

Design of High-Entropy Oxides for Photocatalytic Reactions Using Theoretical Calculations and Experiments

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<https://hdl.handle.net/2324/7396303>

出版情報 : Kyushu University, 2025, 博士 (工学) , 課程博士
バージョン :
権利関係 :



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論 文 名 Thesis Title	Design of High-Entropy Oxides for Photocatalytic Reactions Using Theoretical Calculations and Experiments (理論計算と実験を用いた光触媒反応のためのハイエントロピー酸化物の設計)
論文調査委員 Thesis Review Committee Members	Primary Reviewer: Kaveh Edalati, Associate Professor, Kyushu University Secondary Reviewer: Tatsumi Ishihara, Professor, Kyushu University Secondary Reviewer: Kenji Kaneko, Professor, Kyushu University Secondary Reviewer: Motonori Watanabe, Associate Professor, Kyushu University

論 文 審 査 の 結 果 の 要 旨 Thesis Review Result Summary

Photocatalysis has emerged as a sustainable alternative, enabling green hydrogen production and CO₂ reduction by harnessing solar energy. Despite this promise, photocatalysts generally face challenges such as limited light absorption, poor charge transport, rapid electron–hole recombination, and a limited number of active sites. High-entropy oxides (HEOs), materials composed of five or more elements arranged in single or dual-phase structures, represent a new class of photocatalysts with significant potential for improvement due to their multicomponent nature. So far, these materials have shown desirable properties for photocatalysis, providing enormous active sites, hybridized orbitals, inherent defects and outstanding stability. However, strategies to design highly active high-entropy photocatalysts have not received much attention in the literature. The objective of this thesis is to explore design principles based on the electronic configuration of elements in the periodic table for developing high-entropy photocatalysts with high activity for water-to-hydrogen and carbon dioxide-to-methane conversion.

The thesis presented a variety of strategies for designing HEOs with d⁰, d¹⁰, s⁰, and s⁰p⁰ electronic configurations. The designed HEOs were explored through first-principles calculations and synthesized using a combination of high-pressure torsion and high-temperature oxidation. Their microstructure, composition, optical response, charge carrier dynamics, and photocatalytic performance were systematically analyzed. Overall, this thesis not only reports several new photocatalysts, some capable of functioning without cocatalysts, but also proposes design strategies rooted in periodic table trends for the development of high-entropy photocatalysts with superior activity in hydrogen evolution and CO₂-to-methane conversion.

This thesis involves a systematic investigation to deepen the understanding of the effect of

elements with different electronic configurations on the performance of high-entropy photocatalysts. During the process, nine different entropy-stabilized oxides were successfully synthesized and evaluated for hydrogen evolution and CO₂-to-methane conversion. The photocatalytic activity was efficiently improved, suggesting a deeper understanding of electronic configurations in the periodic table for designing active photocatalysts. Moreover, the candidate could participate in 13 different scientific publications, suggesting a scientifically valuable study about high entropy photocatalysts that make a meaningful contribution to the field.

Therefore, this thesis is recognized as worthy of the degree of Doctor of Engineering.

Final exam

The public defense was carried out on August 9th (Saturday) at 15:00 (JST) in the Lecture Room AMS2 (Room 217, Open Learning Plaza, Ito Campus)

The PhD candidate received feedback from four examiners during the whole review process and diligently revised her thesis accordingly. During the private review, major comments and questions were received related to typographical mistakes, the synthesis method, the obtained crystal structure, and optical properties. Overall, the revisions were appropriately done by the candidate. At the public review, four examiners were present, and 24 other attendees also participated. In this session, several questions were asked by the audience. The questions are summarized below.

- A participant questioned how the d⁰+d¹⁰ configuration works fundamentally at the atomic level?
- One participant asked whether the single atoms with low electronegativity are important or if it is the combination of all the atoms and their work function.
- A participant questions the accuracy of band gaps, specifically whether they were considered direct or indirect band gaps using DFT.
- Some comments related to the importance of the surface heterogeneity and synergy between elements with different electronic configurations were asked by the participants.
- One of the examiners asked the candidate about her opinion on the activity of the separate phases in dual-phase materials.
- One of the committee members also asked the candidate's opinion about controlling the selectivity of the products.
- A participant asked if the models were built by trial and error, or if she considered using machine learning.
- A participant asked about the novelty of her thesis,
- Finally, the candidate was asked about the most difficult times in her PhD process, how she overcame them, and what the best time.

The candidate demonstrated a comprehensive understanding of her research, articulating the influence of elements with different electronic configurations on carrier mobility, the

synergistic interactions between elements, and the inherent limitations of DFT in band gap estimation. She addressed the significance of band structure analysis, interphase boundaries, and strategies to improve selectivity, while clarifying that compositions were systematically designed and subsequently refined through experimental validation. She also acknowledged the potential role of machine learning in advancing high-entropy photocatalyst research. Lastly, she further mentioned that, although DFT calculations represented the most challenging aspect of her study, their successful implementation constituted one of its most rewarding outcomes.

Based on the above results, the author is deemed to have passed the final examination.