ECCS 2025 Conference

The 3rd International Electronic Conference on Catalysis Sciences

23–25 April 2025 | Online

MDPI

Enhancement of hydrogen production activity by constructing heterojunction of TpTSN-COF and Cu-doped ZIS

Yusei Kobayashi[1]*, Hideyuki Katsumata[1], Ikki Tateishi[2], Mai Furukawa[1], and Satoshi Kaneco[1]

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

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

INTRODUCTION & AIM

- In recent years, the development of sustainable energy sources has been called for against the backdrop of problems such as fossil fuel depletion and global warming.
- Among these, photocatalytic reactions that generate hydrogen from water using sunlight are attracting attention as a clean and renewable hydrogen production technology.
- While sulfide semiconductors ($ZnIn_2S_4$) and covalent organic structures (COF) that are responsive to visible light, in contrast to conventional titanium dioxide that responds only to ultraviolet light, have attracted attention, further efforts are needed to improve hydrogen production efficiency because photoexcited electrons and holes easily recombine.

Covalent Organic Framework (COF)

Advantage
- Excellent visile light response
- High surface area
- Tunable structure and bandgap

Disadvantage
- Poor charge transport
- Fast electron-hole recombination

Cu-doped $ZnIn_2S_4$ (Cu-doped ZIS)

Advantage
- Efficient charge separation
- Relatively easy synthesis
- High hydrogen evolution activity

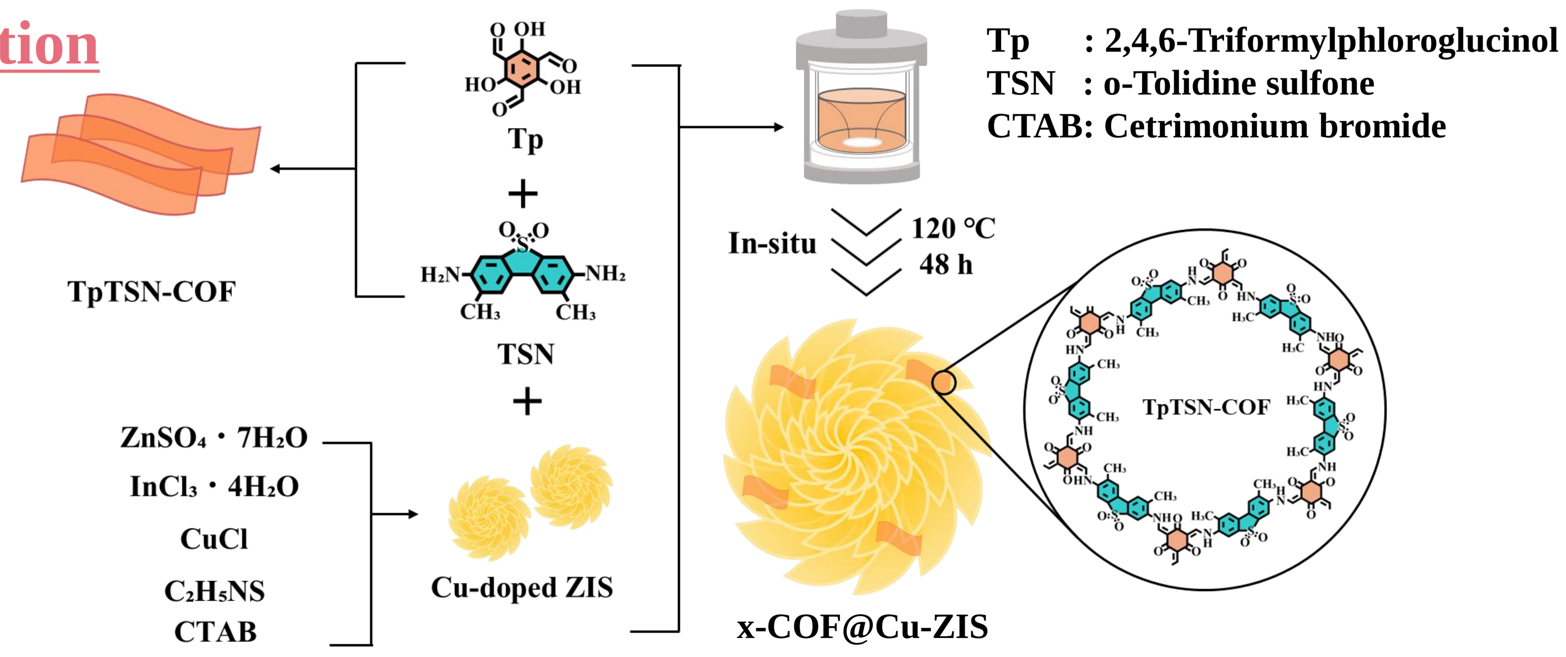
Disadvantage
- Narrow light absorption range
- Limited long-term stability
- Slow career progression

