Multi-Scale Simulations of Dual-Vacancy Effects on Piezoelectric Polarization for Enhanced H_2 Evolution in $ZnIn_2S_4$ Nanosheets

Ming-Yuan Hung,[1] Yen-Ting Kuo,[2] and Hong-Kang Tian*[1,2,3]

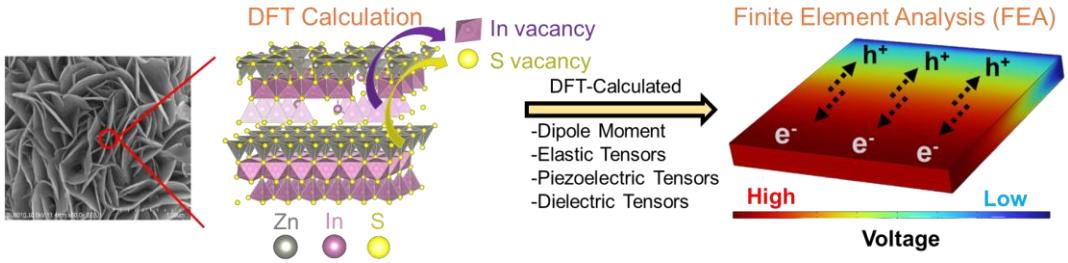
[1] Program on Smart and Sustainable Manufacturing, Academy of Innovative Semiconductor and Sustainable Manufacturing, National Cheng Kung University, Tainan 70101, Taiwan;

[2] Department of Chemical Engineering, National Cheng Kung University, Tainan 70101, Taiwan;

[3] Hierarchical Green-Energy Materials (Hi-GEM) Research Center, National Cheng Kung University, Tainan 70101, Taiwan;

Email: hktian@gs.ncku.edu.tw

$ZnIn_2S_4$ (ZIS) is a highly efficient photocatalyst for light-induced hydrogen generation. Its non-centrosymmetric structure enables polarization under mechanical stress, reducing carrier recombination. Our study[1] shows enhanced hydrogen production in the presence of sulfur and indium vacancies, underscoring the need for a deeper mechanistic understanding of their effects on photocatalysis. However, experimental assessment of ZIS powder is challenging due to its nanoscale dimensions. To address this, we employed a multi-scale computational approach, integrating Density Functional Theory (DFT) and Finite Element Analysis (FEA) to investigate defect-induced effects. DFT calculations identified the most stable S and In vacancy configurations by evaluating vacancy formation energies. The results showed a dipole moment reduction along [001] from 2.07 eÅ to 1.22 eÅ, while vacancies increased dipole moments along [100] (1.07 eÅ) and [010] (0.94 eÅ). Piezoelectric tensors slightly increased, while elastic modulus decreased due to enhanced structural flexibility. Additionally, dielectric tensors significantly decreased with In vacancies, influencing charge polarization. Using DFT-calculated parameters, FEA simulations on a 3D ZIS structure (1 μm × 1 μm × 30 nm) modeled voltage distributions. Two primary voltage sources were analyzed: externally induced piezo-voltage, which increased from 2.4V to 3.4V along [100] and from 0V to 0.9V along [010], and intrinsic dipole-driven voltage, which was higher along [100] and [010] than [001]. These multi-scale computational findings highlight the role of defect engineering in modulating voltage gradients to enhance charge separation and suppress recombination. By bridging quantum-scale DFT with continuum-scale FEA modeling, this study provides a computationally predictive framework for optimizing ZIS-based photocatalysts.



References

1. Zhong, W.-J., **Hung, M.-Y.**, Kuo, Y.-T., **Tian, H.-K.***, Tsai, C.-N., Wu, C.-J., Lin, Y.-D., Yu, H.-C., Lin, Y.-G., & Wu, J.-J.* (2024). ***Advanced Materials***, *36*(36), 2403228.