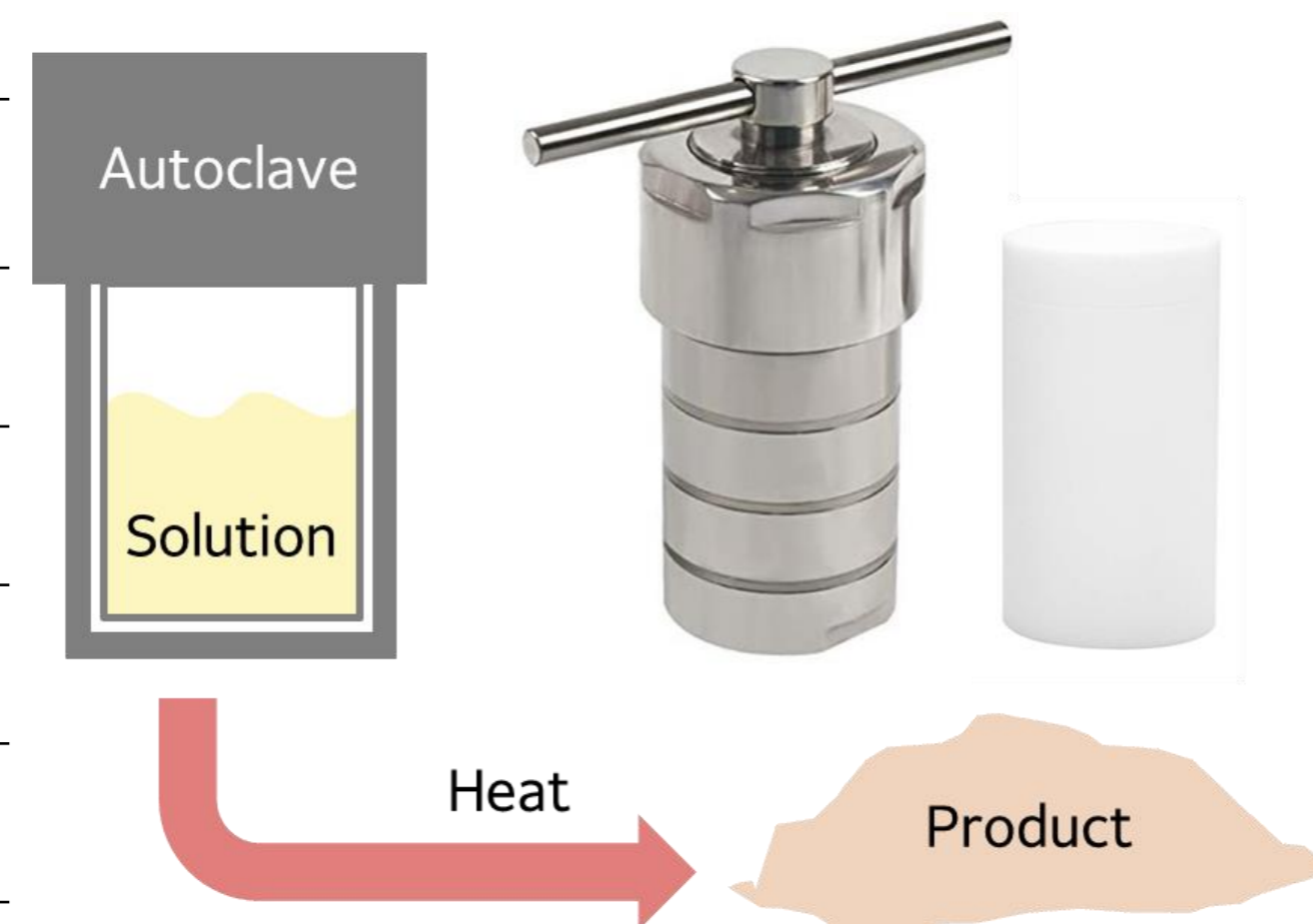
Recently, solar energy is attracting attention as an eco-friendly energy source for the future. In order to enhance hydrogen production efficiency, NiZnS heterostructure photocatalysts are investigated for solar water splitting in this study. In photocatalysts, heterostructures with a ZnS component are widely used due to its high stability. As a co-catalyst, nickel is added to ZnS to improve hydrogen evolution efficiency. In addition, hydrogen productivity is also examined by doping copper precursor. The copper doping improves absorbance of photocatalyst in visible region and helps lower the energy of conduction band. Also, copper is cheaper than other metals. The NiZnS photocatalyst was prepared by a hydrothermal method, the copper doping was proceeded at 8.5 wt% and 10 wt% and is also prepared hydrothermal method. Hydrogen production performance is evaluated by applying the gas chromatography. The highest hydrogen production was resulted 8.5 wt% Cu-NiZnS photocatalyst because it has low band gap.