This Study

In this study, we aimed to construct heterojunctions by in situ synthesis of COF on Cu-doped ZIS to enhance hydrogen production performance by promoting charge separation.

METHOD

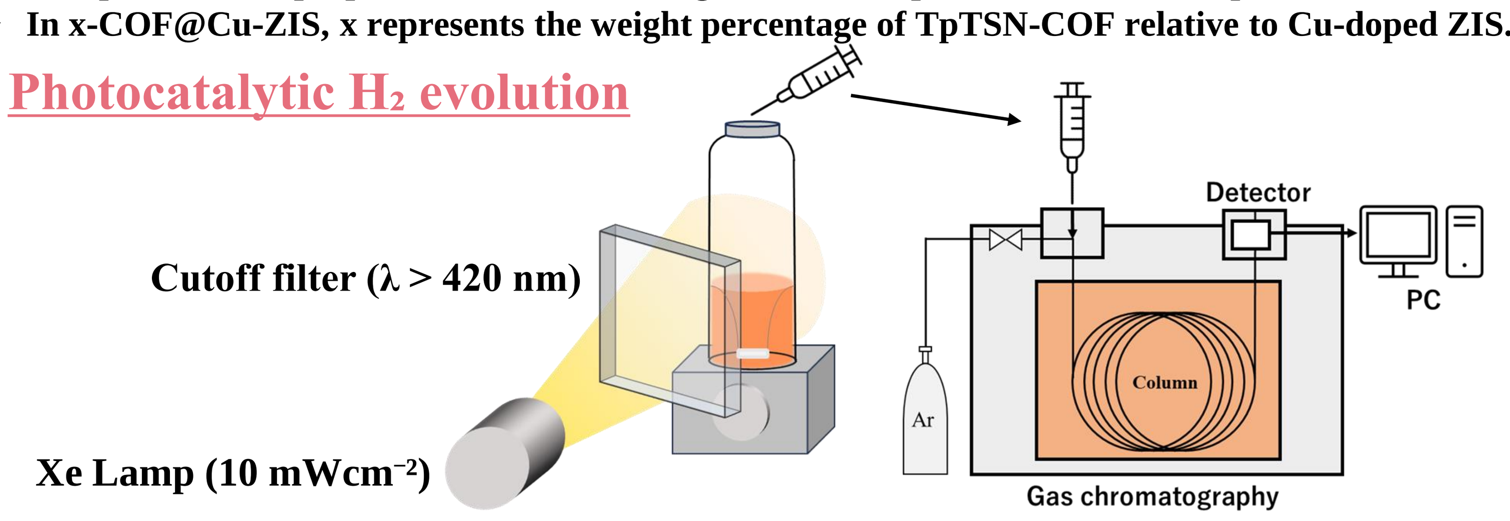
Preparation



Tp : 2,4,6-Triformylphloroglucinol
TSN : o-Tolidine sulfone
CTAB: Cetrimonium bromide

- Composites were prepared with various weight ratios of TpTSN-COF to Cu-doped ZIS.
- In x-COF@Cu-ZIS, x represents the weight percentage of TpTSN-COF relative to Cu-doped ZIS.

