

(続紙 1)

京都大学	博士 (理 学)	氏名	LI HAN
論文題目	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)		
(論文内容の要旨)			
<p>Solar energy conversion into hydrogen and oxygen by photoelectrocatalytic water splitting has been widely investigated, although current research focuses on the utilization of ultraviolet (UV) and visible (Vis) light and the infrared light (IR) accounting for 52% of the sunlight has been abandoned. The photoelectrochemical (PEC) system integrated with plasmonic materials as light absorbing material is one of the promising candidates to convert the IR light energy into chemical energy or electricity. Despite the great progress in development of plasmonic materials and improvement of photocatalysts, an entire use of infrared light using the plasmonic materials is still challenging. To improve the efficiency of the plasmon-induced photoelectrocatalysis by suppressing the ultrafast charge recombination, we need to deeply understand the plasmonic materials and rationally design the plasmonic photoelectrode.</p> <p>Chapter 2. Band Engineering Tuned LSPR in Diverse-Phased $\text{Cu}_{2-x}\text{Se}_y\text{S}_{1-y}$ Nanocrystals</p> <p>Tuning mechanism of localized surface plasmon resonance (LSPR) by band structure of ternary copper chalcogenide nanocrystals (NCs) was investigated. Copper-deficient copper chalcogenide NCs have attracted much attention as a typical degenerated semiconductor. However, how their band structures affect their plasmonic properties has not been thoroughly investigated. Moreover, the synthesis of colloidal $\text{Cu}_{2-x}\text{Se}_y\text{S}_{1-y}$ NCs with diverse crystal phases remains a challenge to date. A facile method to synthesize a variety of $\text{Cu}_{2-x}\text{Se}_y\text{S}_{1-y}$ NCs with different crystal phases was developed and the $\text{Cu}_{2-x}\text{Se}_y\text{S}_{1-y}$ NCs with four distinct phases were successfully synthesized. These $\text{Cu}_{2-x}\text{Se}_y\text{S}_{1-y}$ NCs exhibited different valence band maximum (VBM), conduction band minimum (CBM), and Fermi level (E_F), resulting in the large LSPR peak shift. This result indicates that the modulation of VBM, CBM, and E_F by Se/S alloying and the overlapping of VB and E_F dominate the LSPR properties of alloyed $\text{Cu}_{2-x}\text{Se}_y\text{S}_{1-y}$ NCs. It is noted that not only the change of Cu vacancy but also the negative shift of VBM contribute to the blue shift of LSPR peak.</p> <p>Chapter 3. Tunable Band Structure of $\text{Cu}_{2-x}\text{Se}_y\text{S}_{1-y}$ Promoted Near-Infrared Plasmon Driven Photoelectrocatalytic Oxygen Evolution</p> <p>Photoelectrocatalytic water splitting has been vigorously investigated for efficient utilization of UV and Vis light, while the infrared light accounting for 52% of solar spectrum has been</p>			

abandoned up to date. The plasmonic properties of $\text{Cu}_{2-x}\text{Se}_y\text{S}_{1-y}$ NCs in near-IR (NIR) region was applied to the photoelectrocatalytic water oxidation by the band engineering in the $\text{Cu}_{2-x}\text{Se}_y\text{S}_{1-y}/\text{CdS}$ system. Especially, p-type degenerated semiconductor $\text{Cu}_{2-x}\text{Se}_y\text{S}_{1-y}$ NCs with deep E_F is an ideal material for IR-induced oxygen evolution reaction (OER) reaction. A plasmonic photoelectrode composed of $\text{Cu}_{2-x}\text{Se}_y\text{S}_{1-y}$ and CdS was designed and fabricated 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 irradiation. Change in carrier migration at $\text{Cu}_{2-x}\text{Se}_y\text{S}_{1-y}/\text{CdS}$ interface by tuning the band structure of $\text{Cu}_{2-x}\text{Se}_y\text{S}_{1-y}$ NCs, was found to be important for IR-induced photoelectrocatalytic OER.

Chapter 4. A Flexible CdS Nanorods-Carbon Nanotubes/Stainless Steel Mesh photoanode for Boosted Photoelectrocatalytic Hydrogen Evolution

A flexible reticular photoanode composed of CdS nanorods (NRs) and carbon nanotubes (CNTs) coated on stainless iron mesh was fabricated for efficient photoelectrocatalytic H_2 evolution under visible light irradiation. These CdS-NRs/CNTs-based flexible photoanodes showed a record-breaking 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 and high separation efficiency of electrons and holes. This result suggested that a rational design of the photoelectrode architecture plays a key role in improving the carrier separation and transfer to drastically enhance the performance of solar energy conversion.

(続紙 2)

(論文審査の結果の要旨)

光電気化学的水分解による太陽エネルギーの水素と酸素への変換は広く研究されてきたが、現在の研究は紫外光および可視光の利用に焦点を当てており、太陽光の52%を占める近赤外光は注目されていなかった。LI HAN氏は、近赤外光吸収材料としてプラズモニック材料に着目し、三元系銅カルコゲニドナノ結晶のバンド構造変調が、近赤外局在表面プラズモン共鳴(LSPR)特性に及ぼす影響について検討した。その結果、Se/S原子比に応じ結晶構造の異なる4種類の $\text{Cu}_{2-x}\text{Se}_y\text{S}_{1-y}$ ナノ結晶の合成に成功した。これらの $\text{Cu}_{2-x}\text{Se}_y\text{S}_{1-y}$ ナノ結晶が、異なる価電子帯上端、伝導帯下端、およびフェルミ準位を示し、自由ホール密度の増加に伴いLSPRピークが短波長シフトすることを明らかにした。この結果は、 $\text{Cu}_{2-x}\text{Se}_y\text{S}_{1-y}$ ナノ結晶においてSe/S原子比によりバンド構造が変調可能であり、価電子帯とフェルミ準位のオーバーラップが、 $\text{Cu}_{2-x}\text{Se}_y\text{S}_{1-y}$ ナノ結晶のLSPR特性を決定していることを示している。Cu空孔の変化だけでなく、価電子帯上端の上昇もLSPRピークの短波長シフトに寄与していることを実証した。

次にLI HAN氏は、 $\text{Cu}_{2-x}\text{Se}_y\text{S}_{1-y}$ ナノ結晶の近赤外プラズモニック特性を利用し、光電気化学的水酸化反応に適用した。バイアス下での近赤外光誘起水酸化のために $\text{Cu}_{2-x}\text{Se}_y\text{S}_{1-y}$ とCdSで構成されるプラズモニック光電極を作製し、光電気化学特性を評価した結果、より深いフェルミ準位をもつ $\text{Cu}_{2-x}\text{Se}_y\text{S}_{1-y}$ ナノ結晶が、近赤外光照射下で良好な水酸化触媒能を示すことを明らかにした。また、 $\text{Cu}_{2-x}\text{Se}_y\text{S}_{1-y}$ ナノ結晶のバンド構造変調による $\text{Cu}_{2-x}\text{Se}_y\text{S}_{1-y}/\text{CdS}$ 界面でのキャリア移動の変化が、近赤外光誘起光電気化学的水酸化反応に重要であることを実証した。

よって、本論文は博士(理学)の学位論文として価値あるものと認める。また、令和4年7月12日、論文内容とそれに関連した事項について試問を行った結果、合格と認めた。

なお、本論文は、京都大学学位規程第14条第2項に該当するものと判断し、公表に際しては、当該論文の全文に代えてその内容を要約したものとすることを認める。

要旨公表可能日： 年 月 日以降