Experimental

I. NiZnS Synthesis

Hydrothermal method, 200°C, 24 h

Materials	Formulation
Zinc nitrate hexahydrate	4.6172 g
Nickel nitrate hexahydrate	0.1396 g
Thiourea	2.4358 g
Distilled water	160 mL



II. Cu doped on NiZnS

Hydrothermal method, 160°C, 8 h

Materials	6.5 wt% Cu	8.5 wt% Cu	10.5 wt% Cu
NiZnS photocatalyst	0.4695 g	0.4608 g	0.4525 g
Copper nitrate trihydrate	0.0305 g	0.0392 g	0.0475 g
Distilled water	80 mL		

Conclusion

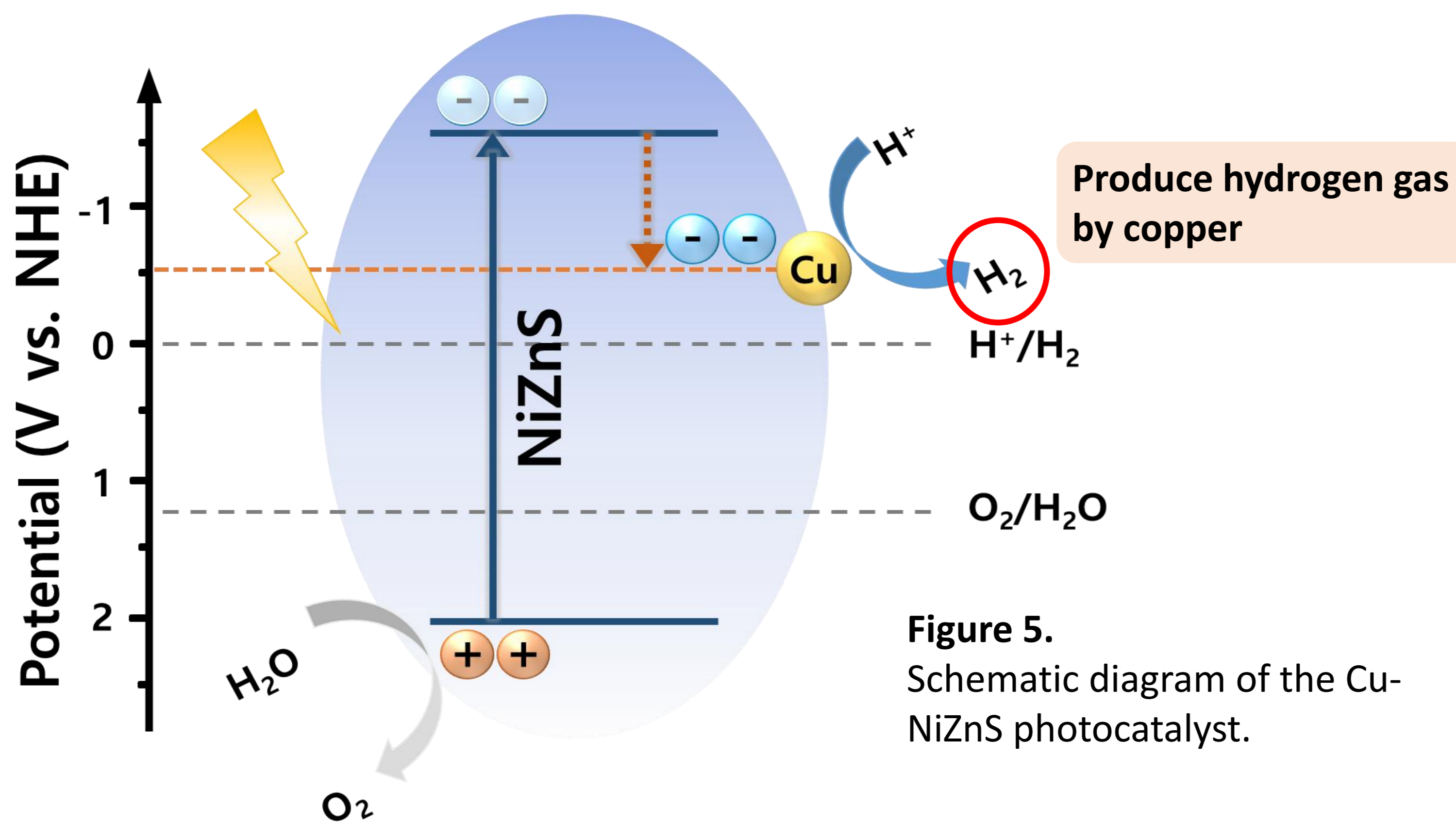


Figure 5. Schematic diagram of the Cu-NiZnS photocatalyst.

- 1) NiZnS photocatalyst and Cu-NiZnS photocatalyst was synthesized hydrothermal method.
- 2) 8.5 wt% Cu-NiZnS photocatalyst showed the highest hydrogen production because the high absorbance in visible region with the narrowest band gap.
- 3) Reproducibility of the 8.5 wt% Cu-NiZnS photocatalyst reveals stable operation mechanism.
- 4) The larger the copper contents, the larger the particle size.
- 5) Through XPS analysis, the binding form of the Cu-NiZnS particles.
- 6) It is estimated that the band gap was narrowed by reducing the energy of the NiZnS conduction band with copper doping.

