（ 続紙 １ ）

京都大学	博 士（ 理 学 ）	氏名	陳　礼輝
論文題目	Synthesis and Plasmonic Properties of Copper-based Nanocrystals （銅基ナノ結晶の合成とプラズモニック特性）		

（論文内容の要旨）

Chapter 1: Introduction

Recently, binary copper-deficient copper sulfide ($Cu_{2-x}S$) nanocrystals (NCs) have attracted numerous attention due to their tunable localized surface plasmon resonance (LSPR) properties. As a new type of plasmonic material, two main difficulties including the assignment of LSPR peak to the corresponding oscillation mode in non-spherical NCs and the morphology control should be investigated carefully. In addition, ternary $CuInS_2$ NCs have also attracted much attention because of their suitable bandgap for the sunlight absorption, low toxicity, and cation deficiency induced LSPR. One major challenge in the $CuInS_2$ NCs is to elucidate the relationship between the carrier dynamics and the LSPR properties. This relationship is an important guideline for an application of the $CuInS_2$ NCs to photo-energy conversion. This research reports the synthesis of the $Cu_{2-x}S$ and $CuInS_2$ NCs and the demonstration of their plasmonic and excitonic properties.

Chapter 2: Plasmon Coupling: Determination of LSPR Mode of Roxbyite-Cu_7S_4 Nanodisks

Plasmonic properties, such as peak position, extinction cross-section, and electric field enhancement, are strongly dependent on the excited LSPR mode. In non-spherical copper chalcogenide NCs, an assignment of the LSPR peaks to the corresponding oscillation modes is under controversy and requires experimental verification. Here, we determined the LSPR mode of roxbyite-Cu_7S_4 nanodisk from plasmon coupling in solution. Compared with individual Cu_7S_4 nanodisks, the self-assembled Cu_7S_4 nanodisk arrays in chloroform exhibited blue-shifted LSPR peak with weaker optical density. This fact strongly indicates that the singular LSPR peak in near-infrared region mainly originates from in-plane oscillation mode. In addition, we demonstrated that the LSPR peak of the Cu_7S_4 nanodisk arrays in chloroform could be finely tuned by controlling the number of disks in the array.

Chapter 3: Tin Ion Directed Morphology Evolution of Copper Sulfide Nanocrystals and Tuning of Their Plasmonic Properties via Phase Conversion

Copper-deficient $Cu_{2-x}S$ NCs have been investigated as important hole-based plasmonic materials because of their size, shape, and carrier density dependent LSPR properties. Morphology and carrier density are two important parameters to determine their LSPR properties. Here, we demonstrated that the foreign metal ion, Sn^{4+}, direct the growth of djurleite $Cu_{31}S_{16}$ from nanodisk to tetradecahedron along the [100] direction. To control the

LSPR properties by tuning the carrier density, the djurleite $Cu_{31}S_{16}$ NCs were pseudomorphically converted into more copper-deficient (higher carrier density) roxbyite Cu_7S_4 NCs by the heat-treatment in the presence of amine. The roxbyite Cu_7S_4 NCs exhibited shorter and stronger LSPR peak with retaining the morphology of the djurleite $Cu_{31}S_{16}$ NCs.

Chapter 4: Investigation on Carrier Dynamics of Oleylamine-Capped Copper Indium Sulfide Nanocrystals Using Transient Absorption Measurement

I-III-VI_2 ternary semiconductors are an important class of materials with wide applications from optoelectronic devices to photo-energy conversion. Among them, non-toxic and highly cost-effective $CuInS_2$ is a striking material attracting the numerous attention due to the potential applications in highly-efficient solar cells. The study on the relationship between photo-induced carrier dynamics and structures of the $CuInS_2$ NCs including shapes, sizes, and protecting ligand is an important guideline for their applications. However, the direct observations of the photo-induced carrier dynamics of the $CuInS_2$ NCs using the laser flash photolysis (LFP) are still rare. Here, we successfully synthesized the typical oleylamine-protected $CuInS_2$ nanospheres and nanodisks and investigated their photo-induced carrier dynamics through the transient absorption measurement. The decay of laser induced excitons in the $CuInS_2$ NCs was not sensitive to the crystal structure nor morphology of the NCs and significantly affected by defect trapping and/or energy transfer to the hole-based LSPR. Our results indicate that the careful selection of protecting ligand is essential to obtain the $CuInS_2$ NCs with optimized optical properties for their applications.

Chapter 5: Summary

In summary, the experimental demonstrations may provide a better way to reveal the plasmonic responses of hole-based binary, ternary, and quaternary semiconductor NCs. In special cases, numerical simulations are no longer suitable because the free holes in these NCs cannot be viewed as full free electrons in plasmonic noble metals. In morphology control of semiconductor NCs, well-developed techniques such as utilization of special organic molecules or foreign metal ions for metals, may be applied to synthesize semiconductor NCs with novel morphologies, which may not be obtained by general methods. Surface passivation is an important parameter determining the lifetime of excitons in some semiconductor NCs. Therefore, a careful selection of protecting ligand is essential to obtain these NCs with optimized optical properties for specific applications.

（続紙　２　）

（論文審査の結果の要旨）

陳礼輝氏は、局在表面プラズモン共鳴（LSPR）が電子だけでなくホールの集団振動でも励起されることに着目し、酸化還元によるホール密度制御が容易な非化学量論硫化銅（$Cu_{2-x}S$）ナノ結晶の合成、ならびに、形状・ホール密度変化による近赤外 LSPR 波長制御について検討した。その結果、近赤外領域に一つの LSPR ピークをもつ単分散ディスク状単斜晶 Cu_7S_4 ナノ結晶の合成に成功した。Cu_7S_4 ナノ結晶の LSPR 波長は空気酸化によるホール密度増大で 90 nm 程度短波長シフトし、還元処理により再度長波長シフトさせることができることを明らかにし、さらに、Cu_7S_4 ナノ結晶一次元鎖の光学特性解析により、LSPR ピークがディスク状 Cu_7S_4 ナノ結晶の in-plane モードに帰属されることを実証した。さらに、Sn^{4+}イオンによる $Cu_{2-x}S$ ナノ結晶の形状制御およびアミンの Cu^{+}イオン引き抜きによる結晶構造制御により、LSPR 波長を制御できることを明らかにした。

一方、陳礼輝氏は、光電変換材料として注目されている $CuInS_2$ ナノ結晶の応用において重要なキャリアダイナミクスー構造相関について検討を行った。球状、ディスク状いずれの場合も、励起子消滅挙動は結晶構造やモルフォロジーには依存せず、欠陥トラップやホール LSPR へのエネルギー移動に大きく影響されることを明らかにし、$CuInS_2$ ナノ結晶の応用に向けて重要な知見を与えた。

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、平成２８年７月２０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