Photocatalytic H_2 evolution

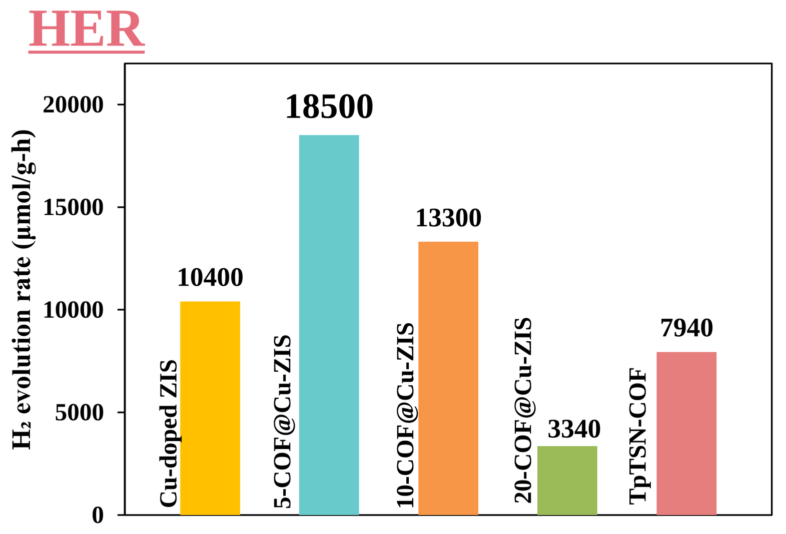


- H_2 evolution test was conducted with 10 mg of photocatalyst in 0.1 M sodium ascorbate solution (pH adjusted to 3 using hydrochloric acid).
- H_2PtCl_6 was added as a co-catalyst precursor and photodeposited onto the photocatalyst as metallic Pt at 2 wt% through photoreduction under light irradiation.
- H_2 was measured by GC with TCD, and the evolution rate was calculated from the 3 h value.