Result & Discussion

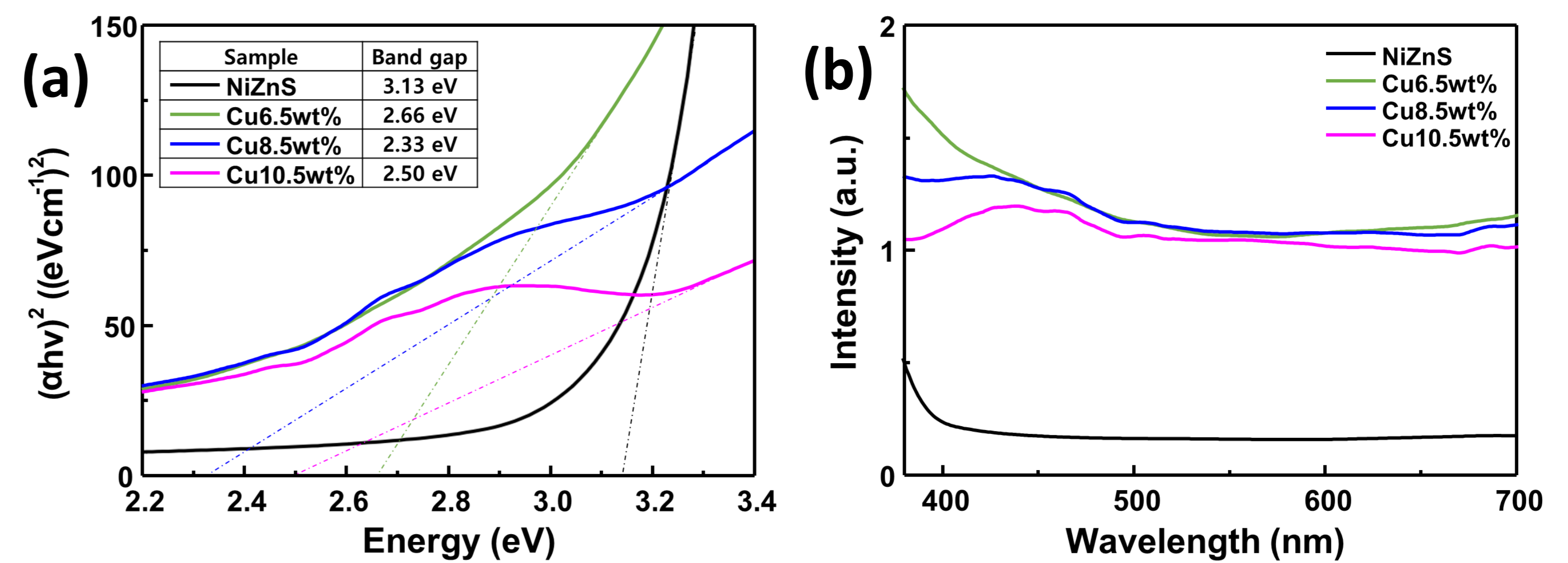


Figure 1. (a) Tauc plots to calculate band gaps of NiZnS and Cu-NiZnS photocatalysts, (b) UV-vis absorbance spectra from the NiZnS and Cu-NiZnS photocatalysts.

