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# 学位論文の要約

題目 Development of Plasmonic Copper Chalcogenide Nanocrystals for Efficient Solar Energy Conversion

(高効率太陽光エネルギー変換を目指したプラズモニック銅カルコゲナイドナノ結晶の開発)

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Converting solar energy into hydrogen (H<sub>2</sub>) and oxygen (O<sub>2</sub>) by photoelectrocatalysis has been widely studied, but current research is suffered by the incomplete utilization of the solar spectrum, and uncontrollable recombination of the photogenerated electrons and holes. In particular, the infrared light (IR) accounting for 46% of the sunlight has been abandoned. The photoelectrochemical (PEC) system integrated with plasmonic materials is one of the promising approaches to achieve the IR light to energy conversion. However, despite the great progress in development of plasmonic materials and improvement of photocatalysts, efficient use of infrared light using the plasmonic materials is still developing. To enhance the plasmon induced photoelectrocatalysis efficiency which is suffered from the ultrafast charge recombination, the deep and comprehensive understanding of the plasmonic materials and rational design of plasmonic photoelectrode realizing the superior photo-induced charge separation still remains as major challenge.

## **Band Engineering Tuned LSPR in Diverse-Phased Cu<sub>2-x</sub>Se<sub>y</sub>S<sub>1-y</sub> Nanocrystals**

This work presents the mechanism of localized surface plasmon resonance (LSPR) tuning by band engineering based on diverse-phased ternary copper chalcogenide nanocrystals (NCs). Cation-deficient copper chalcogenide NCs as a typical degenerated semiconductor have attracted great attention owing to their unique properties. However, the association between band structures and LSPR in such NCs has not been thoroughly studied. Moreover, the synthesis of the colloidal Cu<sub>2-x</sub>Se<sub>y</sub>S<sub>1-y</sub> NCs with diverse crystal phases remains a challenge to date. Hence, we developed a facile method to synthesize a range of Cu<sub>2-x</sub>Se<sub>y</sub>S<sub>1-y</sub>-alloyed NCs with disparate crystal phases. We elucidated the tunable band structures and LSPR shift which results indicated that the modulation of valence band maximum (VBM) position by Se/S alloying and the overlapping of

the valence band and Fermi level ( $E_F$ ) dominate LSPR properties in alloyed NCs. It is noted that not only the variation of Cu vacancy along with the induced free carriers concentration but also the negative shift of VBM contribute to the LSPR shift towards higher energy.

### **Tunable Band Structure of $\text{Cu}_{2-x}\text{Se}_y\text{S}_{1-y}$ Promoted Near-Infrared Plasmon Driven Photoelectrocatalytic Oxygen Evolution**

This work achieved the enhancement of NIR-light driven photoelectrocatalytic water oxidation by the band engineering in the  $\text{Cu}_{2-x}\text{Se}_y\text{S}_{1-y}$  /CdS heterojunction. Photoelectrocatalytic water splitting have been intensely investigated for efficient utilization of clean and sustainable solar energy, while infrared light which accounts for 52% of solar spectrum has been abandoned up to date. A utilization of plasmonic materials with tunable and excellent IR light harvesting ability is promising strategy for the utilization of solar energy in IR region. In contrast to metallic LSPR material, degenerated semiconductive LSPR materials equip the tunable band structure, which is favorable for photoelectrocatalytic reactions. Especially, p-type degenerated semiconductor NCs with deep Fermi level is an ideal material for IR-induced oxygen evolution reaction (OER) reaction, which has been limited. Hence, we design a plasmonic photoelectrode composed of  $\text{Cu}_{2-x}\text{Se}_y\text{S}_{1-y}$  and CdS for NIR-light driven water oxidation under voltage. The  $\text{Cu}_{2-x}\text{Se}_y\text{S}_{1-y}$  with deeper  $E_F$  exhibited good photoelectrocatalytic OER activity under IR light. The tunable band structure of  $\text{Cu}_{2-x}\text{Se}_y\text{S}_{1-y}$ , which lead to the tuning of both carriers migration and oxidation activity are key factors for IR-induced photoelectrocatalytic OER.

### **A Flexible CdS Nanorods-Carbon Nanotubes/Stainless Steel Mesh photoanode for Boosted Photoelectrocatalytic Hydrogen Evolution**

This study accomplished the rational design of the photoelectrode architecture based on a 3 dimensional flexible substrate with remarkable photoelectrocatalytic  $\text{H}_2$  production by visible light irradiation. In this work, an innovative flexible reticular photoanode comprising of CdS-nanorods (NRs) and carbon nanotubes (CNTs) which were coated on stainless iron mesh was designed for efficiently driving photoelectrocatalytic (PEC) hydrogen  $\text{H}_2$  evolution under visible light irradiation. Such CdS-NRs/CNTs-based flexible photoanodes exhibited a record-breaking  $\text{H}_2$  evolution rate ( $728 \text{ mmol h}^{-1} \text{ g}^{-1}$ ) among the reported CdS-based photoanodes under visible-light irradiation owing to the photoelectron transport channels (CNTs) and high separation efficiency of electrons and holes. This work suggested that a rational design of the photoelectrode architecture plays a key role in improving the charge carriers separation and transfer leading to a outstanding performance of solar to chemical.