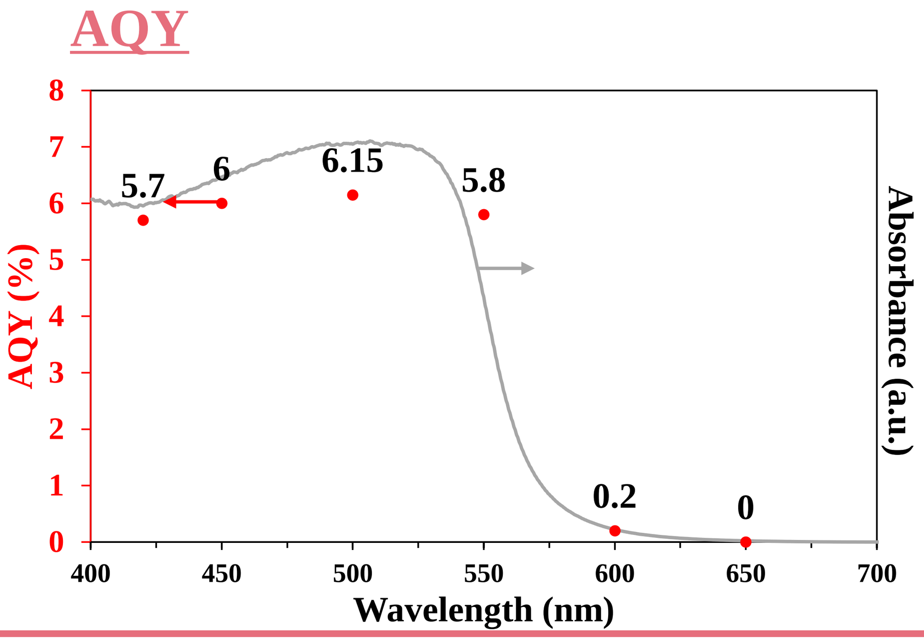
RESULTS & DISCUSSION

Photocatalytic activity

HER

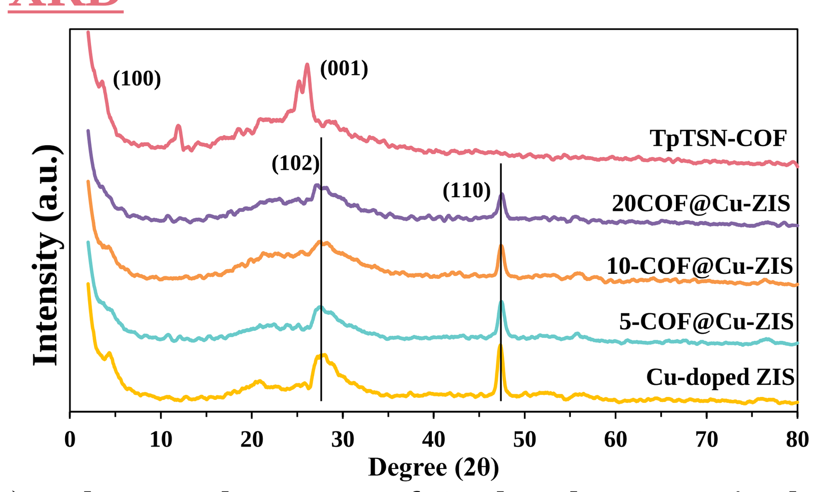


AQY



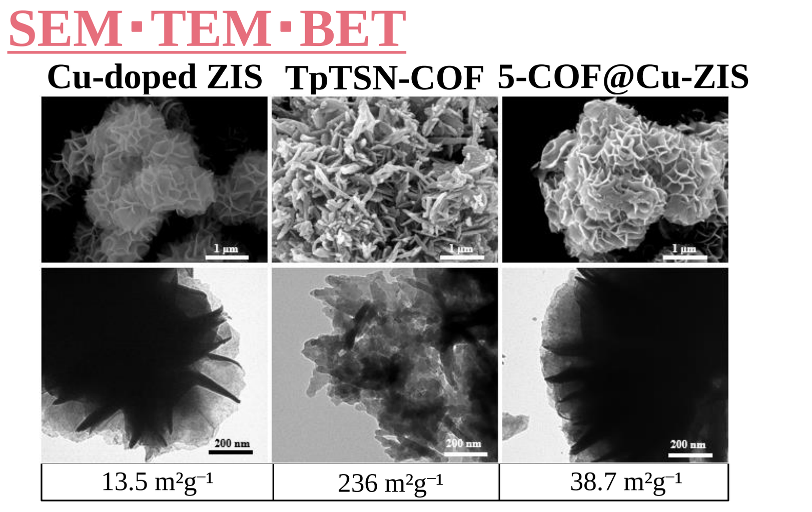