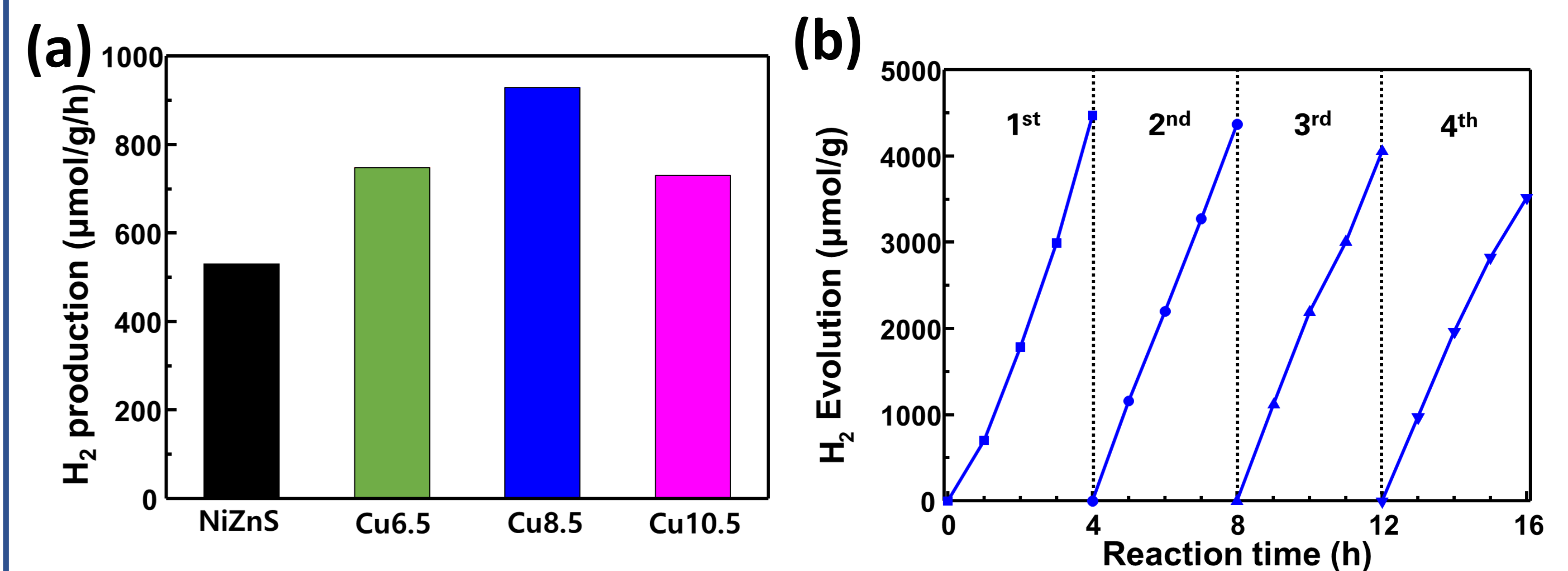


Figure 2. (a) H₂ productions from NiZnS photocatalyst and Cu-NiZnS photocatalysts of various Cu:NiZnS ratios, (b) Reproducibility of H₂ evolutions at 8.5 wt% Cu-NiZnS photocatalyst

