学位論文の要約

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)

氏名　陳　礼輝

序論

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 LSPR 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 optelectronic 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.