Structure

XRD



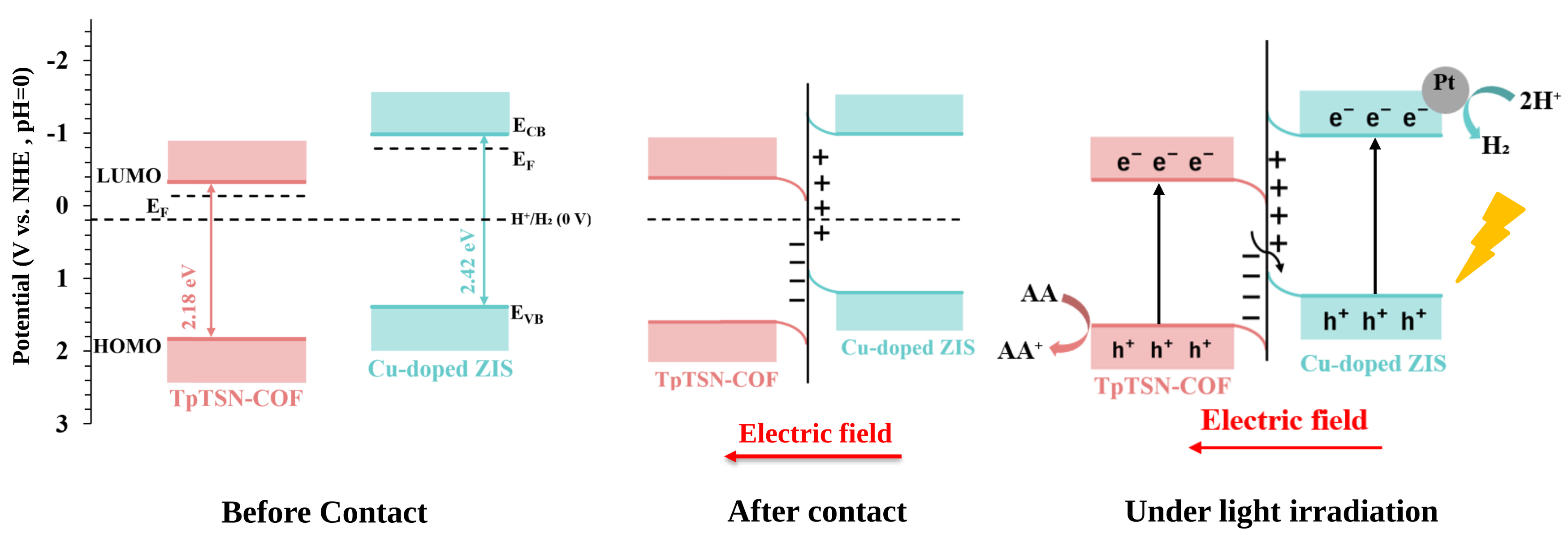
- The crystal structure of Cu-doped ZIS remained unchanged upon heterojunction formation.