Figure 3. SEM images from the NiZnS (a), Cu-NiZnS photocatalyst 6.5 wt% (b), 8.5 wt% (c), 10.5 wt% (d).

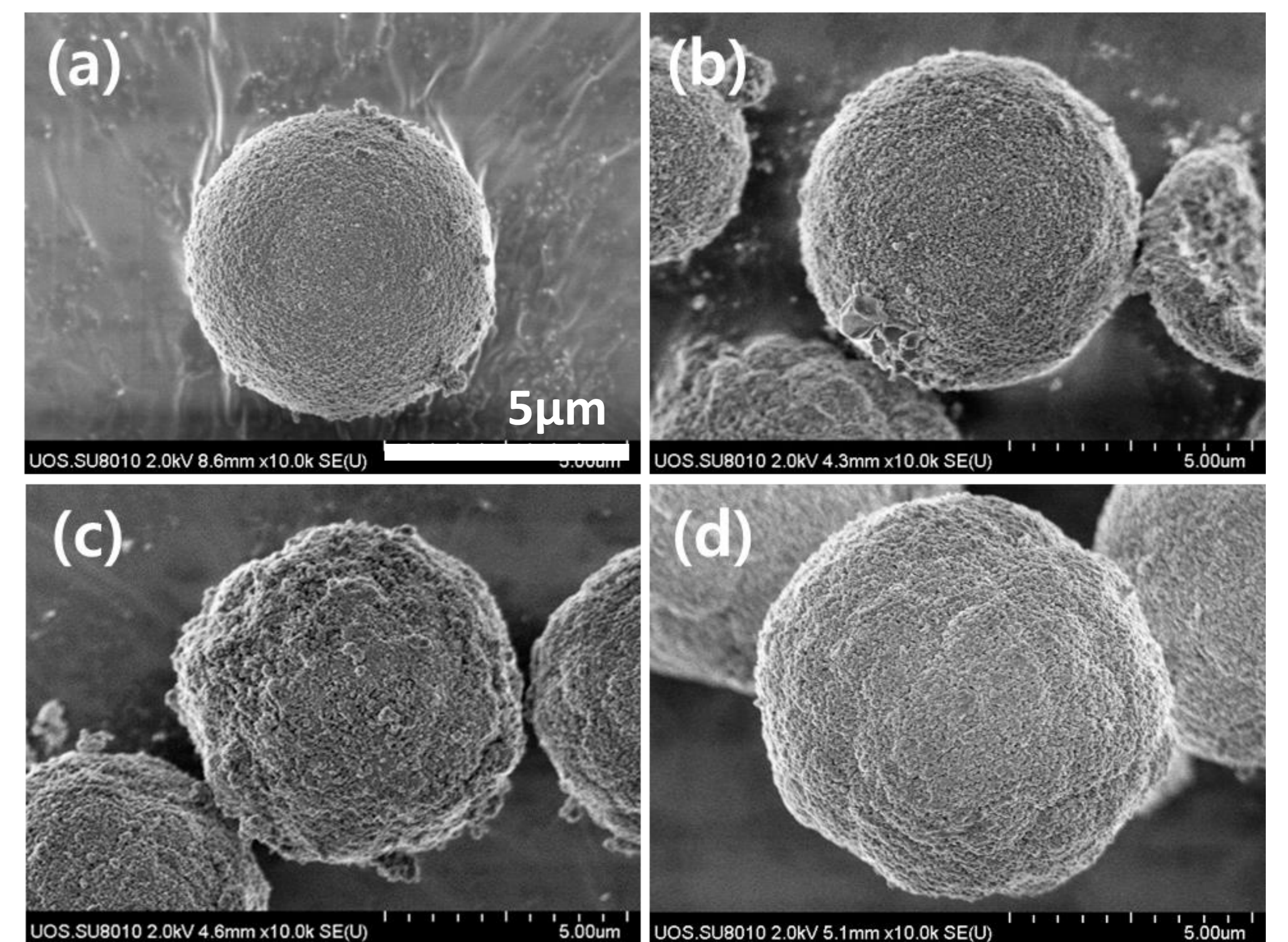
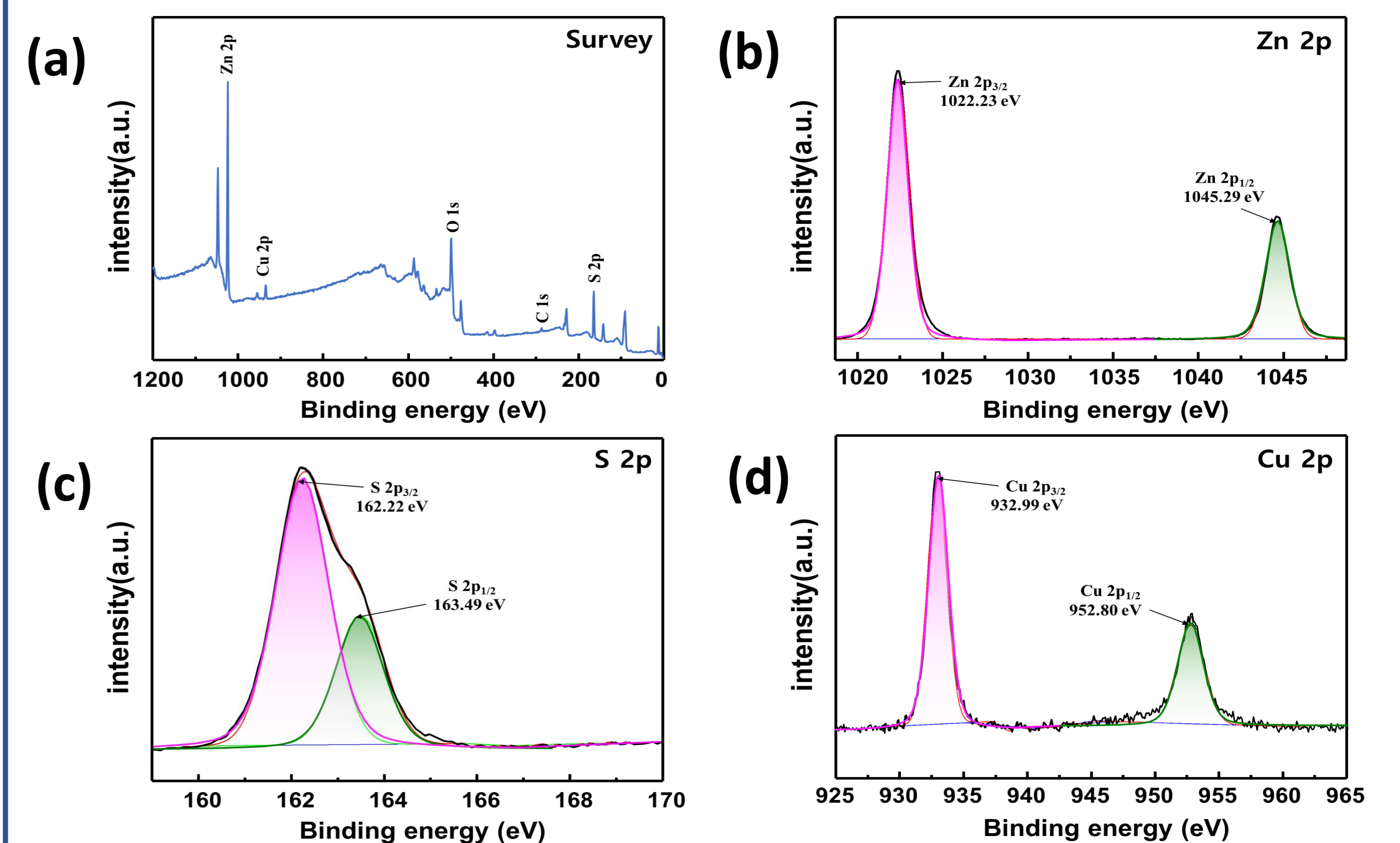