SEM・TEM・BET



- SEM and TEM observations confirmed the intimate interfacial contact between COF and Cu-doped ZIS.

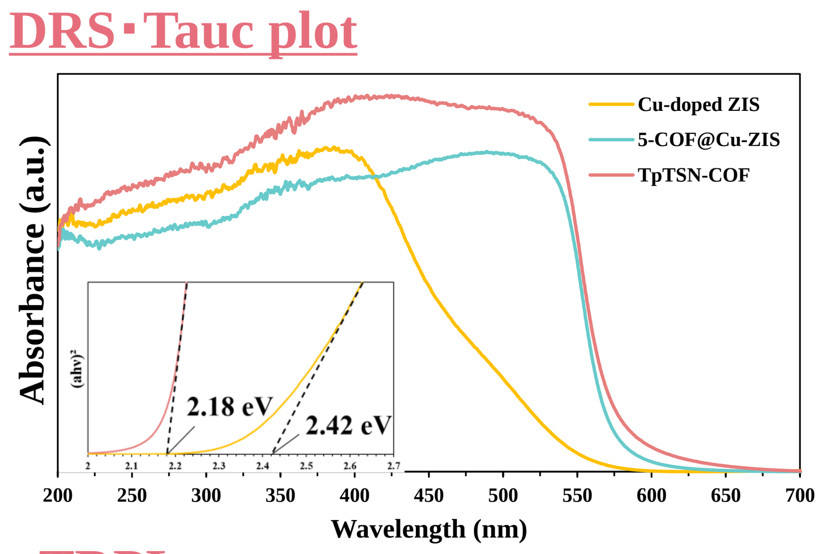
Mechanism



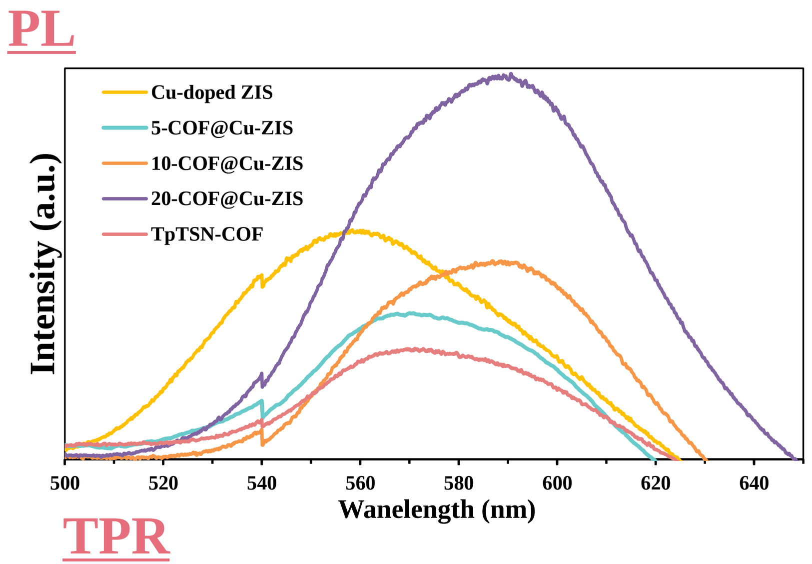
- Band structures of Cu-doped ZIS and TpTSN-COF are shown in the figure above.
- Upon contact, electron transfer from Cu-doped ZIS to TpTSN-COF occurs due to Fermi level equilibration, generating an internal electric field from Cu-doped ZIS to TpTSN-COF.
- When light is irradiated, photo-excited electrons in TpTSN-COF combine with holes in Cu-doped ZIS, suppressing recombination and promoting efficient charge separation.
- The electrons from Cu-doped ZIS reduce protons in the solution, generating hydrogen, while the holes in TpTSN-COF are consumed by the sacrificial agent, ensuring stable reaction progress.

Optical property

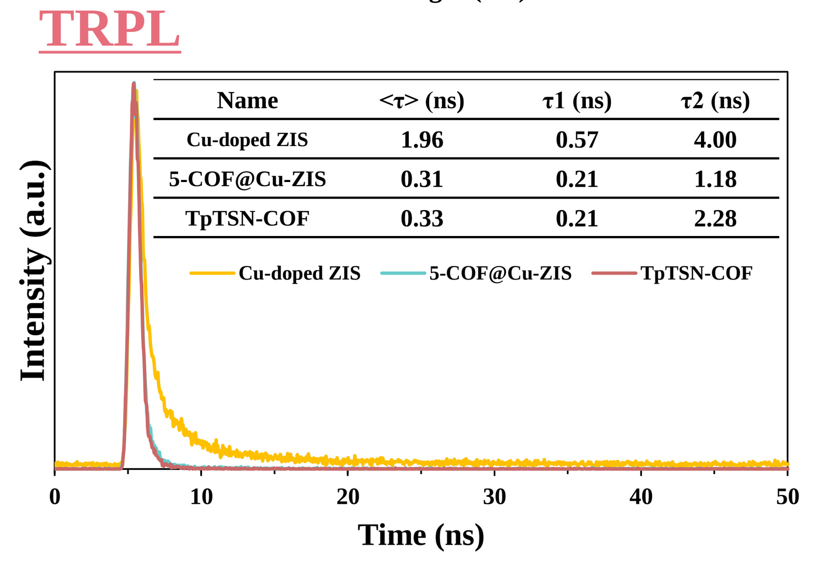
DRS・Tauc plot



PL

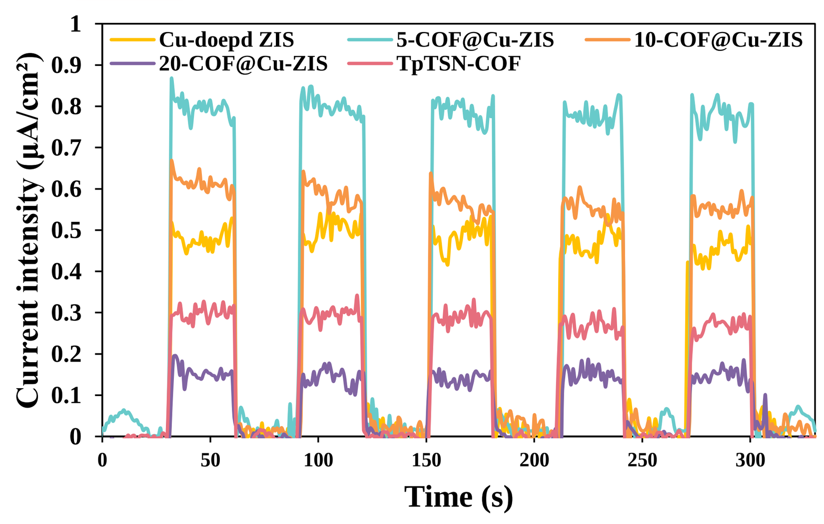


TRPL



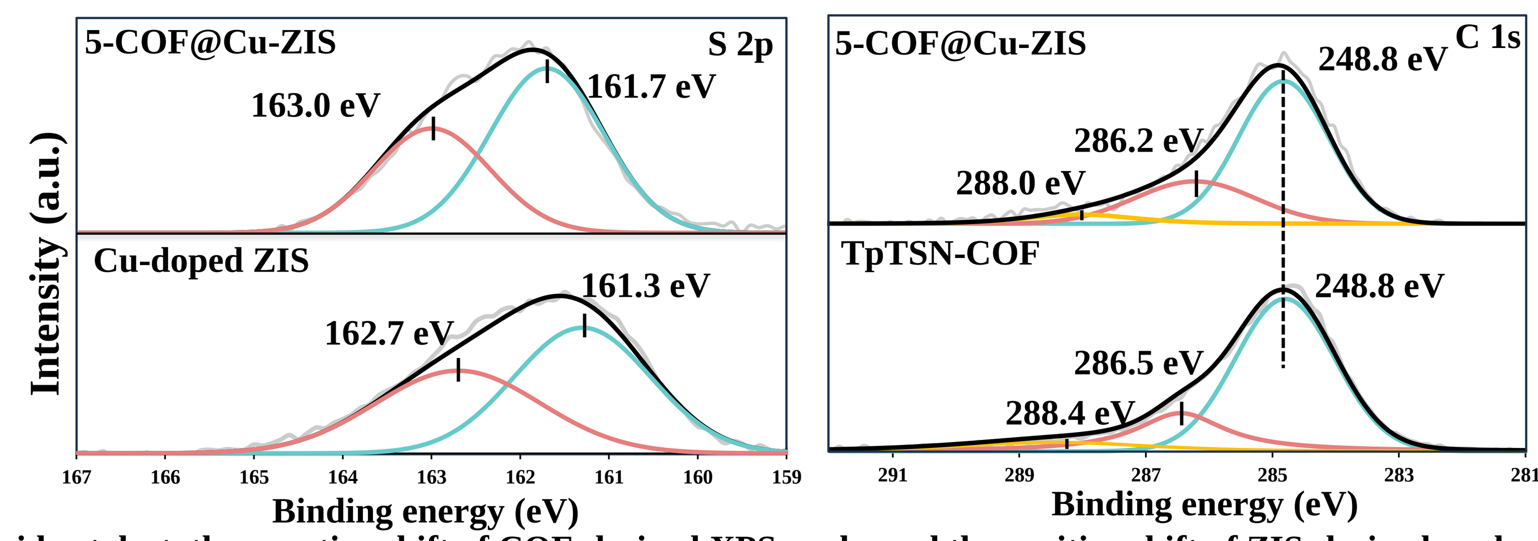
Name	<τ> (ns)	τ1 (ns)	τ2 (ns)
Cu-doped ZIS	1.96	0.57	4.00
5-COF@Cu-ZIS	0.31	0.21	1.18
TpTSN-COF	0.33	0.21	2.28

TPR



- The composite showed an absorption edge almost equal to that of COF.
- The recombination of photogenerated electron-hole pairs was suppressed by the composite.

XPS



- In the hybrid catalyst, the negative shift of COF-derived XPS peaks and the positive shift of ZIS-derived peaks indicate that electron transfer occurs from ZIS to COF after junction formation.

CONCLUSION

- Highly active 5-COF@Cu-ZIS composite catalysts were successfully prepared by an in-situ growth method, achieving an excellent hydrogen production rate of 18500 μmol/g-h and a high AQE of 6.15 % at 500 nm.
- This was attributed to charge separation via an s-scheme heterojunction, where the internal electric field suppressed electron-hole recombination.

REFERENCES

- Huili Ran, Xue Liu, Langhuan Ye, Jiajie Fan, Bicheng Zhu, Quanlong, Yuechang, Journal of Materials Science &Technology, Volume 234, 1 November 2025, Pages 24-30