Figure 4. XPS spectra of (a) Survey, (b) Zn 2p, (c) S 2p, (d) Cu 2p from the 8.5 wt% Cu-NiZnS photocatalyst.



Reference

1. Chang, C. J., Chen, J. K., Lin, K. S., Huang, C. Y., & Huang, C. L. (2021). Improved H₂ production of ZnO@ZnS nanorod-decorated Ni foam immobilized photocatalysts. *International Journal of Hydrogen Energy*, 46(20), 13357-13368.
2. Kim, M., Yulati, L., & Shamsuddin, M. (2016). Preparation and characterization of In and Cu co-doped ZnS photocatalysts for hydrogen production under visible light irradiation. *Journal of Electrochem. Sci.*, 8(4), 5594-5604.
3. Al-Rassoul, K. T., Abbas, N. X., & Shanani, Z. J. (2013). Structural and optical characterization of Cu and Ni doped ZnS nanoparticles. *Int. J. Electrochem. Sci.*, 8(4), 5594-5604.
4. Zhao, W., Chen, Z., Yang, X., Qian, X., Liu, C., Zhou, D., ... & Ok, Y. S. (2020). Recent advances in photocatalytic hydrogen evolution with high-performance catalysts without precious metals. *Renewable and Sustainable Energy Reviews*, 132, 110040.
5. Wei, Z., Xu, M., Liu, J., Guo, W., Jiang, Z., & Shangquan, W. (2020). Simultaneous visible-light-induced hydrogen production enhancement and antibiotic wastewater degradation using MoS₂@ZnxCd1-xS Solid-solution-assisted photocatalysis. *Chinese Journal of Catalysis*, 41(11), 1039-1113.
6. Xu, Y., & Xu, R. (2015). Nickel-based cocatalysts for photocatalytic hydrogen production. *Applied Surface Science*, 351, 779-793.
7. Cao, S., Piao, L., & Chen, X. (2020). Emerging photocatalysts for hydrogen evolution. *Trends in Chemistry*, 2(1), 57-70.
8. Yin, X. L., Li, L., Lu, Y., Han, S. W., Dou, J. M., & Li, D. C. (2022). Pomelo-like ZnO@xS@MoS₂ nano-heterostructure as a stable and efficient photocatalyst for H₂ evolution. *Materials Science in Semiconductor Processing*, 138, 106287.
9. Chang, C. J., Chu, K. W., Hsu, M. H., & Chen, C. Y. (2015). Ni-doped ZnS decorated graphene composites with enhanced photocatalytic hydrogen production performance. *International Journal of Hydrogen Energy*, 40(42), 14460-14466.
10. Liu, X., Zhang, Y., Matsushima, S., Sugiyama, T., Hojo, H., & Einaga, H. (2022). Rational Design of Cu-Doped ZnS Nanospheres for Photocatalytic Evolution of H₂ with Visible Light. *ACS Applied Energy Materials*, 5(2), 1849-1857.
11. Liu, X., & Zhang, H. (2021). Recent progress in photocatalytic hydrogen production: design and construction of Ni-based cocatalysts. *International Journal of Energy Research*, 45(2), 1480-1495.
12. Bharat, T. C., Mondal, S., Gupta, H. S., Singh, P. K., & Das, A. K. (2019). Synthesis of doped zinc oxide nanoparticles: a review. *Materials Today Proceedings*, 11, 767-775.
13. Kahng, S., & Kim, J. H. (2021). Optimal oxidation of CuZn1-xS photocatalysts for enhanced solar H₂ production by efficient charge separations. *Ceramics International*, 47(2), 2848-2856.